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Solvent-assisted coordination driven assembly of a supramolecular architecture featuring two types of connectivity from discrete nanocages†

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The rapid development of supramolecular chemistry provides a powerful bottom-up approach to construct various well-defined nano-architectures with increasing complexity and functionality. Compared to that of small and simple nanometric objects, the self-assembly of larger and more complex nanometric objects, such as nanocages, remains a significant challenge. Herein, we used a discrete nanocage as the monomer to successfully construct a novel three-dimensional (3D) supramolecular architecture, which comprises two types of nanocage building units with different connectivity, using the solvent-assisted coordination-driven assembly approach. The mechanism of this supramolecular assembly process was investigated by electrospray ionization mass spectrometry (ESI-MS) studies, which identified for the first time the formation of a nanocage dimer intermediate during the assembly process. The assembly of discrete nanocages into a 3D supramolecular architecture led to remarkable enhancement of stability and gas adsorption properties.

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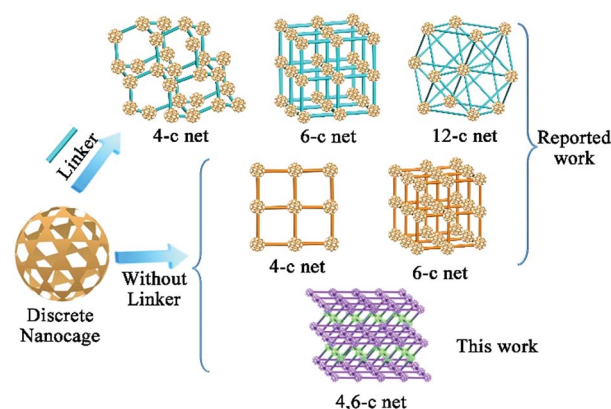
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Introduction

The construction of structurally well-defined nanoarchitectures starting from discrete nanometric scale objects has quickly become an important route for developing functional materials for magnetics, separation, energy storage, and biological applications.¹ From cubes to spheres, various nanometric objects have been used as building blocks to assemble nanoarchitectures for specific applications.² As one type of nano-object, metal-organic cages (MOCs) that feature pre-designed windows and cavities have captured widespread attention³ in the areas of chemical sensing,⁴ catalysis,⁵ molecular encapsulation,⁶ and separation.⁷ The abundant metal sites of the nanocage complex⁸ make MOCs promising candidates for CO₂ adsorption. However, most MOC crystals are unstable, which is presumably due to the weak interaction between the discrete cage molecules. This leads to a collapse of the degassing process, thereby largely restricting their application. Alternatively, assembling the discrete MOCs into 1D, 2D, and 3D

nanoarchitectures through direct bond-formation would significantly boost the stability as compared to discrete MOCs.^{1b,9} While extensive studies have been performed on the assembly of MOCs, understanding the intermediate from discrete MOCs to nanocage architectures and assembling these discrete nanocages into more complex hierarchical structures still remain formidable challenges.

To date, only three different nanocage architecture nets (4-coordinated (abbreviated 4-c), 6-c and 12-c nets) have been obtained *via* coordination interactions between additional linkers and nanocages (Scheme 1).¹⁰ In these structures, all of the



Scheme 1 The summary of current nanocage architectures assembled from discrete nanocages.

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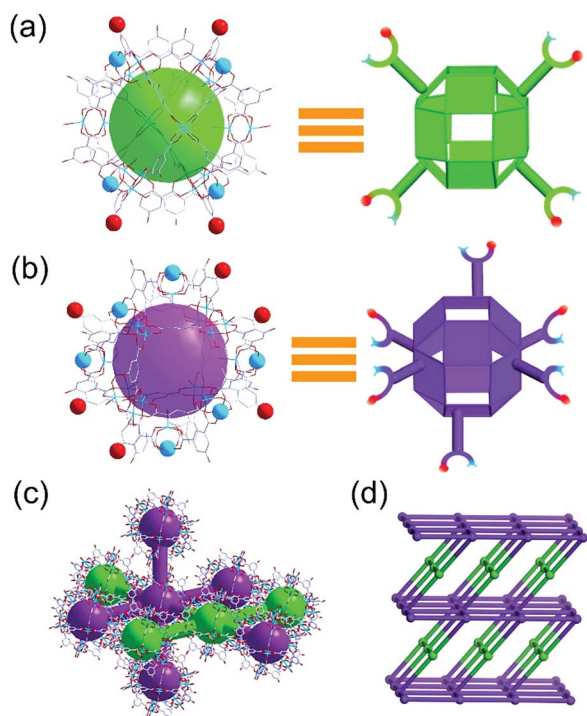


