

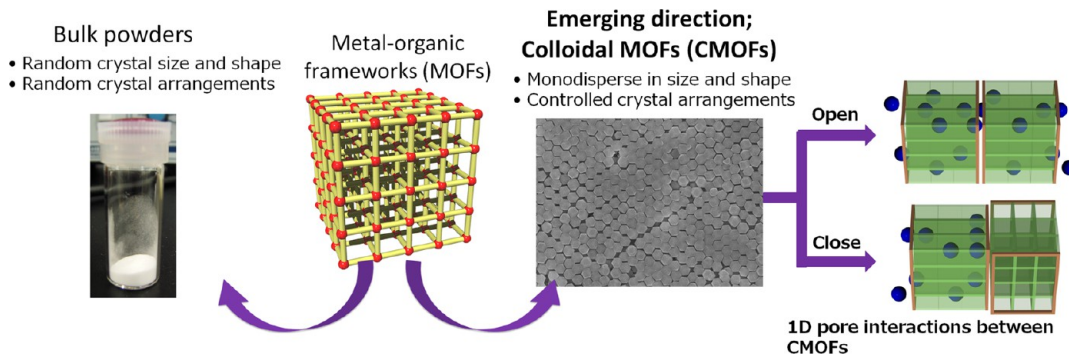
# Colloidal-Sized Metal–Organic Frameworks: Synthesis and Applications

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## CONSPECTUS



Colloidal metal–organic frameworks (CMOFs), nanoporous colloidal-sized crystals that are uniform in both size and polyhedral shape, are crystals composed of metal ions and organic bridging ligands, which can be used as building blocks for self-assembly in organic and aqueous liquids. They stand in contrast to conventional metal–organic frameworks (MOFs), which scientists normally study in the form of bulk crystalline powders. However, powder MOFs generally have random crystal size and shape and therefore do not possess either a definite mutual arrangement with adjacent particles or uniformity. CMOFs do have this quality, which can be important in vital uptake and release kinetics.

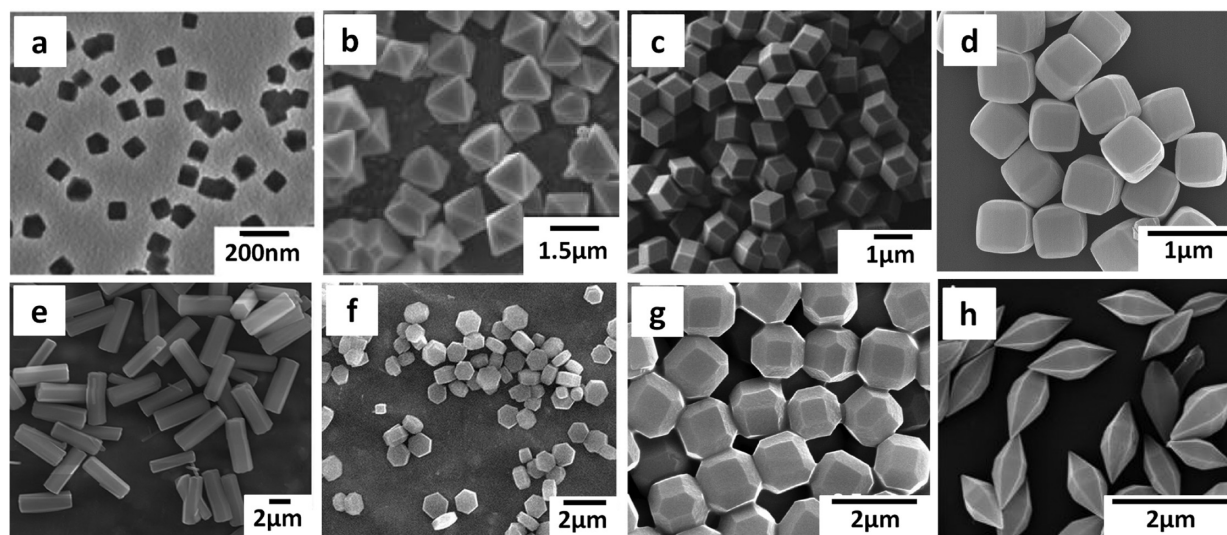
In this Account, we present the diverse methods of synthesis, pore chemistry control, surface modification, and assembly techniques of CMOFs. In addition, we survey recent achievements and future applications in this emerging field. There is potential for a paradigm shift, away from using just bulk crystalline powders, towards using particles whose size and shape are regulated. The concept of colloidal MOFs takes into account that nanoporous MOFs, conventionally prepared in the form of bulk crystalline powders with random crystal size, shape, and orientation, may also form colloidal-sized objects with uniform size and morphology. Furthermore, the traditional MOF functions that depend on porosity present additional control over those MOF functions that depend on pore interactions. They also can enable controlled spatial arrangements between neighboring particles.

To begin, we discuss progress regarding synthesis of MOF nano- and microcrystals whose crystal size and shape are well regulated. Next, we review the methods to modify the surfaces with dye molecules and polymers. Dyes are useful when seeking to observe nonluminescent CMOFs in situ by optical microscopy, while polymers are useful to tune their interparticle interactions. Third, we discuss criteria to assess the stability of CMOFs for various applications. In another section of this Account, we give examples of supracrystal assembly in liquid, on substrates, at interfaces, and under external electric fields. We end this Account with discussion of possible future developments, both conceptual and technological.

