Supraparticles

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Directional Self-Assembly of a Colloidal Metal–Organic Framework**

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Materials science is at an early stage of learning to employ anisotropic interaction in self-assembly.[1–7] One important approach towards this goal involves the study of nm-sized particles, but we note two limitations: first that this is a rather special case as the range of inter-particle interaction in suspensions is typically likewise nm in size, and secondly that the diffraction limit precludes visualizing adjacent nm-sized particles optically at the single-particle level. Among the various nm-sized particles that are known, polyhedra are particularly interesting.[8,9] That new structures might result from the self-assembly of polyhedra was suggested by Monte Carlo simulation predictions of various non-trivial ordered structures or complex mesophase structures.[10–12] Here, we report an experimental approach to extend the self-assembly of polyhedra to larger, colloidal scales. Metal-based particles have already been designed to this end;[13,14] here we consider a different class of materials, which may offer a greater variety of colloidal building blocks and attainable applications.

Metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) are recently developed materials prepared by co-crystallization of metal ions and bridging organic ligands; they offer a wide range of potential applications, among them gas storage, separation, catalysis, and drug delivery.[15–22] These might be augmented if combined with aspects of particle self-assembly, which presents several potential advantages. First, the extension of MOF features to µm-size scales may allow interesting interactions with light, enabling photonic and sensing applications.[23,24] Second, the extension to the volume included in µm-sized particles may allow interesting gas and other adsorption/release features that because the positions of the particles can be controlled, goes beyond present-day applications in which MOF elements are fixed in space. Third, the nontrivial, nonspherical shapes of µm-sized MOFs may be useful for surface patterning and surface templating. While it is true that these applications remain to be realized, they provide motivation for studies of this kind.

The robustness and high porosity of MOFs are suited for colloidal self-assembly, in which materials should have chemical/physical stability in liquid dispersion; moreover, sedimentation should be a minor issue as the density of MOFs is close to that of most solvents. Here we show the first example of supraparticle self-assembly of MOF crystals. A directional facet-to-facet attraction between particles through simple capillary or van der Waals attractions leads to the formation of well-defined clusters and hexagonal arrangements (Figure 1).

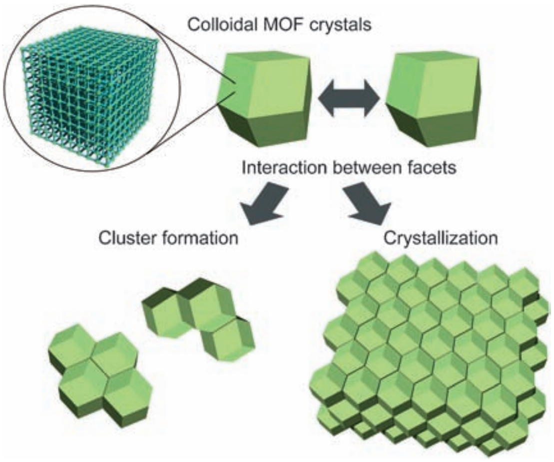

Figure 1. Various pathways for colloidal metal–organic framework (MOF) crystals to self-assemble into supraparticle structures.

For the proof of concept presented here, we worked with prototypical MOF particles, $[Zn(mim)_2]_n$ (ZIF-8;[25] mim = 2-methylimidazolate), which have rhombic dodecahedra morphology.[26,27] Applications of these particles in preparing gas separation membranes and nanofibers are known.[28,29] Infrared (IR) spectra, X-ray powder diffraction (XRPD) measurements, and vapor-uptake experiments shows that the particles are chemically pure and they have good crystallinity and porosity (Supporting Information, Figures S1–S3). Scanning electron microscopy (SEM) images show that monodisperse particles resulted with distinctive morphology and flat rhombic facets (Figure 2a). We found that these particles could be readily suspended in various solvents, including methanol, ethanol, isopropyl alcohol, ethylene glycol, and *N*,*N*-dimethylformamide (DMF), forming stable colloidal dispersions. Particle size analysis by dynamic light scattering showed an average particle size of 830 nm and a relatively narrow size distribution of 9% (Figure S4). The zeta potential of +48 mV, expected to be the same as nanoparticles of the same material as this surface property should not depend on particle size, was confirmed.[26]