Fig. 2 Structure of nanocage architecture 2. The ball-stick representation (left) and simplified model (right) of (a) nanocage building unit A and (b) nanocage building unit B; (c) the interconnection between nanocage building units A and B. (d) The topology of nanocage architecture 2. (The turquoise and red balls stand for coordinated Cu metal sites and phenolic hydroxyl groups between neighboring cages, respectively; the green and purple polyhedra/balls stand for 4-connected nanocage building unit A and 6-connected nanocage building unit B, respectively).

nanocages and two out-of-plane nanocages, thus generating a 6-connected node. In comparison, nanocage building unit A has four Cu metal sites and four phenolic hydroxyl groups coordinating with neighboring nanocages, thus forming a 4-connected node with four neighboring nanocages in the same plane.

In nanocage architecture 2, nanocage building units A and B alternately connect with each other to construct a 3D polymer of nanocages. As shown in Fig. 2c, each nanocage building unit B (purple polyhedron) connects with four B and two A (green polyhedron); meanwhile each nanocage building unit A connects with two A and two B, thus constructing a 4,6-connected structure. Topologically, 2 features a rare *fsg* net¹⁴ (Fig. 2d). To our knowledge, this is the first time that a *fsg* net has been observed in a coordination polymer built with cage or cluster blocks.

Studies of the assembly process from nanocage monomer 1 to nanocage architecture 2

To understand the process for the assembly of nanocage architecture 2 from discrete nanocage 1, electrospray ionization mass spectrometry (ESI-MS) experiments were conducted. The existence of the individual nanocage monomers in the reaction solution (DMSO : MeOH = 1 : 4) was confirmed by ESI-MS studies. As shown in Fig. 3a, the ESI-MS spectrum of the individual nanocage monomer showed a series of doubly charged

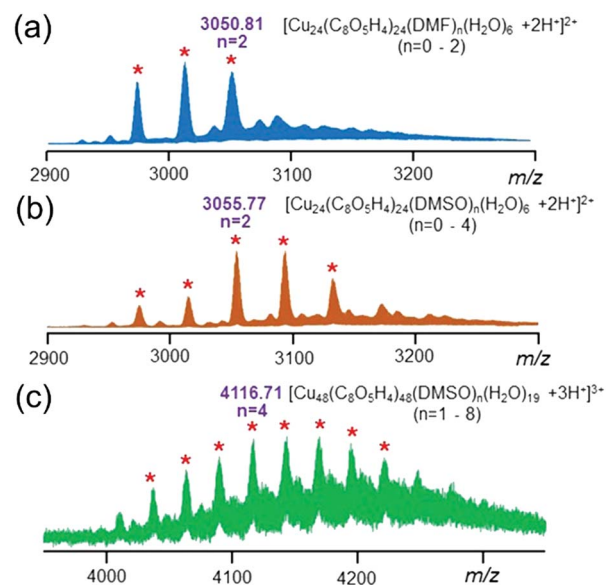
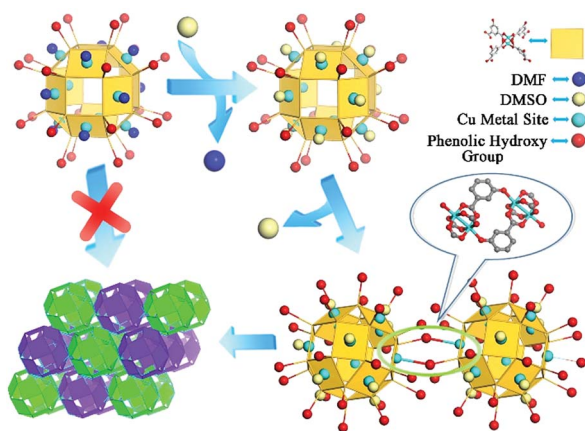