## 1. Introduction

Recent additions to the family of nanoporous materials are crystals composed of metal ions and organic bridging

ligands, known as metal–organic frameworks (MOFs) or porous coordination polymers (PCPs).<sup>1–3</sup> Unlike zeolites and mesoporous silica, the high surface area of MOFs is



**FIGURE 1.** Examples of the variety of monodisperse CMOFs. The shapes include (a) cubes,<sup>17</sup> (b) octahedra,<sup>24</sup> (c) rhombic dodecahedra,<sup>25</sup> (d) truncated cubes,<sup>26</sup> (e) hexagonal rods,<sup>16</sup> (f) hexagonal discs,<sup>16</sup> (g) truncated rhombic dodecahedra,<sup>20</sup> and (h) bipyramidal hexagonal prisms.<sup>27</sup> Reprinted with permission from ref 16 (copyright 2008 American Chemical Society), ref 17 (copyright 2009 John Wiley and Sons), refs 20 and 27 (copyright 2012 American Chemical Society), refs 24 and 25 (copyright 2011 American Chemical Society), and ref 26 (copyright 2013 American Chemical Society).

combined with precisely tunable pore size, chemical make-up, and flexible design of framework structure. MOFs are recognized to have promising potential in applications ranging from energy and environment to biology and medicine. Prior reviews cover their applications, among them storage,<sup>4,5</sup> separation,<sup>6</sup> reaction,<sup>7,8</sup> sensing,<sup>9,10</sup> and drug delivery.<sup>11</sup> Although much activity so far in the MOF field revolves around bulk crystalline powders, such materials possess random crystal size and shape. Powders with random crystal size and shape have no definite mutual arrangement between the neighboring particles and also no uniformity in surface-to-volume ratio.

This Account, focusing on new opportunities from the cross-fertilization with colloid science,<sup>12</sup> concerns MOF crystals whose size and shape are regulated; we refer to them as colloidal MOFs (CMOFs). Uniformity can be important to have when it comes to considering uptake and release kinetics. As another example, it could provide a dense array of oriented MOF crystals that would significantly improve separation efficiency.<sup>13</sup>

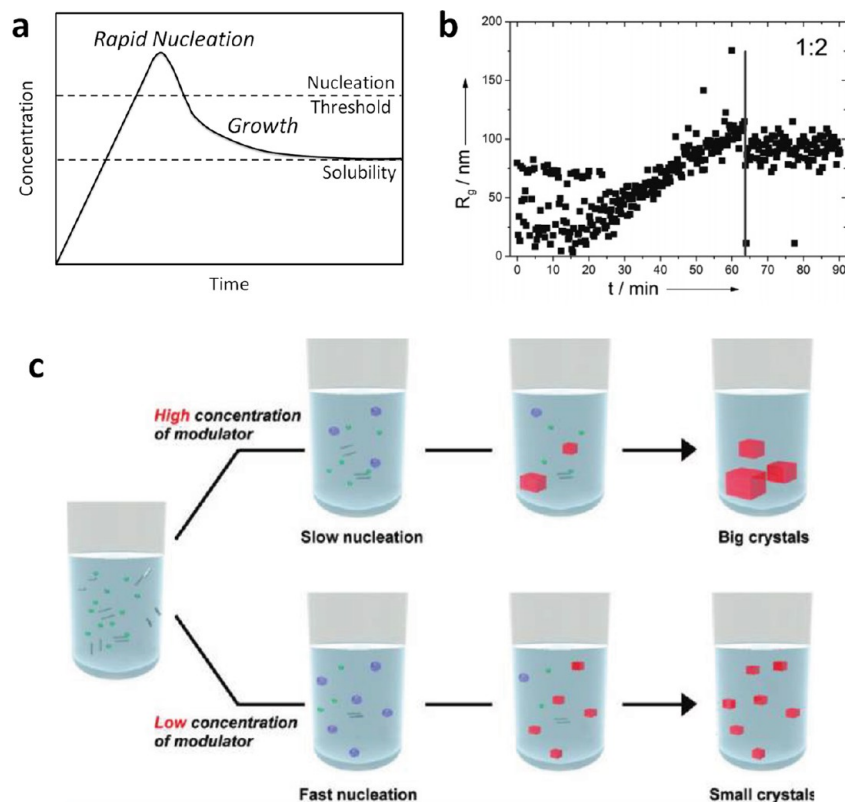
Monodisperse crystals with distinct polyhedral morphologies have been prepared for various families of MOF materials, from nanometers to micrometers in size,<sup>14–20</sup> suggesting that opportunities are not limited to specific classes of MOFs (Figure 1). The controlled synthesis of MOF crystals is in its early stage, however, and the recorded shapes are limited to simple polyhedra. Considering self-assembly, we take note that while much recent attention in

the colloid field focuses on the synthesis and assembly of anisotropic particles, such as nonspherical particles and Janus particles (possessing different surface chemistry on two sides), faceted CMOFs can provide additional levels of complexity<sup>21–23</sup> when used as building blocks for self-assembly, enlarging the scope of colloidal self-assembly with structures unobtainable using conventional particles.

## 2. Synthesis of Monodisperse CMOFs

Monodispersity of size and shape is an important factor not only for in-depth understanding of porous adsorption or separation kinetics, but also for assembling MOF particles into ordered supracrystal structures.<sup>12,20,24,25</sup> The complexity of structures assembled from polyhedra might enlarge functionality beyond what is possible using conventional approaches based on polymers and various oxides such as silica.<sup>21–23</sup>

**2.1. Size Control.** The formation of crystals in solution involves nucleation followed by growth. La Mer *et al.* showed that the production of monodisperse colloids requires a temporally discrete nucleation event followed by slower controlled growth of these nuclei (Figure 2a).<sup>28</sup> The common approach to control the size of crystals, first invented for nonporous coordination polymer crystals<sup>29</sup> and then applied to nanoporous CMOFs, is to add capping ligands that coordinate to metal ions, which decreases the oversaturation of monomers.<sup>30</sup> Since this decreases the difference in chemical potential between solid and monomers,



**FIGURE 2.** Nucleation and growth of MOF crystals. (a) Schematic diagram of nucleation and growth in the La Mer model. (b) Growth of MOF-5 colloids and their termination by modulator addition at the time indicated by the vertical line.<sup>15</sup> (c) Schematic representation of the nucleation-controlled formation of HKUST-1 nanocrystals.<sup>31</sup> The addition of low and high concentrations of modulator results in relatively small and large crystals, respectively. Reprinted with permission from ref 15 (copyright 2007 American Chemical Society) and ref 31 (copyright 2010 American Chemical Society).

