

Organic Nanocrystals of the Resorcinarene Hexamer via Sonochemistry: Evidence of Reversed Crystal Growth Involving Hollow Morphologies

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S Supporting Information

ABSTRACT: Nano- and micrometer-scale crystals of a self-assembled hexamer have been synthesized via sonochemistry. The application of ultrasonic irradiation afforded hollow rhombic-dodecahedral crystals of the C-methylcalix[4]resorcinarene hexamer. The formation of the hollow crystals is attributed to a reversed crystal growth mechanism heretofore described only in the synthesis of inorganic-based materials.

Crystals having nano- and micrometer-scale dimensions are important materials in fields that range from materials science to medicine.^{1,2} An appreciable number of crystals with sizes reduced to nanodimensions exhibit cubic symmetries and shapes at both the molecular and bulk scales. However, in purely organic systems, a cubic lattice is rare.³ A search of the Cambridge Structural Database revealed that less than 0.1% of all reported purely organic crystals are cubic.^{4,5} The lack of organic systems can be attributed to the anisotropy of molecules, which largely prohibits the packing from meeting cubic symmetry requirements.⁶ C-Methylcalix[4]resorcinarene (CMCR) is an organic system that crystallizes in a cubic space group (Figure 1). The bowl-shaped molecule self-assembles to

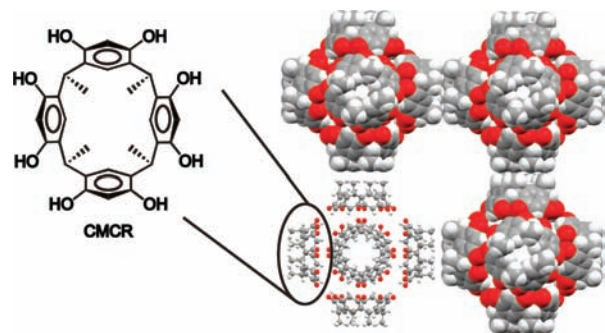


Figure 1. Structure of C-methylcalix[4]resorcinarene (CMCR) and cubic solid-state packing of CMCR hexamers (disordered molecules have been omitted).

form a chiral sphere composed of six resorcinarenes and eight water molecules in the rare space group $I432$.⁷ The field of supramolecular chemistry has shown immense interest in hexameric assemblies of resorcin[4]arenes, as well as related calix[4]pyrroles and pyrogallol[4]arenes, because of their ability

to encapsulate guests with potential applications in fields such as drug delivery.^{8–13} Resorcinarenes have also been identified as excellent surfactants for the dispersion and self-assembly of metal nanoparticles into well-defined structures.¹⁴ However, the development of resorcinarenes and, more generally, host–guest systems as nanocrystals remains largely unexplored.^{15–17}

With this in mind, we report the fabrication of crystals having nano- and micrometer-scale dimensions that are composed of CMCR hexamers. The crystals, with sizes as small as 157 nm, were obtained via a sonochemical approach. The application of ultrasound offers a versatile means to form nanostructured materials that are inaccessible by conventional methodologies.^{18–21} Here we show not only that sonochemistry is critical for forming CMCR nanocrystals but also that ultrasonic irradiation affords hollow crystals. Solids with hollow interiors of interest include dendrimers, graphite, silica, metals, and inorganic materials with applications in a number of fields (e.g., devices).^{18,22–26} The CMCR crystals described here are the first reported hollow, polyhedral crystals composed of purely organic components.²⁷ The formation of the hollow crystals is attributed to a reversed crystal growth mechanism recently elucidated by Zhou and co-workers^{28–31} to account for the formation of hollow zeolite and perovskite crystals. The stages of reversed crystal growth include oriented aggregation of nanoparticles, surface recrystallization, and growth from the surface to the core.

In the original report,⁷ the CMCR hexamer was prepared by crystallization from boiling nitrobenzene (NO_2Ph) over the course of 2 weeks. The result was light-yellow crystals of cubic morphology suitable for single-crystal X-ray diffraction (XRD). When the procedure was repeated, we obtained a yellow precipitate consisting of both crystals and a powder, which powder XRD (PXRD) confirmed to be the CMCR hexamer. A close examination of scanning electron microscopy (SEM) micrographs revealed a mixture of crystalline morphologies consisting of large flakes and rhombic dodecahedra. The rhombic-dodecahedral crystals ranged from 4 to 40 μm in diameter, while the size of the flakes was not uniform and varied on the order of hundreds of micrometers (Figure 2a,b).