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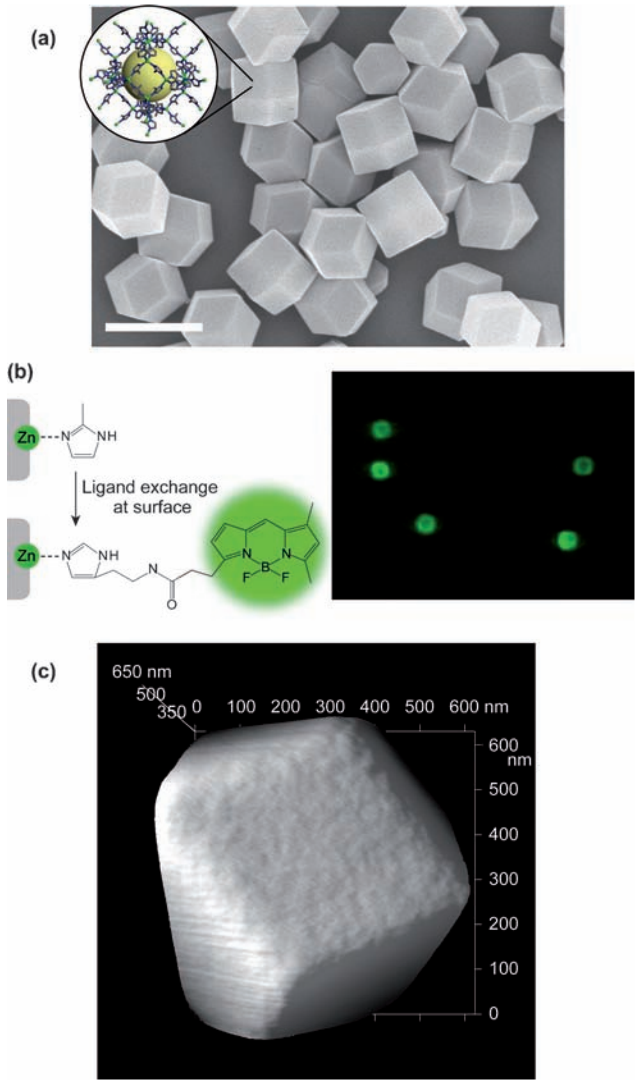

Figure 2. a) Typical SEM image of a dried suspension of original $[Zn(mim)_2]_n$ particles. Scale bar = 1 μm. Inset shows the crystal structure of $[Zn(mim)_2]_n$. b) Dye modification at the crystal surface and fluorescence image, in liquid suspension, of particles whose surfaces are functionalized with fluorescent dye (excitation at 488 nm). c) AFM image of of a typical dye-modified particle.

To visualize the self-assembly of these colloidal-sized objects while still in liquid suspension, first they were functionalized at the surface with fluorescent dye, capitalizing on the recent report that surface carboxylate ligands of submillimeter MOF crystals can be easily exchanged by carboxylate groups attached to fluorescent dye.[30] In this sense, we modified surfaces by dispersing the particles in methanol solution of a BODIPY dye containing an imidazole group (Figure 2b). The porous structure was not affected by the dye modification, as evidenced by IR spectra, XRPD measurements, and vapor-uptake experiments (Figures S1–S3). The morphology, size, and zeta potential of the particles did not change after the surface modification (Figures S4, S5). In confocal microscopy, we observed bright images in which the outlines of the particles were easy to resolve. Atomic force microscopy (AFM) confirmed that the original and dye-modified particles possess flat particle facets—not concave, not convex (Figures 2c, S6, S7). Peak-to-peak surface roughness of the dye-modified particle was ca. 2 nm and the root-mean-square roughness 0.6 nm, and these values are close to those of the original particle. As photolithographic methods do not offer such flat features, this underscores one advantage of crystalline particles relative to other kinds.[2,3] Capillary attraction, used previously to assemble lithographically produced particles,[13] is expected to be augmented in these MOF systems because when they come together, van der Waals attractions between flat surfaces should hold them together.

