Coordination-Driven Polymerization of Supramolecular Nanocages

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**S** *Supporting Information*

ABSTRACT: Controlled assembly of 0D supramolecular nanocages into 2D or 3D architectures has been demonstrated for the first time via a coordination-driven polymerization approach, and the conversion from a 2D to 3D supramolecular architecture has also been successfully achieved via a temperature-induced crystal transformation. The boost of dimensionality for the supramolecular architecture has led to steady yet remarkable enhancement of properties, as reflected from the gas adsorption studies.

The assembly of nanometric objects, which leads to various structurally well-defined nanoarchitectures, has been attracting considerable attention[1] and has been applied in many frontier research areas ranging from optoelectronics[2] and energy storage[3] to life science.[4] Over the past few decades, different types of nanometric objects and building blocks, such as nanoparticles and nanocubes,[5] have been employed to assemble structurally well-defined nanoarchitectures with unique properties; whereas the studies on ordered nanoarchitectures assembled by nanocages remain in the embryonic stage of development. Compared with nanoparticles, nanocages have two different types of surfaces, both of which can enhance the surface area, and thus improve the targeted properties, such as sensing and catalysis.[6] As one kind of supramolecular nanocage, metal–organic cages (MOCs)[7] have been adopted in a wide array of applications in drug delivery,[8] catalysis,[9] and molecular capsulation.[10] Differing from gold and protein nanocages,[11] MOCs have definite and rigid molecular structures, and some MOCs have potential open metal sites and coordinative active functional groups[12] which afford the possibility of assembling MOCs into nanoarchitectures and to study the assembling mechanism in detail. Albeit the assembly of MOCs into one-dimensional (1D) chains has recently been reported,[13] the controlled arrangement of the supramolecular nanocages into an ordered 2D or 3D framework structure remains a challenge.

Here, we report how to address such challenge via coordination-driven polymerization through controlling the coordinated auxiliary solvent molecules at vertices, as exemplified in the context of hierarchical construction of both 2D and 3D variants of MOC nanocages on the basis of the discrete small rhombihexahedron MOC unit, $[Cu_{24}(L)_{24}(H_2O)_{16}(DMA)_8]\cdot$ 15MeOH·42DMA (**1**, H_2L = 5-hydroxy-1,3-benzenedicarboxylic acid).

As shown in Scheme 1, the nanocage **1** features both an open metal site and a distinctive functional group, thus serving as a monomer which extends to 2D and 3D polymers. More

Scheme 1. Concept of Controllable Assembly Processes from Monomer Nanocage to 2D/3D polymers
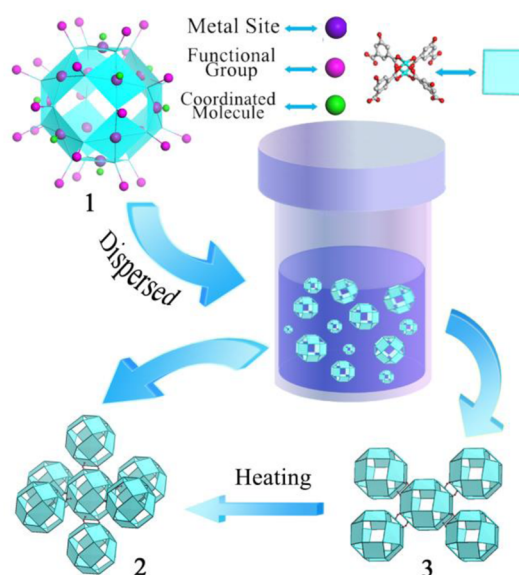
specifically, the dimensionality of the polymers has been successfully controlled by certain small molecules. Moreover, the conversion from 2D to 3D has also been achieved via the control of temperature. Compared to the discrete nanocage, the afforded 2D and 3D polymers exhibit significant enhancement of particular properties, especially structural stability, gas adsorption, and separation capability.