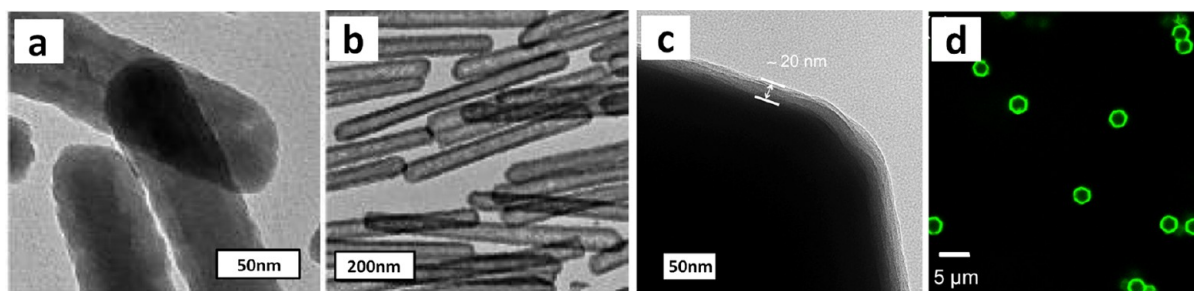
the nucleation rate is reduced (fewer nuclei), resulting in the formation of larger crystals. As expected from this argument, higher concentrations of capping ligands increase the crystal size.

Such additives can also affect growth rate. Monodentate ligands, called modulators, compete with multidentate bridging ligands at metal centers of crystal surfaces.<sup>15,17</sup> They often have similar chemical functionality as the linkers and impede the coordination interaction between metal ions and organic linkers. This competitive situation regulates the rate of crystal growth and the final crystal size. From these arguments, one sees that additives can play two opposite roles: increasing crystal size by reducing nucleation points and decreasing crystal size by suppressing crystal growth.<sup>25,26</sup> Which one dominates can be controlled by proper choice of the strength of metal–additive coordination and the concentration of the additive.

An early example of size control by regulating crystal growth was reported for MOF-5 [ $\text{Zn}_4\text{O}(\text{terephthalate})_3$ ] by Fischer and co-workers.<sup>15</sup> *In situ* time-dependent light scattering measurements indicated narrow size distribution and

highly symmetrical shape. Interestingly, the addition of a monodentate capping ligand (*p*-perfluoromethyl benzenecarboxylate) terminated the crystal growth and produced crystals limited in size, 100–200 nm (Figure 2b).

Kitagawa and co-workers systematically controlled the crystal size of carboxylate-based MOFs by modulating crystal nucleation.<sup>17,31</sup> They finely tuned the size of  $[\text{Cu}_3(\text{btc})_2]$  crystals (HKUST-1;  $\text{btc}$  = benzene-1,3,5-tricarboxylate) by changing the concentration of modulator ligand (dodecanoic acid).<sup>31</sup> Since the higher concentration of modulator provided fewer nuclei, larger crystals resulted (Figure 2c). In the similar spirit of coordination modulation, monodisperse nanocrystals of  $[\text{Zn}(\text{mim})_2]$  (ZIF-8;  $\text{mim}$  = 2-methylimidazole) were synthesized in the presence of various monodentate ligands (carboxylate, *N*-heterocycle, alkylamine) by Wiebcke and co-workers.<sup>18,25</sup> The obtained crystals were monodisperse in size and shape. These extensive studies suggest that the function of monodentate ligands can be understood as modulation of complex formation and deprotonation equilibria during crystal nucleation and growth. A complementary study by Zhang et al.



**FIGURE 3.** Polymer-protected CMOFs and their faceted capsules. TEM images show (a) 8–9 nm silica coating of  $\text{Ln}(\text{BDC})_{1.5}(\text{H}_2\text{O})_2\text{-SiO}_2$  and (b) the hollow shell after dissolving away the interior.<sup>36</sup> LBL-coated ZIF-8 after LBL deposition with  $(\text{PSS-PA})_4\text{-PSS}$  multilayers observed under (c) TEM and its rhombic dodecahedron capsule in (d) 2D-CLSM after removal of the particle showing preservation of the template morphology.<sup>37</sup> Reprinted with permission from refs 36 (copyright 2007 American Chemical Society) and ref 37 (copyright 2013 John Wiley and Sons).

analyzed the relation between pH, regulated by the presence of basic capping ligand, and the rate of crystal growth. Nanocrystals were produced using a combination of appropriate capping ligand and fast deprotonation.<sup>32</sup>

When the desired crystal size cannot be achieved using a single additive, the employment of multiple additives provides further rational control.<sup>19,20,26,32</sup> This laboratory showed an example of controlling ZIF-8 crystal size by combining two modulators, 1-methylimidazole (1-MI) and poly(vinyl pyrrolidone) (PVP).<sup>26</sup> In this system, large crystals ( $>1 \mu\text{m}$ ) could not be grown merely by modulating 1-MI concentration since the crystal size decreases with increase of the 1-MI concentration above a certain concentration, probably because 1-MI suppresses not only nucleation but also crystal growth. Instead we took the strategy of introducing a weaker ligand (PVP), which helped to further decrease the number of nucleation points without suppressing crystal growth. Remarkably, the concurrent employment of both 1-MI and PVP resulted in substantially increased crystal size. The increase of particle size with increasing concentration of 1-MI and PVP mixtures suggests that 1-MI and PVP suppressed nucleation cooperatively. These large micrometer-sized crystals enabled the *in situ* observation of supracrystal assembly processes (see section 5, Assembly).

