

Synthesis and Self-Assembly of Monodispersed Metal-Organic Framework Microcrystals

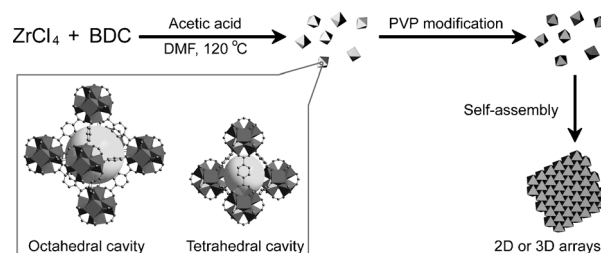
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Self-assembly of monodispersed objects with sizes ranging from nanometers to millimeters offers a useful route to new functional materials and devices featuring two-dimensional (2D) or three-dimensional (3D) ordered structures that are not easily achieved with conventional photolithography-based microfabrication techniques.^[1] Beyond classic spheres,^[2] non-spherical building blocks^[3] such as ellipsoids,^[4] dumbbells,^[5] rods,^[6] stars,^[7] octapods,^[8] and polyhedrons^[9–12] have attracted increasing interest due to advances in colloidal synthesis that enable the precise control over the size and shape of colloidal particles. In particular, self-assembly of polyhedrons made of crystalline materials such as metals,^[9] oxides,^[10] and semiconductors^[11] has been extensively investigated from both the theoretical^[12] and experimental viewpoints in recent years.

Metal-organic frameworks (MOFs), a new class of crystalline materials, are synthesized by assembly of metal ions or clusters with organic linkers.^[13] MOFs display permanent microporous structures with large surface areas, regular but tunable cavity sizes, and tailorable chemistry, and thus show great promise for wide applications including gas storage,^[14] molecule separation,^[15] heterogeneous catalysis,^[16] chemical sensing,^[17] and drug delivery.^[18] In the past few years, many efforts have been undertaken in MOF synthesis to control the size^[19–22] and shape^[23] of MOF crystals since these parameters can significantly impact certain properties of bulk materials, for example, gas sorption,^[19] and indeed are critical for biological applications.^[18,20] Meanwhile, MOF crystals with small sizes can be processed easily into thin films and membranes through dip-coating^[24] or spin-coating,^[25] and further, oriented MOF films can also be prepared with crystals of regular shapes and with the aid of the Langmuir–Blodgett (LB) technique.^[26] In this regard, MOF crystals with uniform size and shape will facilitate not only the control over the thickness of oriented films but also the formation of 2D or 3D ordered structures by bottom-up self-assembly. Nevertheless, relevant work is just beginning, and

only 2D self-assembly of MOF microcrystals has been realized recently.^[27] Challenges in this emerging area are the synthesis of monodispersed MOF crystals with uniform sizes and shapes as well as the exploration of appropriate assembly techniques.

Here, we report 1) the acetic acid-modulated synthesis of monodispersed octahedral microcrystals of a zirconium-carboxylate MOF material, UiO-66 (UiO stands for University of Oslo), 2) the preparation of oriented MOF films with controlled thickness based on the assembly of large-area 2D monolayers of a microcrystal, and 3) the formation of long-range 3D superlattices of MOF microcrystals through a sedimentation technique (Scheme 1). UiO-66 is a chemically



Scheme 1. Schematic representation for the synthesis, modification, and self-assembly of monodispersed UiO-66 octahedral microcrystals that possess tetrahedral and octahedral cavities.

robust and thermally stable MOF material and was first synthesized in intergrown crystal form by Lillerud et al.^[28] Subsequent work by Behrens et al. showed that shapes of UiO-66 crystals can be effectively modulated from intergrown morphologies to well-defined octahedrons by adding benzoic acid or acetic acid.^[23g] However, monodispersed crystals were not obtained under the investigated experimental conditions. We found that this acetic acid-modulated synthesis is indeed capable of producing octahedral UiO-66 microcrystals with uniform sizes if concentrations of metal ions, organic ligands, and modulators in the reaction are carefully chosen.

In a typical synthesis, ZrCl_4 and 1,4-benzendicarboxylic acid (BDC) were dissolved in *N,N*-dimethylformamide (DMF) containing acetic acid and then placed at 120 °C for 24 hours. With a fixed molar ratio of metal ion/ligand of 1, concentrations of ZrCl_4 , BDC, and acetic acid were systematically varied (see the Supporting Information). Products

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were collected by centrifugation and washed consecutively with DMF and methanol. Scanning electron microscopy (SEM) measurements revealed that the optimal concentrations of reactants for producing monodispersed UiO-66 octahedral crystals are 1.6 to 3.2 M for acetic acid and 7 to 20 mM for ZrCl_4 (or BDC), respectively (see the Supporting Information). Figure 1a shows a typical SEM image of inter-

