

## Self-assembly and interconversion of large polyhedral cages with highly entangled motifs

Self-assembly driven by reversible metal coordination is a mutually complementary method to organic/inorganic synthesis via covalent bond formation and has been developed contemporaneously with advanced technologies for molecular structural characterization, enabling the precise control of the construction of tailor-made molecular frameworks. One- to two-dimensional (1D-2D) and relatively simple three-dimensional (3D) coordination materials were intensively studied during the first two decades of the 21<sup>st</sup> century, targeting a wide spectrum of applications in molecular storage, energetic materials, and catalysis.

However, we have recently explored the self-assembly of large, complex 3D structures to establish synthetic strategies similar to those adopted in the formation of natural complicated molecules including proteins. Initially, we focused on metal–acetylene  $\pi$ -coordination using conventional coordination elements such as nitrogen-containing heterocycles and oxygen donors (Fig. 1(a)). As summarized in our recent review [1], acetylene  $\pi$ -coordination frequently appears in small organometallic compounds and host-guest systems, but its binding energy is typically too weak for the stabilization of larger assemblies. Therefore, we discovered that the cooperative ability of acetylene  $\pi$ -coordination is applicable to the discrete self-assembly of complex nanostructures, supported by its high structural flexibility and diversity.

After the serendipitous discovery of the smallest  $(M_3L_2)_2$  cage ( $M = Cu(I), Ag(I)$ ), this method was extended to the construction of a series of polyhedral molecular cages  $(M_3L_2)_n$  based on hierarchically oligomerized  $M_3L_2$  subunits ( $n = 4, 6$ ) [2]. *Small-to-large* interconversion to a 5-nm-class cubic cage ( $n = 8$ , Mw: 18,768, except for the free counter anions) was developed by combining the current method with an anion-exchange protocol that strengthens the stability of the  $M_3L_2$  subunit electrostatically capturing the nitrate anion (Fig. 1(b)) [3].

In this study, this strategy was applied to *large-to-*

*large* interconversion of polyhedral cages [4]. After additional anion exchange of the  $(Ag_3L_2)_8$  cube using tetrabutylammonium nitrate in a nitromethane- $d_3$  solution, platelet crystals were experimentally obtained via a vapor-diffusion protocol at low temperature. We examined several types of protocols at SPRING-8 BL26B1 and BL41XU to realize single-crystal X-ray analysis of relatively fragile crystals, partly because of the large structure of the main framework providing porous regions inside and outside. Finally, helical scanning ( $\sim 200 \mu\text{m}$ ) of the platelet crystals introduced into a borosilicate glass capillary enabled us to obtain acceptable diffraction data on the reduction of radiation damage.

The obtained  $Ag_{21}L_{12}$  cage (Mw: 14,585) was revealed to have the concave framework ( $\sim 4.0 \times 4.0 \times 3.2 \text{ nm}^3$ ) topologically transformed from the  $(M_3L_2)_6$  prism (Fig. 2(a)), which was also supported by  $^1\text{H}$ ,  $^{13}\text{C}$ , 2D nuclear magnetic resonance spectroscopy (NMR) studies in solution and atomic force microscopy imaging. The numbers of vertices ( $v = 21$ ), edges ( $e = 33$ ), and faces ( $f = 14$ ) followed Euler's polyhedron formula ( $v - e + f = 2$ ), exhibiting a concave tetrakaidecahedral structure. Formally, this polyhedron was formed via the insertion of three nitrate–silver–nitrate triads into all three lateral edges of the truncated prism shape, as observed for the  $(M_3L_2)_6$  prism. In addition, the structure of the  $Ag_{13}L_8$  concave decahedron ( $v, e, f = 13, 21, 10$ ), as a modified form of the  $(M_3L_2)_4$  tetrahedron (Fig. 2(b)), was also determined by X-ray analysis by merging two diffraction data sets to compensate for the rapid degradation of the crystals.

Importantly, the current assemblies based on flexible cooperative acetylene coordination afforded a series of unprecedented 3D structural motifs (Fig. 3) that are related to emerging molecular entanglements [5]. First, the smallest  $(M_3L_2)_2$  cage exhibited an entangled  $\theta$ -shape topology composed of two interlocked (connected via acetylene coordination) cage-like components. Second, the  $(M_3L_2)_n$  polyhedra ( $n = 4, 6, 8$ ) included entangled motifs resembling a trefoil knot

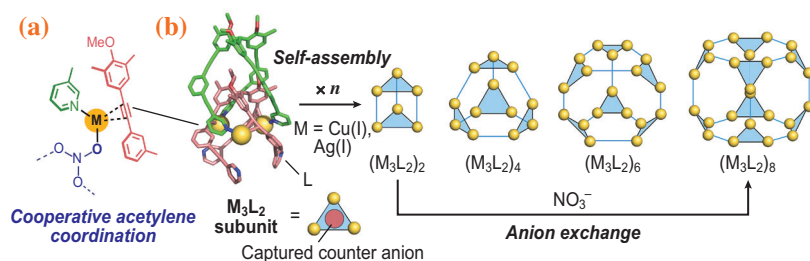


Fig. 1. (a,b) Self-assembly of the  $(M_3L_2)_n$  polyhedral cages based on cooperative acetylene coordination.