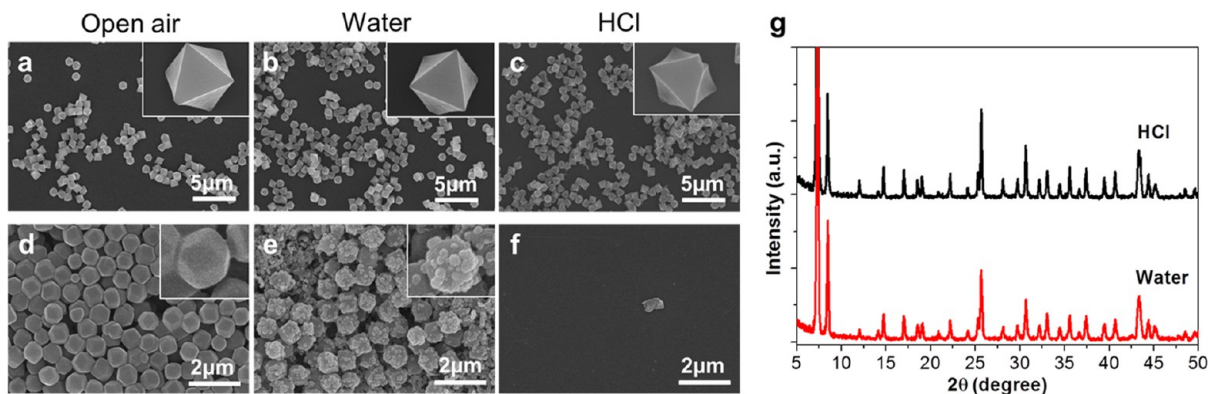
**2.2. Morphology Control.** The polyhedral morphology of CMOFs opens, in principle, a pathway to construct new functional complex structures, especially as recent developments show that coordination modulation can control not only size but also crystal morphology. Early work by Oh et al. reported shape tuning of In-based MOF crystals by a capping reagent (pyridine).<sup>16</sup> In the absence of pyridine, long ( $16 \mu\text{m}$ ) hexagonal rods formed. With increasing pyridine concentration, crystal growth in the direction of the hexagonal facet was effectively blocked, resulting in short hexagonal rods (Figure 1f), hexagonal lumps, and hexagonal discs (Figure 1g).

Kitagawa and co-workers demonstrated the morphological transition (octahedron (Figure 1b)–cuboctahedron–cube) in HKUST-1 crystals with an increase of modulator concentration (lauric acid).<sup>24</sup> This was attributed, based on Monte Carlo coarse-graining modeling study, to the tuning of growth rates in  $\langle 100 \rangle$  and  $\langle 111 \rangle$  directions. The selective capping of specific crystal faces of  $[\text{Cu}_2(\text{ndc})_2(\text{dabco})_2]$  ( $\text{ndc} = 1,4\text{-naphthalene dicarboxylate}$ ;  $\text{dabco} = 1,4\text{-diazabicyclo}[2.2.2]$  octane) was also shown by selectively modulating one node of Cu–ndc with monocarboxylic acid,<sup>17</sup> producing anisotropic structures such as nanocubes (Figure 1a) and nanorods. It is useful to keep in mind that depending on the crystal, a given surfactant may prefer different facets. For example, cetyltrimethylammonium bromide stabilizes  $\{111\}$  facets of HKUST-1 but interacts most strongly with the  $\{100\}$  facets of ZIF-8.<sup>33,34</sup>

Another route to prepare different morphologies is influencing the crystallization process. This laboratory observed  $\text{Al}_{12}\text{O}(\text{OH})_{18}(\text{H}_2\text{O})_3(\text{Al}_2(\text{OH})_4)[\text{btc}]_6 \cdot 24\text{H}_2\text{O}$  (MIL96) in variants of hexagonal bipyramid crystals, such as truncated, nontruncated, rounded, or elongated, by means of changing the reaction solvents.<sup>35</sup> From the crystallization point of view, stable intermediates are alternative viable option for new morphologies. Wiebcke and co-workers isolated gradual shape evolution from cubes with  $\{100\}$  crystal facets to rhombic dodecahedra with  $\{110\}$  facets (Figure 1c) during ZIF-8 microcrystal formation.<sup>25</sup>

### 3. Surface Modification

The structural elements of all MOFs consist of pores constructed by organic ligands; this determines properties such as stability, absorption, selectivity, hydrophobicity, and surface charge. From the synthetic point of view, these properties can be altered by incorporating small molecules or surfactants onto the crystal surface. For example, ZIF-8



**FIGURE 4.** SEM micrographs of UiO-66 (a–c) and ZIF-8 (d–f) CMOFs. Both were (a, d) incubated in open air for 1 month, (b, e) immersed in water for one day, and (c, f) immersed in aqueous hydrochloride solution for one day. The insets show that the UiO-66 particles underwent only minimal changes while ZIF-8 particles were etched significantly by water and completely dissolved by HCl. (g) Powder XRD pattern of UiO-66 after immersion in water and HCl, showing that XRD measurements correlate poorly with direct microscopy-based measures of surface morphology. Unpublished results.

intermediates synthesized using a PVP modulator were found to be more stable than those without modulator.<sup>26</sup> However, additives may interfere with crystal growth.<sup>19,20,24,30,33,34</sup> Hence, postsynthetic surface modification is favored in order to transform the exterior of the crystal without interfering with the overall crystallinity and morphology.

Shell encapsulation by polymers is readily adapted as a method to avoid aggregation or flocculation, because polymers can be physically or chemically adsorbed onto pre-synthesized crystals without altering their postsynthetic shape or morphology. The CMOF zeta potential shifts to near neutral owing to charge screening by adsorbed PVP.<sup>26</sup> Introducing a polymer layer also allows further functionalization because the polymer-wrapped crystal has different surface affinity than the untreated crystal. Extensively, Lin et al. showed that silica shells of tunable thickness can be formed on CMOFs after wrapping them with PVP (Figure 3a).<sup>36</sup>

