

# Controllable Coordination-Driven Self-Assembly: From Discrete Metallocages to Infinite Cage-Based Frameworks

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**CONSPECTUS:** Nanosized supramolecular metallocages have a unique self-assembly process that allows chemists to both understand and control it. In addition, well-defined cavities of such supramolecular aggregates have various attractive applications including storage, separation, catalysis, recognition, drug delivery, and many others. Coordination-driven self-assembly of nanosized supramolecular metallocages is a powerful methodology to construct supramolecular metallocages with considerable size and desirable shapes. In this Account, we summarize our recent research on controllable coordination-driven assembly of supramolecular metallocages and infinite cage-based frameworks.

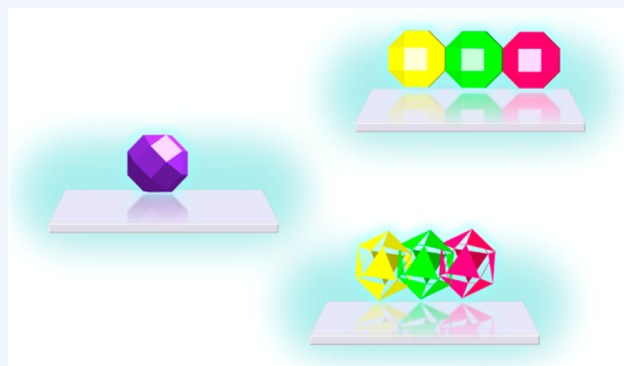
To this end, we have chosen flexible ligands that can adopt various conformations and metal ions with suitable coordination sites for the rational design and assembly of metal–organic supramolecular ensembles. This has resulted in various types of metallocages including  $M_3L_2$ ,  $M_6L_8$ ,  $M_6L_4$ , and  $M_{12}L_8$  with different sizes and shapes. Because the kinds of metal geometries are limited, we have found that we can replace single metal ions with metal clusters to alternatively increase molecular diversity and complexity. There are two clear-cut merits of this strategy. First, metal clusters are much bigger than single metal ions, which helps in the construction and stabilization of large metallocages, especially nanosized cages. Second, metal clusters can generate diverse assembly modes that chemists could not synthesize with single metal ions. This allows us to obtain a series of unprecedented supramolecular metallocages.

The large cavities and potential unsaturated coordination sites of these discrete supramolecular cages offer opportunities to construct infinite cage-based frameworks. This in turn can offer us a new avenue to understand self-assembly and realize certain various functionalities. We introduce two types of infinite cage-based frameworks here: cage-based coordination polymers and cage-based polycatenanes, which we can construct through coordination bonds and mechanical bonds, respectively.

Through either directly linking the unsaturated coordination sites of metallocages or replacing the labile terminal ligands with bridging ligands, we can produce infinite cage-based frameworks based on coordination bonds. We introduce several interesting cage-based coordination polymers, including a single-crystal-to-single-crystal transformation from a  $M_6L_8$  cage to an infinite cage-based chain. Compared with discrete metallocages, these kinds of materials can give us higher structural stability and complexity, favoring the applications of metallocages.

In addition, we discuss how we can use mechanical bonds, such as interlocking and interpenetrating, to construct extended cage-based frameworks. So far, study in this field has focused on polycatenanes constructed from  $M_6L_4$  and  $M_{12}L_8$  cages, as well as a controllable and dynamic self-assembly based on  $M_6L_4$  metallocages. We also discuss cage-based polycatenanes, which can give dynamic properties to discrete metallocages.

We hope that our investigations will bring new insights to the world of the supramolecular metallocages by enlarging its breadth and encourage us to devote more effort to this blossoming field in the future.



## 1. INTRODUCTION

Supramolecular aggregates with well-defined cavities have attracted considerable attention due to their aesthetically fascinating structures and their intriguing applications such as recognition, catalysis, separation, drug delivery, and gas storage. Coordination-driven self-assembly, which is based on the formation of metal–ligand bonds, has proven to be a powerful method to construct supramolecular metallocages, featuring considerable synthetic advantages such as few steps, fast and facile construction of the final products, and inherent self-correcting, defect-free assembly. Based on coordination-driven

self-assembly, design strategies including edge-directed and face-directed self-assembly, symmetry interaction model, and molecular library approach have been developed, and many elaborate metallocages with various sizes and shapes, such as tetrahedra, octahedra, cubes, cuboctahedra, dodecahedra, truncated tetrahedra, truncated octahedra, and others, have been produced.<sup>1–17</sup>