1 was synthesized from DMA/MeOH solution under solvothermal conditions. Single crystal X-ray diffraction (SCXRD) studies reveal that the nanocage of **1** is constructed by twelve $Cu_2(CO_2)_4$ paddlewheels and twenty-four 2,4-isophthalate bridging ligands. These ligands consequently enclose to form a small rhombihexahedron cage with twelve squares. The outer diameter of the nanocage **1** is ~3.0 nm, and the inner void diameter is ~1.5 nm. The outer vertices of $Cu_2(COO)_4$ paddlewheel are occupied by DMA molecules, as depicted in Figure 1a. The attempt of direct polymerization of **1** was unsuccessful due to the steric hindrance effect of coordinated DMA molecules, although **1** has both a potential metal site (vertices of $Cu_2(COO)_4$ paddlewheels) and phenolic hydroxyl groups.
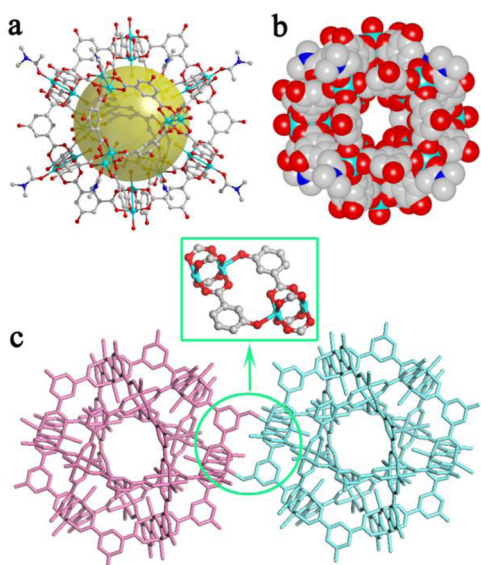
Figure 1. (a) The nanocage structure of **1**. (b) The space-filling mode of **1**. (c) Connectivity between two neighboring nanocages in **2** (inset: the building block).

1 can be well dissolved in MeOH, and it has been demonstrated that the discrete cages are dispersed uniformly in solution as individual molecules.[14] Within 24 h of the addition of a small amount of dimethyl sulfoxide (DMSO) (V(DMSO):V-(MeOH) < 1:10) into the solution, dark green crystals were obtained. The SCXRD analysis indicates that the nanocages of **1** fabricate a 3D architecture with a formula of $\{[Cu_{24}(L)_{24}(DMSO)_3(MeOH)_2(H_2O)_{13}]\cdot67MeOH\cdot7DMSO\}_n$ (hereafter denoted as **2**). In **2**, each nanocage connects to six neighboring cages, including four coplanar nanocages and two out-of-plane nanocages, to form a 3D framework structure (see Supporting Information, Figures S1 and S2). In the structure of the nanocage polymer, a new type of orbicular connection unit is observed, which is constructed through two phenolic hydroxyl groups from one nanocage with two $Cu_2(COO)_4$ paddlewheel vertices from the neighboring nanocages (Figure 1c). The substitution of DMA by DMSO on nanocage **1** reduces the steric hindrance effect around the metal sites, thus facilitating the polymerization of the nanocages.

When the molar ratio of DMSO increases (V(DMSO):V-(MeOH) > 1:7), a new type of blue crystal is obtained with a formula of $\{[Cu_{24}(L)_{24}(DMSO)_{4.5}(H_2O)_{15.5}]\cdot95MeOH\cdot12DMSO\}_n$ (**3**). Notably, **3** represents the 2D polymerization manner of the nanocages. Differing from what was observed in **2**, four neighboring nanocages in the same plane are connected to the central nanocage to expand as a 2D layer in **3** (see Supporting Information, Figures S3 and S4). Given that the vertices out of the plane are occupied by DMSO molecules and prevent the extension along the axial direction, no connection is formed between neighboring layers. Interestingly, when the ratio of V(DMSO):V(MeOH) increases to 1:1, the isolated product is purely the discrete cage, **1-DMSO**,[15] in which all of the DMA molecules of **1** are substituted by DMSO.