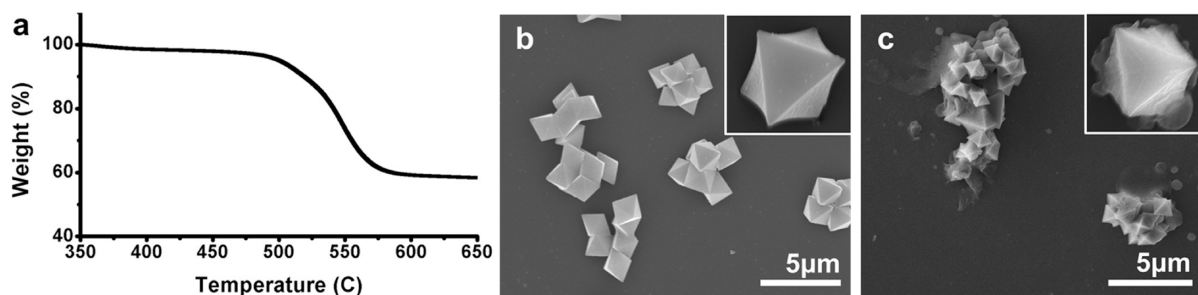
The surface composition and shell thickness of CMOFs can also be tailored down to nanometer thickness using layer-by-layer (LBL) polymer deposition. In this method, complementary polymers are alternately adsorbed using electrostatic or hydrogen bond interactions. Caruso et al. showed that templating a polymer shell onto CMOFs followed by removal of the particle is a viable path to create faceted capsules with high fidelity (Figure 3c, d).<sup>37</sup> These hollow polyhedra present desirable constructs to study nonspherical flow dynamics (Figure 3b, d), as well as shape-specific cellular interactions and uptake. We anticipate that the capacity to fine-tune shell thickness and uniformity on porous structures may also be used to control the selectivity of capture–release of guest molecules and their exit diffusion rate.

Some CMOFs have metal–ligand coordination with surface coordination bonds that can be exchanged with a new incoming ligand of similar coordination strength.<sup>12</sup> This exchange enables incorporation of other functional groups for improving hydrophobicity or incorporating monolayer dye on the surface. Nevertheless as a practical matter, chemical modification is limited by finding a choice of specific reaction conditions that activate only the surface layer without competing with ligands in the inner layers.

## 4. Stability

Because of relatively weak coordination bonds, it is typical for pores to degrade during long exposure to moisture in air; this manifests itself as diminished surface area. Similarly, MOF crystallinity may be destroyed upon contact with water. This creates a challenge in potential applications of CMOFs since water is often unavoidable, and even desirable, in common applications of colloidal chemistry.

**4.1. Water and Chemical Stability.** Bulk crystallinity measurements (X-ray diffraction, IR and Raman spectroscopy, UV–vis fingerprints, or X-ray photoelectron spectroscopy) are not very informative about surface morphology and its stability, which is a serious problem considering that colloidal systems demand structural integrity for further studies and applications. For example, a slight decrease of intensity in X-ray diffraction (XRD) gives no clear mechanistic interpretation about interfacial defects. This of course is an issue already when dealing with bulk MOFs, but when dealing with CMOFs, the problem is exacerbated as surface properties are so important in these systems made up of micrometer-scale particles, whose surface-to-volume ratio is relatively large. To assess surface stability directly, one



**FIGURE 5.** (a) Thermal gravimetric analysis of colloidal UiO-66 in this laboratory indicates that the 2 µm particles have comparable thermal stability to their bulk counterpart. SEM images taken in this laboratory show that the particle morphology was retained after heating at (b) 400 °C for 3 h, whereas amorphous carbon formed around the microcrystals, and (c) 600 °C for 3 h. Unpublished results.

needs morphology-specific measurements such as SEM, TEM, or AFM of which sample properties are repeatable from place to place.<sup>35</sup> For example, Yang et al. sought to use SEM to infer stability of MOF-177 upon exposure to water vapor in air,<sup>38</sup> but the SEM comparisons were ambiguous since the MOF morphology was variable, and the large standard deviation of the MOF size worked against their conclusion that MOF-177 is unstable, in spite of the fact that the average size seemed to decrease. In order to assess stability of MOFs, it is desirable to synthesize uniform and well-defined crystals and to inspect them both in local spots and over wide areas.

Among thin film MOF systems, UiO-66 has exceptional water stability.<sup>39</sup> This laboratory has compared, using SEM, the stability of ZIF-8 and UiO-66 surface morphology by immersing the samples in water, aqueous hydrochloride solution (pH = 1), and air. Exposure to ambient moisture for one month caused the facets of ZIF-8 crystals to become blunt at their previously sharp edges (Figure 4d). Immersion in water was even worse; the surface of ZIF-8 was etched severely after one day immersion and dissolved under acidic conditions (Figure 4e,f). On the other hand, we found no major change in the surface morphology of UiO-66 when exposed to air or immersed in water (Figure 4a,b). The UiO-66 particles were only slightly etched in strong acid solution as shown by the damaged particle in Figure 4c, inset. It is instructive to contrast these SEM findings with power XRD measurements, where all diffraction peaks were still observed and their intensity did not significantly decrease (Figure 4g). This lack of correlation with degradation of surface morphology highlights the importance of checking the surfaces by direct microscopic characterization.

**4.2. Physical Stability.** Most MOFs can withstand temperatures up to 150–350 °C without losing their framework stability, despite their susceptibility to chemical etching.

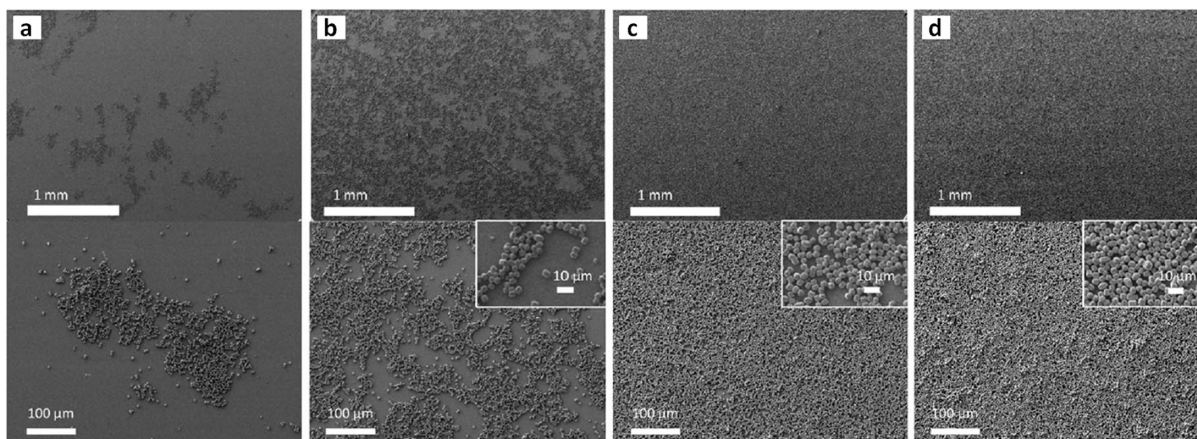
However, prolonged exposure to higher temperature will decompose the organic ligand into amorphous carbon and will degrade the metal ion into oxide. We found that CMOFs retain the physical properties of the bulk MOF material. As an example, UiO-66 particles were subjected to thermal gravimetric analysis (TGA) at the rate of 10 °C/min (Figure 5). The thermal stability was shown to be equal to the known reported value (>500 °C).<sup>39</sup>