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Scheme 1. Using Flexible Tripodal Ligands and Suitable Metal Ions to Construct Supramolecular Ensembles in Which the Selected Metal Ions Mainly Focus on Linear Two-Coordinated Metal Ions and Planar Four-Coordinated Metal Ions

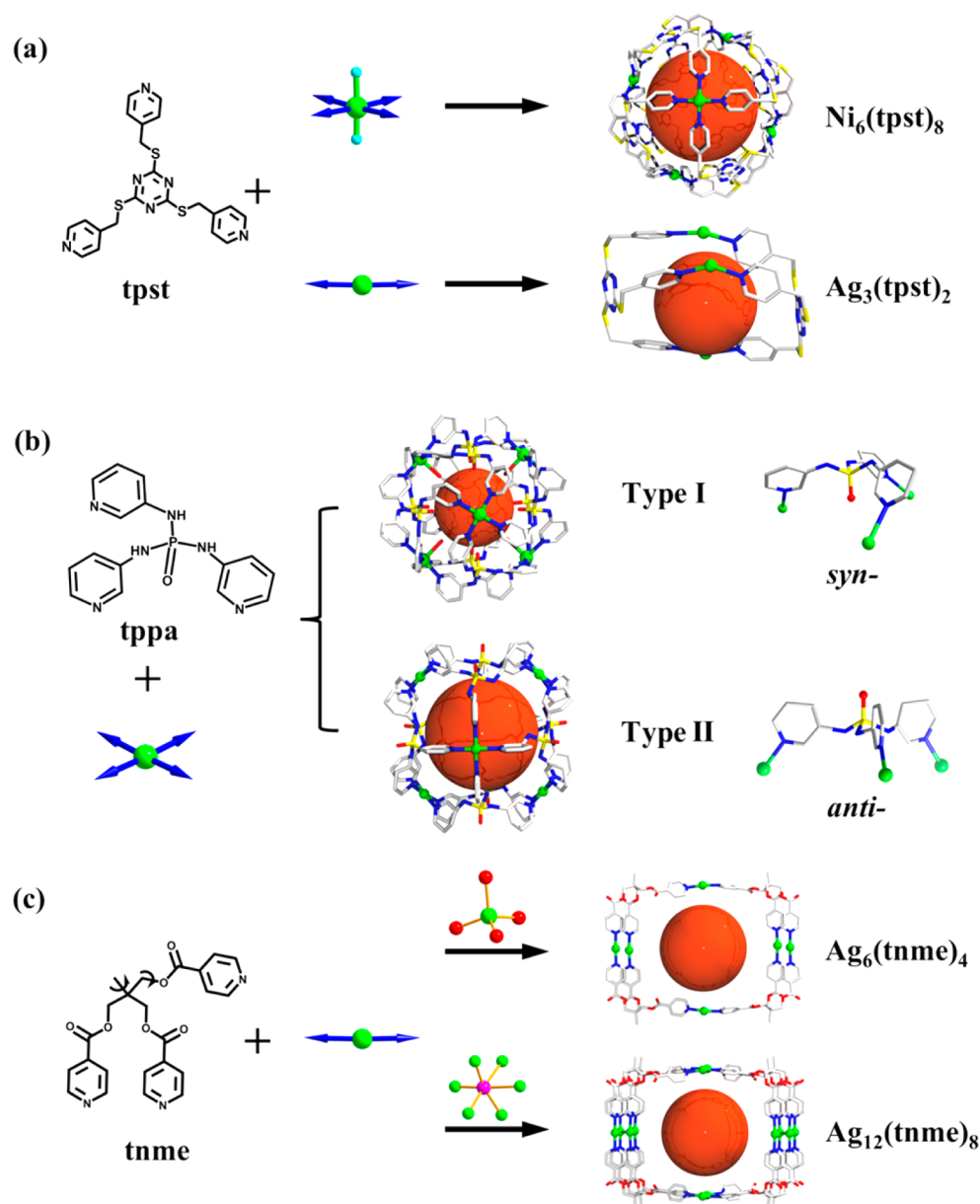
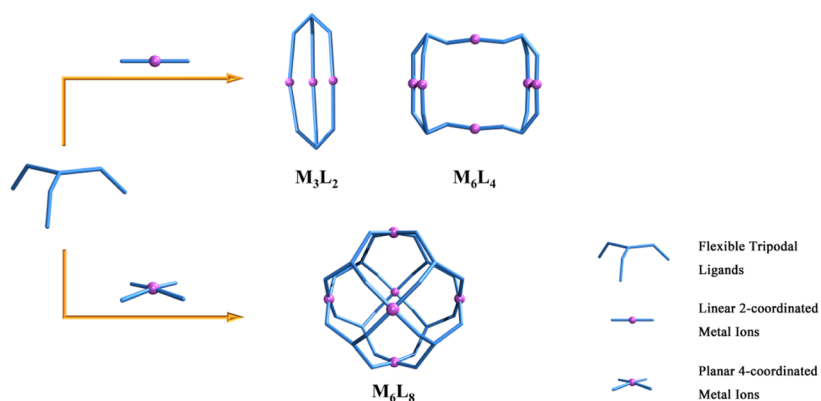


Figure 1. Self-assembly of selected flexible ligands with metal ions of different coordination geometries.