Further examination of the structures indicates that the arrangement of the coplanar nanocages in **2** is similar to that of the layered nanocages in **3**. As shown in Figure 2, the Cu1 atom of $Cu_2(COO)_4$ paddlewheel unit coordinates with DMSO molecule in **3**, yet the distance between O1 and Cu1 is only 3.78 Å. In **2**, O1 atom of the phenolic hydroxyl group is coordinated
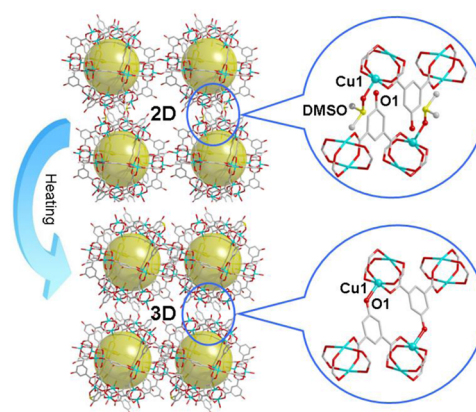

Figure 2. Transformation process from 2D to 3D nanocage polymers and the detail molecular structures of 2D and 3D nanocage polymers, respectively.

with the Cu1 atom of $Cu_2(COO)_4$ paddlewheel. It has been documented that the small coordinated molecules could be readily removed from the metal sites of the coordination compound at relative high temperatures.[16] Bearing this in mind, we anticipate that the conversion from 2D **3** to 3D **2** can be achieved via a temperature-induced crystal transformation process. Accordingly, selected crystals of **3** were put into the mixed solution (V(DMSO):V(MeOH) = 1:10) and kept at 160 °C for 12 h. Afterward, dark green crystals were obtained and identified as 3D nanocage polymers of **2**, confirming the successful conversion of **3** to **2** as expected (see Supporting Information, Figure S5).

Evidently the controlled synthesis of the discrete nanocage and 2D and 3D nanocage polymers can be achieved by adjusting the concentration of DMSO, which can occupy the vertices of the nanocage. This tunes its connectivity through coordination, and the tunability of the connectivity of the nanocage also allows the conversion of the 2D dimensional array into a 3D architecture via temperature elevation. This type of coordination-driven polymerization process can be interpreted from the perspectives of cooperation and competition of thermodynamics and kinetics.

As shown in Scheme 2, under solvothermal conditions, the DMSO molecules could compete with DMA molecules on coordinating sites at the vertices of nanocage **1**, thus forcing the removal of coordinated DMA molecules. High concentration of DMSO can promote the exchange reaction between DMSO and DMA and prevent other molecules or functional groups from exchanging with coordinated DMSO. Consequently, the DMA molecules of **1** are substituted completely by DMSO to give the discrete DMSO coordinated cage. However, decreasing the concentration of DMSO provides the opportunity for the phenolic hydroxyl groups on the ligand to compete with the DMSO molecules in coordinating with Cu(II) ions, resulting in the polymerization of the cages and thereby the formation of a 2D layered structure. When the concentration of DMSO is diluted as low as 1:10 (V(DMSO):V(MeOH)), the reaction equilibrium of the exchange reaction between phenolic hydroxyl groups and coordinated DMSO shifts further to facilitate the substitution of coordinated DMSO molecules for phenolic hydroxyl groups. This shift results in the polymerization of the cages from the whole triaxiality of the space to form a 3D architecture. Raising the temperature can also facilitate the competition of phenolic hydroxyl groups with coordinated DMSO molecules on the Cu(II) sites, thereby allowing the

Scheme 2. Mechanism of Coordination-Driven Polymerization Progresses
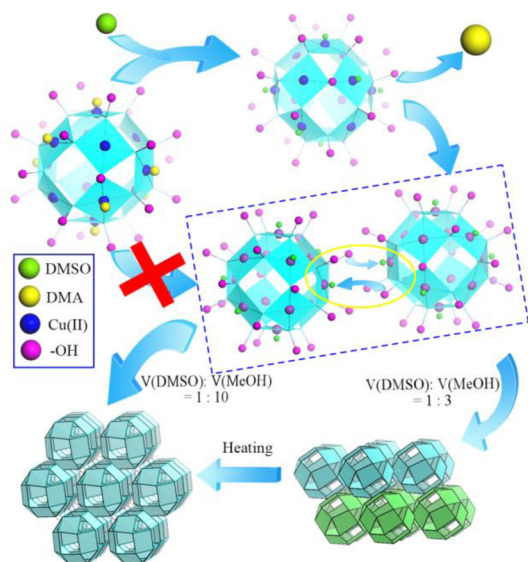
conversion of 2D **3** into 3D **2** as observed experimentally. The results and the mechanism discussed above therefore suggest a new perspective to control the polymerization of nano objects or other building units through the combination of thermodynamics and kinetics means.