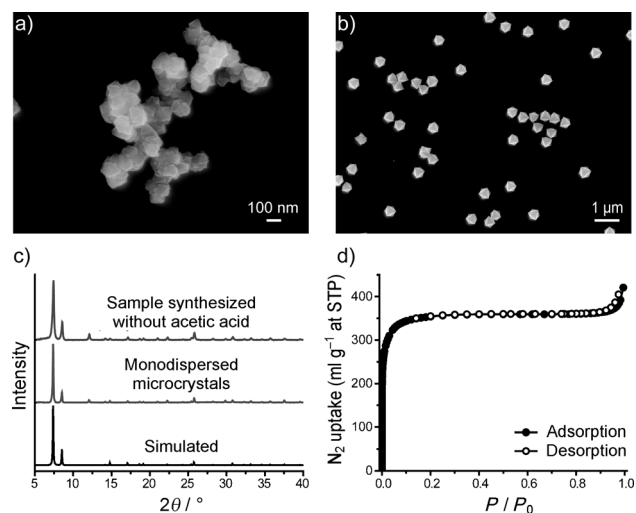


Figure 1. SEM images of a) intergrown crystals synthesized in the absence of acetic acid and b) monodispersed octahedral microcrystals synthesized with 15 mM ZrCl_4 , 15 mM BDC, and 2.4 M acetic acid. c) XRD patterns of the samples shown in panels a and b. d) Nitrogen sorption isotherm for monodispersed UiO-66 octahedral microcrystals at 77 K up to 1 bar.

grown crystals in a sample synthesized in the absence of acetic acid. Figure 1b shows a representative SEM image of monodispersed octahedral microcrystals with an average edge length of 409 ± 29 nm prepared with 15 mM ZrCl_4 , 15 mM BDC, and 2.4 M acetic acid. Under optimized conditions, competitive coordination of acetic acid molecules to zirconium ions influences not only the shape^[23 g] but also the nucleation of MOF crystals. SEM measurements of samples obtained at reaction times of 90 minutes, 6 hours, and 10 hours, respectively, under optimized experimental conditions (see the Supporting Information) indicate that all products consist of particles with a narrow size distribution, thereby suggesting that UiO-66 MOF microcrystals nucleate in a short period of time and grow gradually in size without the occurrence of new (or secondary) nucleation. X-ray diffraction (XRD) measurements (Figure 1c) show that the sample consisting of monodispersed octahedral microcrystals shown in Figure 1b contains narrower peaks in its diffraction pattern than that of the sample synthesized without acetic acid, suggesting larger grain sizes in octahedral microcrystals. In nitrogen sorption measurements (Figure 1d), type I isotherms with steep increases in N_2 uptake at a low relative pressure (<0.01) were observed for all activated UiO-66 samples, thereby indicating a microporous nature. The calculated gravimetric Brunauer–Emmett–Teller (BET)

surface area of octahedral microcrystals was $1376 \text{ m}^2 \text{ g}^{-1}$, a value much larger than that of the sample synthesized in the absence of acetic acid ($773 \text{ m}^2 \text{ g}^{-1}$, see the Supporting Information), consistent with a previous report.^[23 g]

Very recently, Granick et al. have demonstrated the 2D self-assembly of monodispersed rhombic dodecahedral crystals of a zeolitic imidazolate framework material, ZIF-8, by casting the colloidal solution on a solid platform.^[27 a] In fact, however, it is not easy to produce a large-area uniform 2D monolayer with the casting technique. An alternative strategy is to utilize techniques based on liquid–air interfacial assembly, for example, the LB technique.^[26] We used a method^[29] that is similar to the LB technique in principle but accessible to common laboratories as it does not require specialized equipment. Briefly, a loose monolayer of crystals is first formed on a still water surface through surface tension gradient-driven spreading of a suspension of polyvinylpyrrolidone (PVP)-modified crystals (PVP modification improves the phase stability of crystals in a dispersant; herein, a mixture of ethanol and water was used). Subsequently, crystals are consolidated by adding a few drops of an aqueous solution of sodium dodecyl sulfate (SDS) to change the surface tension of water. Figure 2a shows a 2D monolayer with a continuous area larger than 10 cm^2 formed on the water surface. The obtained monolayer is robust enough to be easily transferred to a solid platform. Figure 2b shows a typical SEM image of the transferred 2D monolayer on a silicon platform. The monolayer consists of small domains where octahedral crystals are ordered in a hexagonal close-packed array with their {111} facets contacting the platform.