Self-assembly was examined in two situations, solvent drying and in situ suspension. We began with solvent drying as if particles would fail to self-assemble under this severe condition, they could hardly be anticipated to do so in liquid suspension. As the original $[Zn(mim)_2]_n$ particles were slowly dried over a Si wafer, we found that evaporation from methanol and isopropyl alcohol dispersions left no regular structure behind, but that drying 1 wt% dispersions in DMF at 60 °C produced close-packed hexagonal arrangements with crystal orientation in the $\langle 111 \rangle$ direction, implying the existence of directional capillary forces between the facets (Figure 3a).[13,31] This is reasonable upon considering that the slower evaporation of DMF might allow sufficient time for particles to rearrange to form the most stable structure. Defects were of course observed: there were some cracks between the ordered particle due to shrinkage of liquid bridges between the facets, and different orientations close to the surface were observed, which might be attributed to capillary attraction between the particle facets and the substrate surface (Figure S8).[32] Some particle multilayers were observed at this concentration, but by reducing the particle concentration to 0.05 wt%, it was possible to fabricate monolayers (Figure 3b). Interestingly, the particles emerged arranged in loose hexagonal packing that contained short-range translational order but mesophase orientational disorder, which is understandable because directional capillary forces between the particle facets and the substrate surface might dominate, resulting in $\langle 110 \rangle$ orientation of crystals. The overall crystal orientation was evaluated from out-of-plane X-ray diffraction (XRD) patterns of these hexagonal assemblies. In addition to the 222 reflection, we also found other peaks such as 110 and 220 for multilayers of particles, probably stemming from disordering close to the surface and cracks, but for monolayers, it was better: just three dominant peaks were observed, from the $\{110\}$, $\{220\}$, and $\{440\}$ planes, confirming that crystal orientation had been controlled in the $\langle 110 \rangle$ direction preferentially.[21,29] This proof of concept potentially might expand the feasibility of using colloidal MOFs as functional patterning materials.

For in situ confocal optical examination of the dye-modified particles, the solvent was selected to be ethylene glycol in part because of its non-volatile nature, in part because its refractive index of 1.43 is closer than that of many organic solvents to that of the particles themselves, which has been estimated to be 1.54,[28] thus reducing the magnitude of van der Waals attraction relative to what it would be in those other liquids. Electrostatic repulsions between the particles