#### 4.3. Designing Environmental Stability into CMOFs.

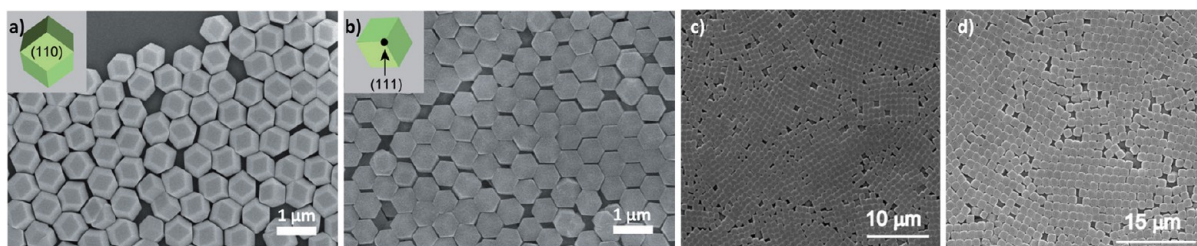
Water stability, chemical tolerance, and strong endurance to harsh conditions are some CMOF prerequisites that still need development to suit particular end-use purposes. Aside from the underlying crystal network stability,<sup>40</sup> it is possible to modulate the coordination bond strength or surface energy by using the methodology of colloidal chemistry. For example, ZIF-8 intermediate crystals with exposed {100} facets lose their morphology upon prolonged immersion time; however, this can be prevented by surface stabilization with PVP.<sup>26</sup>

## 5. Assembly

When thinking of the porous structure of MOFs, it is not traditional to consider how pores between different grains of the same material meet one another. On the other hand, in the field of colloids, there is intense interest to achieve anisotropic assembly. In that context the available shapes are mainly based on chemical anisotropy (Janus and patchy spheres), physical deformation (stretched, swelled, and dimpled particles), and template-assisted synthesis (spindles, peanuts, and cubes).<sup>23</sup> Attaining shape anisotropy with CMOFs is easier because these faceted crystals are intrinsically anisotropic and their sizes fall in the convenient size range of nanometers to micrometers. The assembly of CMOF-based polyhedra is attractive from another point of view also: their porosity imparts to them a density considerably less than oxide or metal particles, so sedimentation is



**FIGURE 6.** Surface coverage of  $[\text{Al}_{12}\text{O}(\text{OH})_{18}(\text{H}_2\text{O})_3(\text{Al}_2(\text{OH})_4)(\text{btc})_6]_n$  particles after transfer from a LB trough.<sup>41</sup> The surface area was progressively decreased from panels a to d. Reprinted with permission from ref 41. Copyright 2012 Royal Society of Chemistry.



**FIGURE 7.** Monolayer lattice orientation formed by capillary induced assembly.<sup>12,20</sup> SEM images of dried ZIF-8 show crystal orientation on a silica substrate: (a)  $\langle 110 \rangle$  and (b)  $\langle 111 \rangle$ . SEM images of lattice orientation in (c) edge- and corner-rounded cubes and (d) truncated cubes of soc-MOF crystals after drying on substrate. Reprinted with permission from ref 12 (copyright 2012 John Wiley and Sons) and ref 20 (copyright 2012 American Chemical Society).

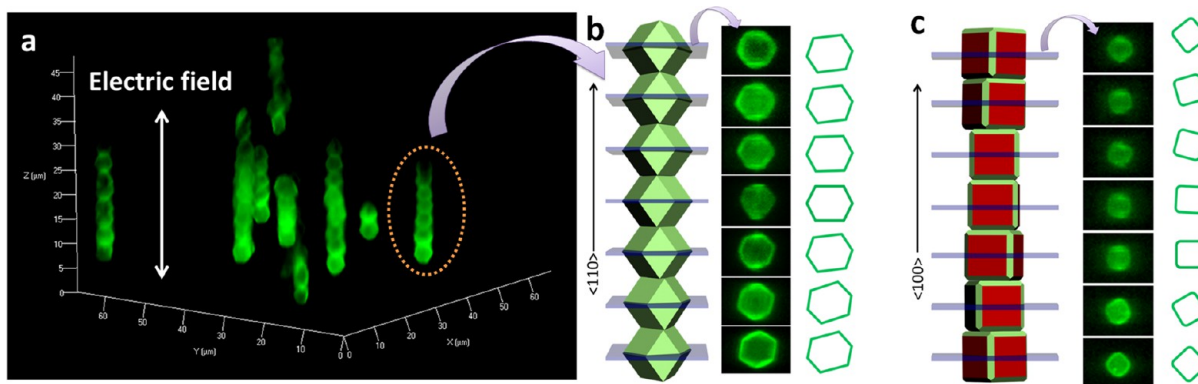
less severe. Beyond simply the creation of MOF arrays by *in situ* approaches, CMOF assembly into superstructures is still at an early stage.