The formation of discrete metallocages can be regarded as a simplified version of a self-assembly process. The infinite cage-

based frameworks, which can be obtained from the connection of discrete metallocages, give access to supramolecular

assemblies with various degrees of hierarchy and sophistication, bringing new insight into the self-assembly of metallogages. A number of reviews and papers have been published on the construction or applications of discrete supramolecular metallogages.<sup>1–6,9–17</sup> In the present Account, we would like to highlight our research not only on discrete metallogages but also on infinite cage-based frameworks and discuss their controllable self-assembly.

## 2. COORDINATION-DRIVEN SELF-ASSEMBLY OF DISCRETE METALLOGAGE UNITS

### 2.1. Discrete Metallogages Based on Single Metal Ions

Considering that the assembly of supramolecular ensembles mainly relies on the directional and predictable nature of the metal–ligand coordination sphere, in our lab, both flexible ligands, which can adopt various conformations, and metal ions with suitable coordination sites are carefully chosen for rational design and assembly of metal–organic supramolecular ensembles. For example, the  $M_3L_2$  and  $M_6L_4$  metallogages are expected to be constructed from linear two-coordinated metal ions with suitable flexible tripodal ligands, while planar four-coordinated metal ions prefer to connect such ligands to generate  $M_6L_8$  metallogages (Scheme 1). To realize this coordination-driven self-assembly, three flexible tripodal ligands (tpst, tppa, tnme) showing moderate, less, and more flexibility, respectively, have been introduced.

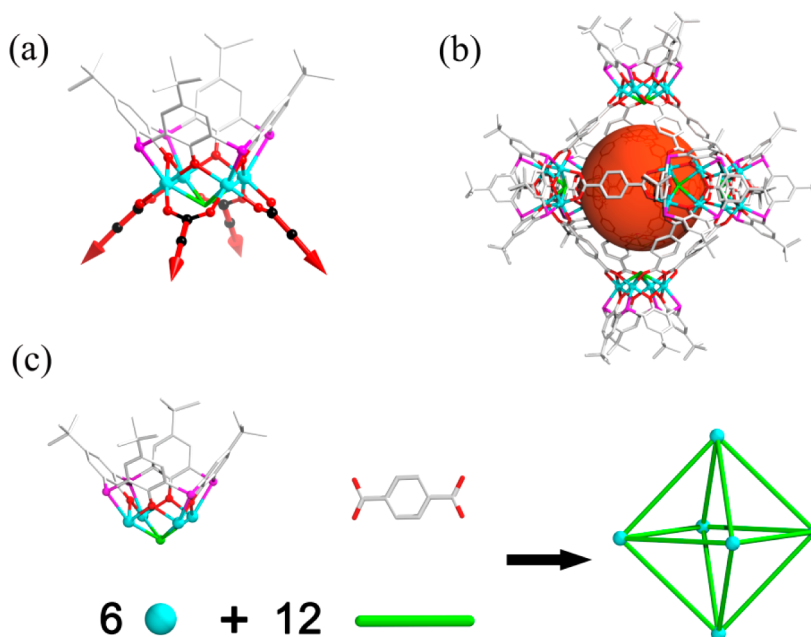
2,4,6-Tri[(4-pyridyl)sulfanylmethyl]-1,3,5-triazine (tpst), a flexible tripodal ligand with its three pyridyl rings and central spacer connected by sulfanylmethyl groups, can act as the trigonal pyramidal corner of a cube when it combines with square-planar metal ions. Only a few metal ions such as Pd(II) and Pt(II) have square-planar geometries naturally, while the other transition metal ions generally exhibit octahedral six-coordinated geometries. An alternative planar four-coordinated node can be realized by preferentially occupying the two axial positions of octahedral metal ions with suitable groups. Reaction of  $NiCl_2 \cdot 6H_2O$  and tpst leads to the first example of a discrete  $M_6L_8$  metallogage<sup>18</sup> (Figure 1a). As expected, the axial positions of the octahedral coordination geometry of Ni(II) ion are occupied by two chloride anions, whereas four nitrogen atoms from four tpst ligands are on the equatorial plane, which finally results in a gorgeous  $O_h$ -symmetric  $Ni_6(tpst)_8Cl_{12}$  cube. The centroids of the eight triazinyl rings in the ligand are very close to the corners of the cube, and six Ni(II) ions occupy the centers of the six faces of the cube. The distance from the cavity center to the triazinyl centroid is 13.2 Å, and the volume of the inner cavity is estimated to be ca. 1000 Å<sup>3</sup>. This structure is also the first X-ray structure of the discrete nanometer-sized metallosupramolecular cage with  $O_h$  symmetry.