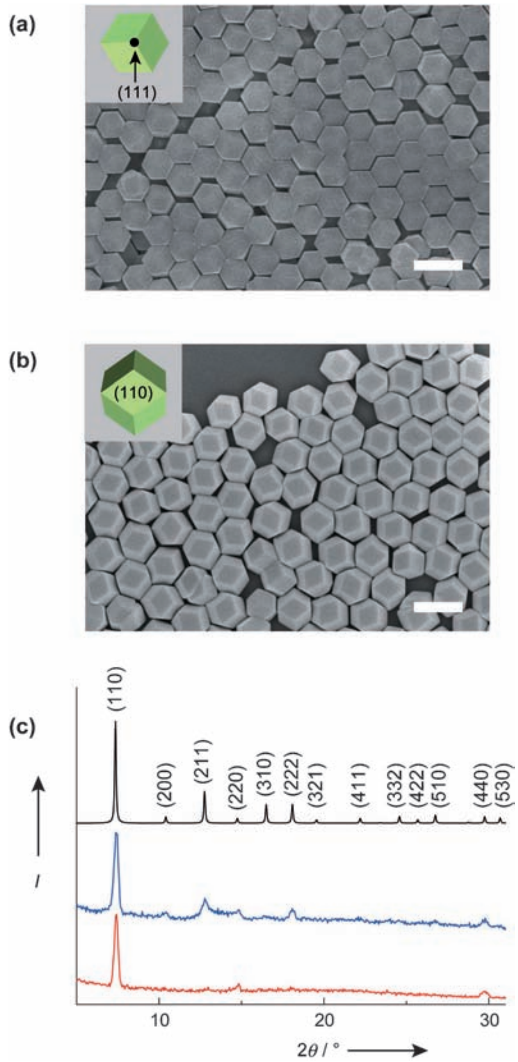

Figure 3. SEM images of assembled original particles after evaporation from a) a 1 wt% DMF dispersion and b) an 0.05 wt% DMF dispersion. Insets show the underlying crystal orientation. Scale bar = 1 μm. c) XRD patterns of simulated ideal powder (black) and actual self-assembled structures after evaporating a 1 wt% DMF dispersion (blue) and an 0.05 wt% DMF dispersion (red) of the original particles.

were screened by adding 1 mM sodium nitrate, resulting in a Debye length of 6.7 nm. We observed linear, triangular, and U-shaped trimers (Figure 4a), and linear, rhombic, and square tetramers (Figure 4b). A key point was that we always observed regularity: regular distance between the particles, regular mutual orientation. For example, that in the U-shaped trimers the bond angle was always the same highlights the fact that orientational order was the rule. It should be noted that these clusters can be portions of a face-centered-cubic (fcc) lattice in which rhombic dodecahedra completely fill space. In addition to clusters, we also observed fcc packing of the particles (Figure 4c). Note that the BODIPY dye is used just for imaging and does not affect the assembled structures, because particle size and shape, surface roughness, and zeta potential were not changed by the dye modification.

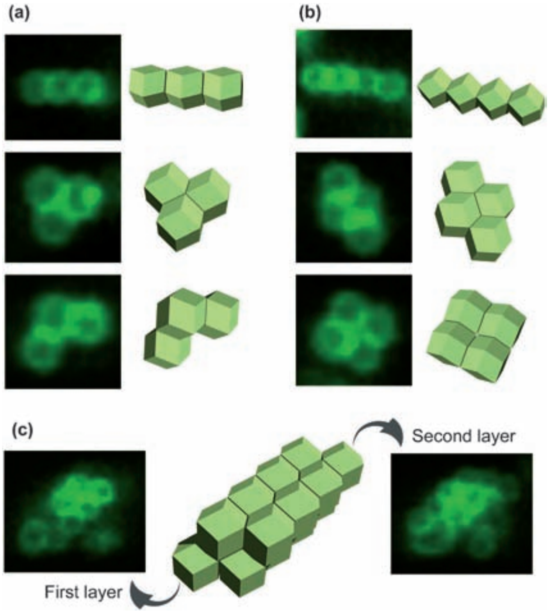

Figure 4. Confocal microscopy images of dye-modified particles and accompanying schematic illustrations. a) Trimers were linear, triangular, and U-shaped. b) Tetramers were linear, rhombic, and square. c) Larger structures exhibited a fcc packing.

These observations show that directional facet-to-facet attraction produced not just positional but also orientational order, requiring only the proper choice of solvent and salt concentration, the van der Waals attractions between flat facets appearing to be sufficient to drive directional self-assembly without need for depletion or other externally-driven sources of attraction.[2,3] Though in the present study all facets of the polyhedral were chemically equivalent, we imagine generalization based on rendering them chemically inequivalent; this could be implemented by directional coating of the monolayers demonstrated in this paper.[4,33] Although the development of long-range 3D periodicity will require additional development, the possible generalization of this concept to include building blocks of other polyhedral shape is evident.

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