Fig. 3 ESI-MS spectra of (a) nanocage monomer (charge state 2+, loss of DMF molecules); (b) DMSO substituted nanocage monomer (charge state 2+, loss of DMSO molecules); (c) dimer nanocage intermediate (charge state 3+, loss of DMSO molecules).

signals corresponding to the loss of encapsulated solvent molecules including DMF and H₂O (*i.e.*, $m/z = 3050.81$ for $[\text{Cu}_{24}(\text{C}_8\text{O}_5\text{H}_4)_{24}(\text{DMF})_2(\text{H}_2\text{O})_6 + 2\text{H}^+]^{2+}$). Interestingly, after heating the solution at 120 °C for 1 h, the peaks belonging to individual nanocage monomers shifted slightly towards a higher m/z region and a new series of peaks appeared in the ESI-MS spectrum (Fig. S6–S8†). As depicted in Fig. 3b, the doubly charged peaks correspond to the loss of solvent molecules including DMSO and H₂O (*i.e.*, $m/z = 3055.77$ for $[\text{Cu}_{24}(\text{C}_8\text{O}_5\text{H}_4)_{24}(\text{DMSO})_2(\text{H}_2\text{O})_6 + 2\text{H}^+]^{2+}$). These results indicated that the encapsulated DMF molecules were substituted by DMSO molecules during the assembly process. In particular, a new sets of peaks (Fig. 3c) between 4000 and 4300 (m/z) with triple charge was attributed to the nanocage dimer based on calculation (*i.e.*, $m/z = 4116.71$ for $[(\text{Cu}_{24}(\text{C}_8\text{O}_5\text{H}_4)_{24}(\text{DMSO})_2(\text{H}_2\text{O})_{9.5})_2 + 3\text{H}^+]^{3+}$). The isotope pattern of all the assigned peaks agreed well with the calculated values (Fig. S9†), indicating the composition of the proposed structure.

On the basis of SCXRD and ESI-MS results, the detailed assembly process of the nanocage architecture is illustrated in Scheme 2. When the nanocage 1 was dispersed in the DMSO/MeOH solvent mixture, the Cu metal sites were still occupied by DMF molecules. After heating the solution at 120 °C for 1 h, the DMF molecules were substituted by DMSO molecules, which implied that the DMSO coordinated nanocage was favored when increasing the temperature. Meanwhile, two phenolic hydroxyl groups from one nanocage coordinated with two $\text{Cu}_2(\text{COO})_4$ paddlewheel vertices from the neighboring nanocages to construct an orbicular connection unit, thus forming the novel nanocage dimer intermediate. This intermediate indicated that the substitution of DMF by DMSO on nanocage 1 reduces the steric hindrance effect around the metal





Scheme 2 The detailed assembly process of nanocage architecture 2 from discrete nanocage 1 and the nanocage dimer.

sites, thus facilitating the polymerization of the nanocages to form the nanocage architecture 2.