To synthesize CMCR hexamer crystals reduced to nanometer dimensions, we turned to sonochemistry.¹⁸ The coupling of rapid precipitation and sonochemistry has been shown to

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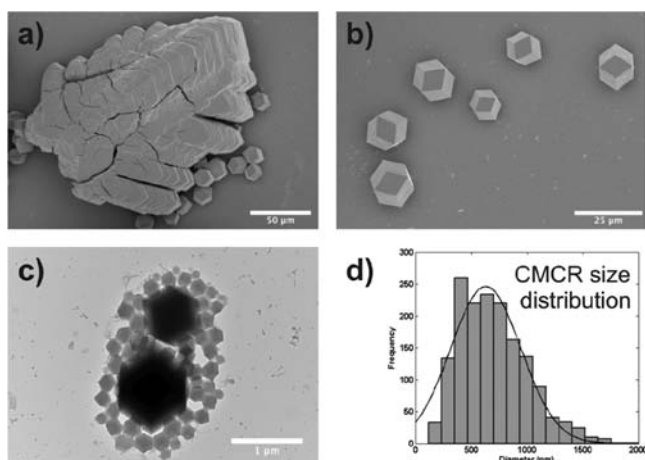


Figure 2. (a, b) Rhombic-dodecahedral CMCR crystals formed via slow solvent evaporation. (c) TEM micrograph of nanocrystals. (d) Particle size distribution of the solid prepared via sonochemistry.

afford multicomponent nanocrystals, or cocrystals, containing purely organic components.^{20,21} A typical preparation consisted of dissolving CMCR (0.003 g, 5.5 mmol) in boiling NO_2Ph (1 mL) and rapidly injecting the solution into water (10 mL). During the injection, the water was simultaneously stirred and exposed to ultrasonic irradiation. After 2 min, an aliquot was removed for analysis by PXRD, SEM, and transmission electron microscopy (TEM).

Close examination of SEM and TEM micrographs revealed crystals of rhombic-dodecahedral morphology (Figure 2c). The crystal sizes were reduced relative to the original recrystallization and could be fit to a Gaussian distribution characterized by an average diameter of 630 nm (s.d. 315 nm) with well-defined morphologies as small as 157 nm (Figure 2d). PXRD analysis confirmed that the solid formed using the sonochemical approach consisted of CMCR hexamers (Figure S1 in the Supporting Information). Additional peaks in the powder pattern were assigned to a hydrate of the resorcinarene. Indeed, a solid with a PXRD pattern that matched these additional peaks was obtained directly from a water suspension after equilibration for 3 days.³² The propensity of CMCR to form hydrates (and solvates in general) is well-documented.³³

When the nanocrystallization of the CMCR hexamer was repeated with vigorous stirring in water alone, the resulting solid was composed of smooth spherical particles that ranged from 40 to 900 nm in diameter (Figure S2). When the suspension was allowed to age for 2 months, no change in size or morphology was observed (Figure S3). However, the smooth spheres could be converted to rhombic dodecahedra upon exposure to ultrasound. SEM analysis clearly demonstrated the presence of well-defined crystals, albeit of micrometer dimensions (Figure S4). From these observations, we concluded that the combined application of ultrasonic irradiation^{18,19} and rapid precipitation is required to obtain the well-defined nanosized crystals of CMCR.

During the sonochemical preparation of CMCR nanocrystals, we observed rhombic dodecahedra exhibiting a hollow morphology (Figure 3). SEM micrographs displayed dodecahedra that were likely fragmented into two pieces¹⁹ (Figure 3a–c) or, remarkably, were formed with a hole to reveal a hollow interior (Figure 3d). The fragmented polyhedra exhibited a spherical interior and had approximate shell thicknesses ranging from 70 to 230 nm. The occurrence of

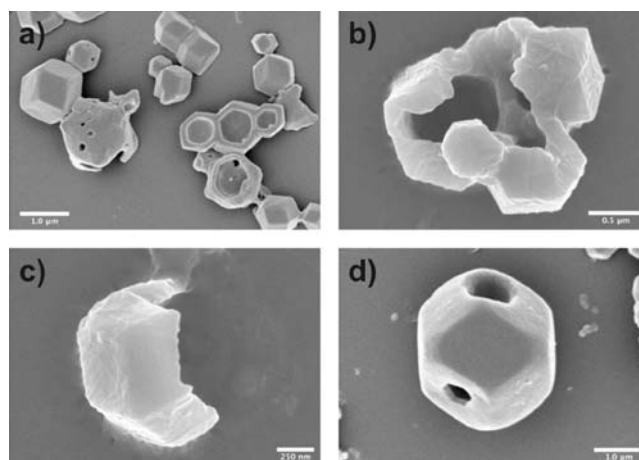


Figure 3. SEM micrographs of (a–c) fragmented hollow rhombic dodecahedra and (d) a rhombic dodecahedron formed with a hole.