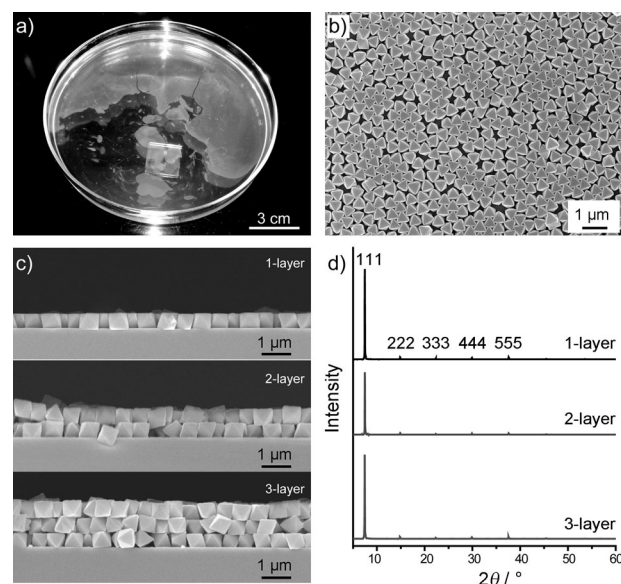


Figure 2. a) Photograph of 2D monolayer assembled from monodispersed UiO-66 octahedral microcrystals on the water surface in a Petri dish of 14 cm diameter. b) SEM image of a 2D array of monodispersed UiO-66 octahedral microcrystals in a transferred monolayer on a silicon platform. c) Cross sectional SEM images and d) out-of-plane XRD patterns of silicon platform-supported thin films comprising one, two, and three monolayers of microcrystals prepared by repetition of the transfer process.

The lack of a long-range crystalline order in the obtained 2D monolayer is presumably because the consolidation process upon addition of SDS is too fast for microcrystals to pack together with an identical orientation in all directions; this might be improved by consolidating crystals slowly using the standard LB technique.^[9d] Films composed of multiple monolayers supported on solid platforms can be made in a layer-by-layer manner by simply repeating the transfer process (Figure 2c) without disturbing the orientation of the crystal monolayers (Figure 2d). An advantage of the use of monodispersed crystals is that the thickness of films prepared with this technique can be precisely tuned by the number of transfer cycles.

Yang et al. have recently investigated experimentally and computationally the 3D self-assembly of PVP-modified silver octahedral crystals by sedimentation.^[9a] Millimeter-sized 3D superlattices were successfully prepared, and the polymer layer adsorbed on the surface of silver octahedrons was found to play an important role in the self-assembly process: it provides silver crystals with strong entropic repulsion to prevent them from forming disordered aggregates caused by van der Waals attractions. Inspired by this work, we dispersed PVP-modified UiO-66 microcrystals in water and allowed them to sediment slowly under gravity in a glass pipette with a flame-sealed tip. SEM measurements show that long-range 3D superlattices comprising PVP-modified UiO-66 octahedral crystals can be obtained after removal of the supernatant and drying of the samples (Figure 3a). In a cleaved facet of an obtained 3D superlattice, MOF octahedrons are ordered in a hexagonal array and form close-packed, oriented layers that, in turn, stack in a face-to-face fashion (Figure 3b).

In summary, we have demonstrated that monodispersed octahedral microcrystals of UiO-66 can be synthesized, under optimized experimental conditions, by using acetic acid as a modulator. Taking advantage of the uniform size and shape of the obtained MOF crystals, we have produced large-area 2D oriented monolayers on a water surface through a liquid-air interfacial assembly technique. The obtained monolayers can be further transferred easily to a solid platform to form oriented MOF films with a controlled thickness. More importantly, self-assembly of monodispersed MOF crystals into long-range 3D superlattices has also been realized for the first time by simple sedimentation. Previous^[27] and present work illustrates that self-assembly will be a useful route for preparing MOF-based functional materials and devices with ordered structures.^[30]

Experimental Section

A mixture of ZrCl_4 and BDC was dissolved in 10 mL of DMF containing acetic acid in a 9 dram borosilicate glass vial. The molar ratio of metal ion/ligand was fixed at 1, and concentrations of ZrCl_4 , BDC, and acetic acid were systematically varied (see Table S1 in the Supporting Information). The vial was capped and placed at 120°C for 24 h. Subsequently, the product was collected by centrifugation, washed three times with DMF, and soaked in methanol at 60°C for three days with replacing the

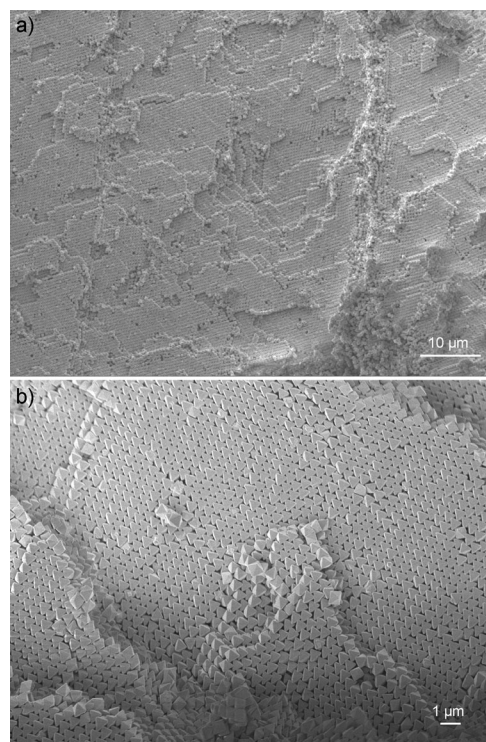


Figure 3. a) Low-magnification and b) high-magnification SEM images of a cleaved facet of a long-range 3D superlattice assembled from monodispersed UiO-66 octahedral microcrystals by sedimentation.

soaking solvent every 24 h to exchange DMF. Finally, the product was washed three times with methanol. It should be noted that the average size of microcrystals varies slightly from batch to batch even under the same experimental conditions.

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