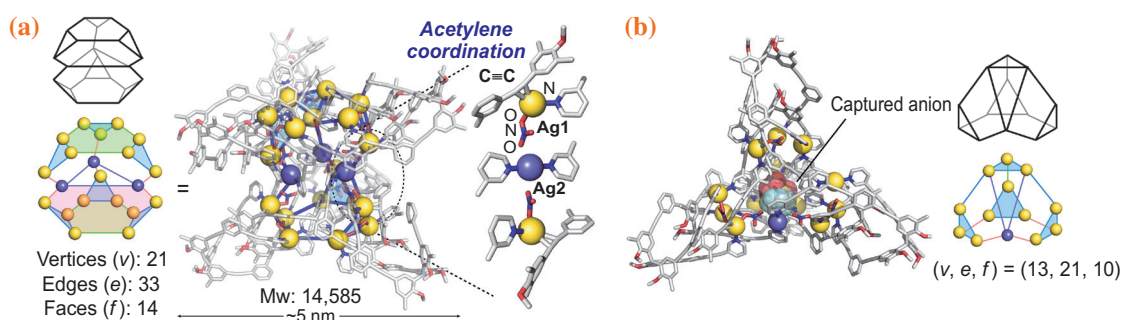


Fig. 2. Single crystal X-ray structures of (a)  $\text{Ag}_{21}\text{L}_{12}$  and (b)  $\text{Ag}_{13}\text{L}_8$  concave polyhedra.

and Solomon link, on each face of the polyhedra. Each assembly forms a complicated but well-ordered 3D structure (Fig. 3(a)) with an inner cavity capturing the anions and a topologically chiral character, which can be controlled by accumulating small chiral groups on its surface [1]. Furthermore, the current  $\text{Ag}_{21}\text{L}_{12}$  and  $\text{Ag}_{13}\text{L}_8$  cages also exhibit unique ‘edited’ structures: Solomon link-like motifs dissociated in the  $\text{Ag}_{21}\text{L}_{12}$  framework, while its trefoil knot-like motifs are maintained (Figs. 3(b,c)). In addition, in  $\text{Ag}_{13}\text{L}_8$ , a trefoil motif dissociated during the maintenance of the three neighboring motifs (Fig. 3(d)). Such an interconversion may be applied as a prototype for the skeletal editing of large and complex polyhedral structures, inducing new properties and functions.

3D entanglements have recently attracted considerable attention, not only as substructures in some natural proteins, but also as fascinating motifs in artificial nano-to-macro-scale functional materials. The establishment of synthetic strategies is an essential step in the elucidation of potential physical and chemical properties for applications in stimuli-responsive molecular containers, molecular machines, and other hierarchically manufactured functional materials. We also emphasize that the precise design of future complex materials requires appropriate structural characterization utilizing emerging methodologies and techniques, including those offered by the next-generation facilities at SPring-8/SACLA.

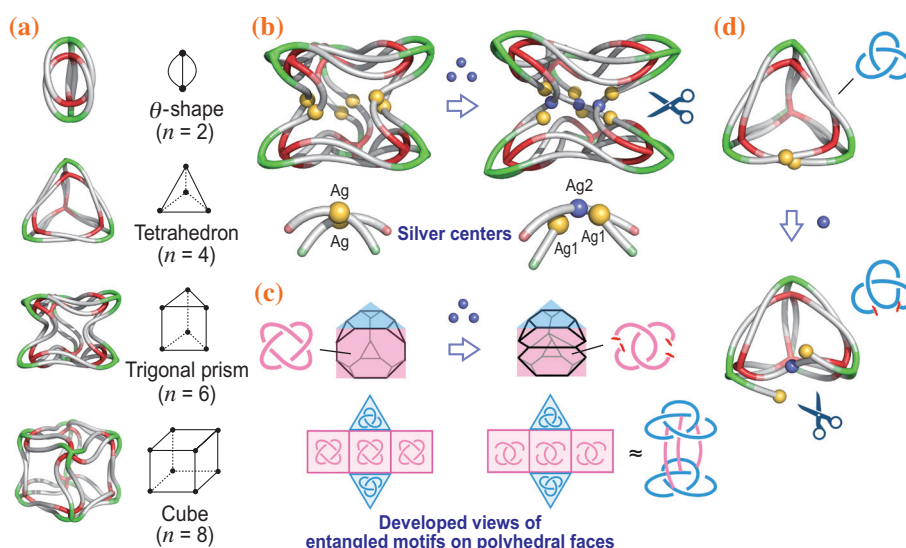


Fig. 3. (a) 3D entangled structures of the  $(\text{M}_3\text{L}_2)_n$  cages ( $n = 2, 4, 6, 8$ ). Acetylene coordination connecting each component is omitted for clarity. (b-d) Partial modification of the entangled motifs in the  $\text{Ag}_{21}\text{L}_{12}$  and  $\text{Ag}_{13}\text{L}_8$  concave polyhedral frameworks.

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## References

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