Kitagawa et al. used the Langmuir–Blodgett (LB) technique to produce good packing of CMOFs at the liquid–air interface.<sup>41</sup> The area of CMOF particles spread on the liquid was reduced incrementally to compress the particles into a monolayer film. Preferential crystal orientation was observed upon transferring the layer onto solid substrates, but close packing was not observed due to particle polydispersity (Figure 6). Similar methods of interface assembly were also shown by Huo and co-workers.<sup>42</sup>

Directional capillary forces can be used to pull crystal facets together. This laboratory<sup>12</sup> and Eddaoudi et al.<sup>20</sup> showed that drying uniform CMOFs on a solid substrate creates two-dimensional alignment (Figure 7) and domains of close-packed monolayer. This interaction is also relevant in considering three-dimensional packing under the influence of sedimentation.<sup>42</sup> Facet-to-facet alignment makes CMOFs viable candidates as templates for surface patterning or filling without the need for lithography.

The versatility of facet-to-facet ordering presents an approach to build 3D structures. To accomplish this, interactions between particles must be induced *in situ*, and the attraction source should acknowledge the anisotropic nature of the CMOF. The simplest *in situ* directed assembly was demonstrated by screening the surface charge between ZIF-8 rhombic dodecahedra<sup>12</sup> by adding salt to reduce the Debye length to the point that electrostatic repulsion overwhelmed van der Waals attraction. Orientational alignment of flat facets produced regular clusters and fcc packing. Most important of all, the regular dimensions and regular angles of the CMOF building blocks were preserved and transferred.

Complexity in aligning CMOF facets can be introduced when dipolar attraction is induced by an external electric field.<sup>3</sup> Alternating voltages at appropriate frequencies induce dipoles, causing CMOF particles to collapse into linear chains, while van der Waals attraction ensures that particles join facet-to-facet. This directional preference maintains the  $\{110\}$  facets of rhombic dodecahedra in linear chains. In contrast, truncated rhombic dodecahedra formed with random facets of  $\{100\}$  and  $\{110\}$  along the chain, which



**FIGURE 8.** Directional assembly of ZIF-8 driven by external AC electric field at 1 MHz.<sup>26</sup> (a) Confocal images of linear chains parallel to the direction of electric field. Confocal cross sections of chains made from (b) rhombic dodecahedra and (c) truncated cubes illustrate random orientation in the plane perpendicular to electric field. Reprinted with permission from ref 26. Copyright 2013 American Chemical Society.

remain linear, indicating equal chance of joining these facets. Dipole-induced selectivity, favoring one facet over the other, is effective only when the area differences between facets is rather large. In this case, chains assemble to join the largest facets. In principle, the assembly preference between  $\{110\}$  and  $\{100\}$  facets in turn should influence which pores connect from one particle to another (Figure 8).

## 6. Future Directions

This Account has summarized the present state of the art regarding preparation and assembly of CMOF materials, with specific attention to CMOF assembly over large areas, at interfaces, and in an anisotropic fashion (Figure 9). In this rapidly developing field, it is anticipated that potential applications will follow from other aspects of this interdisciplinary concept. Here we propose an anticipated prediction of potential applications in various research fields from the predicted potentials of colloidal MOFs in this early stage.

The various distinct shapes of CMOFs provide an encouraging system in which to produce new ordered structures (Figure 9a) that could provide an experimental platform in which to test various predictions from computer simulations whose existence awaits experimental verification.<sup>43,44</sup> Till the present, only a few simple ordered structures have been prepared from CMOFs,<sup>12,20,26,42</sup> but clearly, there are other possibilities. These include open structures such as diamond and zeolite, anisotropic structures such as graphite, and quasicrystal orderings, all of which remain major challenges in assembly using colloidal particles whose shape is traditional.<sup>21</sup>

It is also an exciting challenge to make dynamic ordered structures, such as liquid crystals and plastic crystals and rotator phases, which are predicted to be formed for

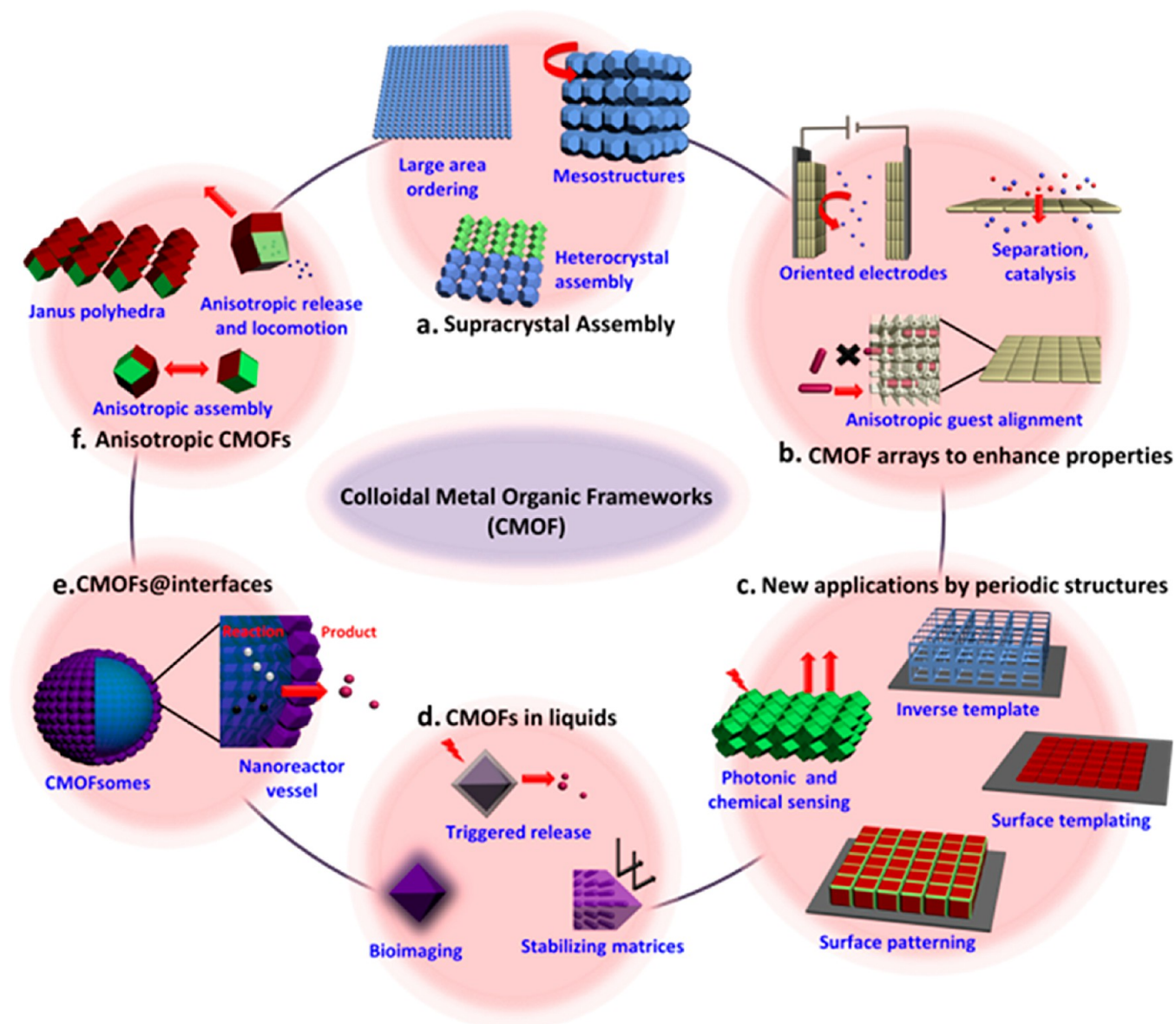
some polyhedra in certain ranges of volume fraction (Figure 9a).<sup>43,44</sup> Note that in the theoretical simulations to date, the polyhedra that have been considered are “hard” particles without interparticle attractions, and entropy maximization is the only force to order them. However, facet-to-facet attraction is found to be significant in the laboratory systems investigated to date.<sup>12,26</sup> The issue is especially relevant practically, when it comes to achieving large-scale (centimeter scale) ordered structures without many defects, which will be necessary to fulfill the promise of real applications based on self-assembly.