The CO_2 adsorption isotherms were collected to investigate the adsorption properties of different dimensional architectures based on the nanocages. As shown in Figure 3, the CO_2 adsorption isotherms at 195 K of 0D **1**, 2D **3**, and 3D **2** all exhibit the type-I adsorption behavior, a characteristic of microporous materials. Derived from the CO_2 adsorption data, the Brunauer−Emmett−Teller (BET) surface area is only 85 m^2/g for 0D **1**, whereas that of 2D **3** and 3D **2** is 244 and 471 m^2/g, respectively. This means the expansion of 0D discrete nanocage to a 2D layered structure can triple the surface area,

and the extension of the 2D layer to a 3D architecture can further double the surface area. A similar trend of improvement is also observed for CO_2 uptake at 273 and 298 K. Given the limited N_2 uptake by the 3D nanocage polymer **2**, the separation ratios of CO_2 versus N_2 are calculated from the ratio of the initial slopes of the adsorption isotherms,[17] which are 46 at 273 K and 45 at 298 K.

In summary, we have demonstrated for the first time the successful conversion assembly of 0D supramolecular nanocages into 2D or 3D architectures via coordination-driven polymerization, as well as the conversion from a 2D to 3D architecture via a temperature-induced crystal transformation. The mechanism for the coordination-driven polymerization process has also been proposed from the thermodynamic and kinetic perspectives. Our work thereby paves a new way for controllable supramolecular assembly of nano objects or other building units into targeted architectures with enhanced properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b10815.

> Synthetic procedures of related compounds; PXRD and TGA data; the figures related to crystals and transformations; gas adsorption isotherms and related data processing (PDF)
> Crystallographic data of **1** (CIF)
> crystallographic data of **2** (CIF)
> crystallographic data of **3** (CIF)

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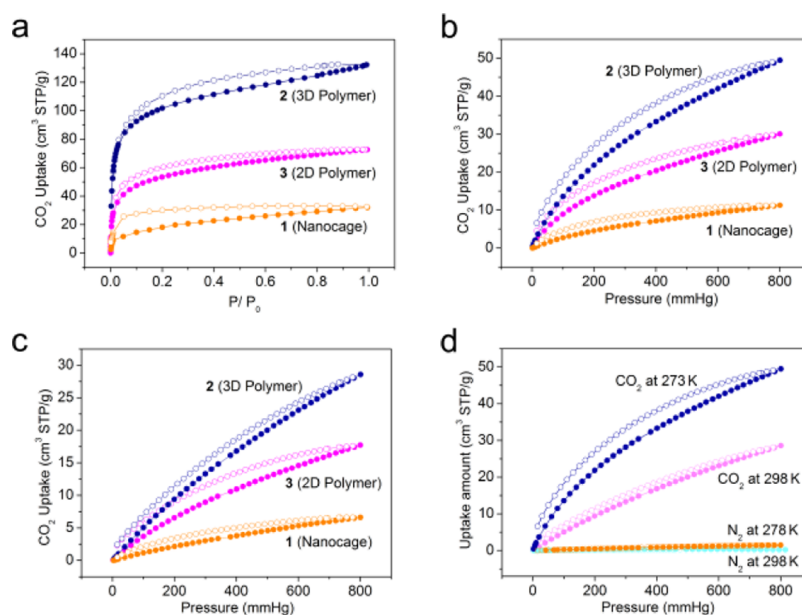The authors declare no competing financial interest.

Figure 3. The CO_2 adsorption isotherms about 0D nanocage (**1**), 2D (**3**), and 3D (**2**) polymers at (a) 195, (b) 273, and (c) 298 K. (d) N_2/CO_2 adsorption isotherms for 3D nanocage polymer.

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