the hollow crystals was not size-dependent, as crystals from 500 nm to 4 μm in diameter exhibited hollow morphologies. Crystals with hollow polyhedral topologies have been observed for inorganic materials,^{28–31} with zeolite analcime and zeolite A being examples based on a porous structure. The zeolites formed according to a reversed crystal growth mechanism that began with oriented aggregation of nanoparticles, proceeded by surface recrystallization, and concluded with growth from surface to core via Ostwald ripening.^{29,34}

To gain insight into the formation of the hollow CMCR crystals, crystallization studies were performed in NO_2Ph at 20-fold dilution. A dilution was employed to decrease the rate and observe the stages of crystallization, but the crystal growth remained rapid in comparison with zeolites.^{34,35} SEM analysis revealed platelike crystals upon only 45 s of sonication, which included sizes as small as 70 nm (Figure 4a). Exposure to

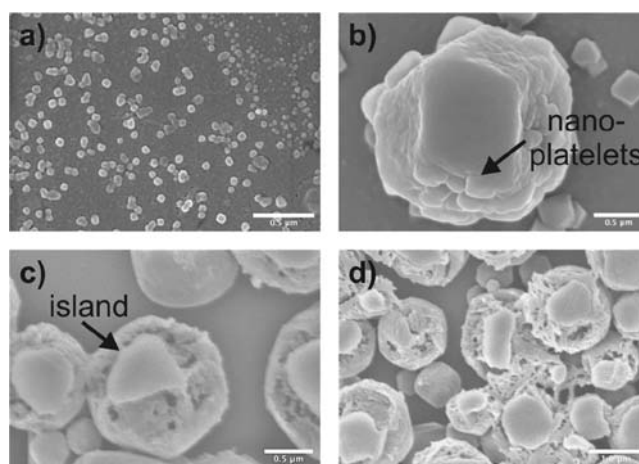


Figure 4. (a, b) Comparison of SEM micrographs of organic nanocrystals of CMCR after sonication for (a) 45 s and (b) 2 min at 20-fold dilution in NO_2Ph . (c, d) SEM micrographs showing partial surface crystallization of islands having a triangular shape.

ultrasonic irradiation for 2 min converted the plates to the rhombic-dodecahedral morphology. Building units in the form of nanoplatelets were visible, with clear boundaries on the surface of the polyhedra (Figure 4b).²⁹ The presence of platelets is consistent with an oriented aggregation process in

which nanocrystallites organize to share identical orientations, whereupon fusion occurs at the interface to form a single crystal.^{36–39} Indeed, SEM micrographs taken in our original attempts to form nanocrystals of CMCR, *without dilution* and as in the case of preparing zeolites,²⁸ revealed disordered aggregates with crystalline “islands” having an approximately triangular shape (Figure 4c,d). The islands likely correspond to partially formed polygons and coincide with partial surface crystallization that continues to grow over the surface and self-adjust until the entire surface corresponds to the faces of a rhombic dodecahedron (e.g., Figure 3d). To our knowledge, the reversed growth mechanism displayed by a purely organic material in the form of CMCR is a unique occurrence. These observations are particularly important given that surface-adsorbed organics are typically used only to enhance interparticle interactions of inorganic components that are known to exhibit such a mechanism.²⁹

In this report, we have presented a sonochemical preparation of CMCR host–guest crystals having nano- and micrometer-sized dimensions achieved with rapid nucleation of a crystalline phase. The crystals undergo oriented aggregation to yield rhombic dodecahedra and hollow dodecahedral crystals. The mechanism is attributed to a reversed crystal growth process heretofore observed only in inorganic-based materials. Efforts are underway to identify additional organics, as well as metal–organics,^{40,41} that exhibit such nonclassical crystal growth to afford nanocrystalline solids. Nano- and micrometer-scale crystals of additional and controlled morphologies based on the self-assembled hexamer are also under investigation.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental details, sample characterization, PXRD data, and SEM micrographs. This material is available free of charge via the Internet at <http://pubs.acs.org>. Supplementary crystallographic data (CCDC reference code LIWQIR) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html.

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Notes

The authors declare no competing financial interest.

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