Beyond the assembly of polyhedra of just one kind, there is great potential to mix polyhedra: different sizes, shapes, or materials (Figure 9a). This will require particles quite monodisperse in size and shape, but if successful, one could find surprises.

Ordered arrays of CMOFs present another direction of opportunity (Figure 9b). For example, the control of crystal orientation in densely packed CMOF arrays could align the pores and maximize not only their separation capabilities but also their catalysis capabilities.<sup>13</sup> The ability to produce such orientational control of CMOFs could also enhance the photonic and electric properties intrinsic to such frameworks. Aligned MOF channels could also be useful to orient functional guest molecules anisotropically. This could produce anisotropic luminescence, nonlinear optic properties, and electric properties. The recently reported remarkable redox capacity and high ionic conductivity of MOFs could be improved by engineering crystal arrangements, with a view toward applications as battery electrodes and solid electrolytes.

Other applications follow logically (Figure 9c). It has been proposed that periodic supracrystal architectures can serve





**FIGURE 9.** Perspective on colloidal metal–organic framework particles (CMOFs).

as photonic band gap materials. Unlike existing photonic crystals, these new materials possess internal porosity. Selective adsorption of specific molecules could modulate photonic properties of the material, perhaps providing efficient chemical sensing.<sup>9,45</sup> Lithography techniques cannot provide periodic complex three-dimensional nano- or micrometer-scale surface patterns of this kind (Figure 9c). As templating materials, the combination of macroscale and nanopore structure may be interesting for transcription to target materials.

The monodisperse, nanoporous makeup of CMOFs can be attractive for engineering the uptake and release kinetics in liquids (Figure 9d). It should be possible to control release profiles after surface modification; to accomplish this, possibilities include modification with polymers, silica,

and molecular amphiphiles including lipids.<sup>14</sup> Another interesting challenge is triggered release; guest actives could be released from CMOF nanopores by chemical and physical stimuli after CMOF surfaces are modified with stimuli-responsive materials (triggered gate-opening). In potential biomedical contexts, surface functionalization of CMOFs with cell-targeting moieties may enhance their delivery to cancer cells to allow for target-specific bioimaging.<sup>11</sup>

As shown in Figure 9e, CMOFs offer potential applications when bound to liquid/liquid or liquid/air interfaces.<sup>46,47</sup> They could work as solid surfactants to stabilize emulsions to produce colloidosomes (CMOFsomes), in which small oil (water) droplets surrounded by CMOFs are stably dispersed in water (oil). The advantage over conventional colloidosomes

is the potential to become reaction systems when molecules in either oil or water phases enter the CMOF nanopores and react inside.<sup>48</sup> Considering the huge surface area of CMOFs, one can expect highly efficient reactions.

Selective facet functionalization is insufficiently developed. Presently there is growing interest in Janus particles for colloidal engineering through anisotropic interparticle interactions,<sup>22</sup> but the shapes of conventional Janus particles are limited to simple shapes such as spheres and rods. Janus polyhedral CMOFs can be fabricated by directional deposition of metal or metal oxides onto CMOF monolayers that have been prepared previously (Figure 9f). With this approach, one could selectively modify a limited subset of facets, for example, 5 of 12 facets of rhombic dodecahedra. Presently it is very challenging to make monodisperse clusters comprised of defined numbers of Janus particles, and simple tetrahedra are the only known example.<sup>49</sup> Predicated on selective as well as directional facet-to-facet attraction, Janus CMOFs could become a promising platform for producing new exotic structures.

The emerging field of active materials is also relevant when one considers particles whose surface chemical makeup is asymmetric. For example, metal-coated Janus CMOFs could show chemotaxis: asymmetric release of preloaded guest molecules from noncoated surfaces should cause concentration gradients in solution (or at liquid–air interface, asymmetric change in surface tension of surrounding liquid), and these may be sufficient to produce self-sustained motion, potentially with feedback resulting in collective “schooling” behavior.

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#### FOOTNOTES

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