Gas adsorption studies of nanocage monomer 1 and nanocage architecture 2

Similar to the 4-c and 6-c nanocage architectures, nanocage architecture 2 is stable in common organic solvents, such as

MeOH, EtOH, DMA, DMF, and DMSO. The good stability of nanocage polymer 2 prompted us to examine the gas adsorption properties of the discrete nanocage 1 and the nanocage architecture 2. The Brunauer–Emmett–Teller (BET) surface areas of nanocage 1 and nanocage architecture 2 were derived from the CO₂ adsorption isotherms at 195 K. As presented in Fig. 4a, the CO₂ isotherms at 195 K of both nanocage 1 and nanocage architecture 2 show type-I adsorption behavior, indicating the microporosity of both. The BET surface area of nanocage architecture 2 reaches 604 m² g^{−1}, which is 8 times higher than that of nanocage 1 (73 m² g^{−1}). In particular, the surface area of 2 (4,6-c nanocage architecture) is also much higher than that of 4-c and 6-c nanocage architectures (244 m² g^{−1} and 471 m² g^{−1}, respectively). The higher BET surface area of 2 can be attributed to the 4,6-c net, which provides a more stable 3D framework than the 4-c 2D net as well as more porosity compared to the 6-c net. The CO₂ adsorption measurement of the nanocage and nanocage architectures further underscores the advantage of the 4,6-c net in gas adsorption. As shown in Fig. 4b, the CO₂ adsorption capacity at 298 K for the nanocage architecture 2 is 35 cm³ g^{−1}, which is not only much higher than that of nanocage 1, but also higher than that of 4-c and 6-c nanocage architectures (17 cm³ g^{−1} and 27 cm³ g^{−1}, respectively). The gas adsorption results indicate that the assembly of the discrete nanocages into a 3D nanoarchitecture with the 4,6-c net not only drastically increases the surface area, but also shows better CO₂ gas adsorption performance compared with the nano-architectures with a single node net.

Conclusion

In summary, we have successfully constructed a 3D supramolecular architecture featuring dual nanocage building units through solvent-assisted coordination-driven assembly of one type of nanocage for the first time. The nanocage dimer intermediate formed during the assembly process was also identified for the first time *via* ESI-MS studies. The two types of nanocage building units feature different connectivity, thus enabling the construction of a complex 4,6-c nanocage architecture with the rare *fs**g* topology. The 4,6-c nanocage architecture showed an enhanced surface area and CO₂ adsorption performance compared with nanocage 1 and the 4-c and 6-c nanocage architectures. Our work thereby paves the way for controlled construction of complex nano-object architectures from discrete nano-objects for a broader range of applications.

Conflicts of interest

There are no conflicts to declare.

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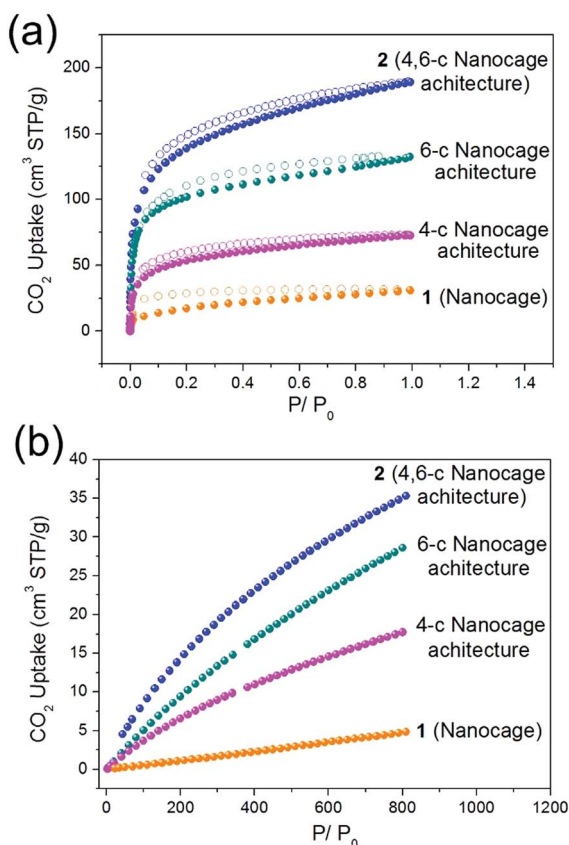


Fig. 4 The CO₂ adsorption isotherms of the nanocage (1), 4-c nanocage architecture, 6-c nanocage architecture and 4,6-c nanocage architecture (2) at (a) 195 K and (b) 298 K.



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