Because tpst is an exotridentate ligand with the ability to bind three metal ions via three pyridyl N atoms of the three flexible arms, a  $M_3L_2$  metallogage is expected to be achieved when a metal ion with linear coordination geometry is employed instead of a square-planar metal ion. Self-assembly of tpst and Ag(I) ions generates  $Ag_3(tpst)_2$  metallogage units with triangular prism shape.<sup>19</sup> As Figure 1a shows, each of the three Ag(I) metal ions is two-coordinated with pyridyl N atoms of pendent arms from two different tpst ligands, forming the three pillars of the triangular prism, while the triazinyl rings of the two ligands occupy the upper and lower planes of the triangular prism, respectively.

Since  $M_6L_8$  and  $M_3L_2$  type coordination cages have been assembled by a moderate flexible ligand with tailored octahedral and linear metal ions, a less flexible tripodal ligand,  $N,N',N''$ -tris(3-pyridinyl)phosphoric triamide (tppa), is introduced for comparison. Reaction of tppa with  $Cu(ClO_4)_2$  in EtOH/ $H_2O$  solution leads to a discrete  $Cu_6(tppa)_8$  (type I) nanocage with the volume of the internal cavity ca. 900 Å<sup>3</sup> (Figure 1b).<sup>20</sup> In this type of metallogage, each of the Cu(II) metal ions is five-coordinated with one water molecule and four nitrogen atoms from different tppa ligands. The coordinated water molecules and all P=O moieties of eight tppa ligands point inward to the center of the cage, providing a hydrophilic environment inside the cavity. The nanocage encompasses 12 large rectangular windows with the size of  $4.3 \times 7.9$  Å<sup>2</sup>, each of which is adjustable along with the rotation of pyridyl rings. The reactions of tppa with other transition metal ions, Ni(II), Co(II), Zn(II), and Cd(II), result in a series of isostructural  $M_6(tppa)_8$  (type I) nanocages except that the metal ions here are all six-coordinated.<sup>21</sup> The functionalities of these metallogages can be tuned by different metal ions involved, of which it is worth noting that strong blue emissions are observed from Zn(II) and Cd(II) compounds under UV irradiation. Compared with the free ligand, the intensity of the emission increases remarkably and is approximately 1 order of magnitude higher than that of the free ligand.

When  $K_2PdCl_4$  is employed, a different discrete  $M_6(tppa)_8$  (type II) cage with truncated octahedral geometry is obtained in MeOH/DMF solution (Figure 1b).<sup>21</sup> In this  $Pd_6(tppa)_8$  cage, the distance of the axial metal centers is 15.45 Å, which is 2.27 Å longer than that of the above-mentioned  $M_6(tppa)_8$  type I cage, resulting in a larger cavity volume of ca. 1300 Å<sup>3</sup> and a remarkably increased window size of  $8.2 \times 10.7$  Å<sup>2</sup>. In the type II  $M_6(tppa)_8$  cage, all P=O moieties of the ligands point outward from the inner cavity. The increase in both the window size and the internal cavity may be ascribed to the conformation of the tppa ligand. With the free rotation of pyridine rings, the pyridyl N and phosphoryl O of the tppa can be arranged on the same or opposite side, defining the *syn/anti* conformation. In the type I cage, the inner cavity of the cage is occupied by free water molecules, which tend to form hydrogen bonding interactions with the oxygen atoms of P=O groups, inducing the *syn*-conformation of the ligand. In contrast, the tppa ligand adopts an *anti*-conformation in the type II cage under nonaqueous conditions. All of the above compounds (type I and type II metallogages) based on tppa ligand were characterized by <sup>1</sup>H NMR spectroscopy and ESI-MS. The results reveal that only Pd(II) compound (type II metallogage) maintains its structural integrity in solution.

Both the formation of  $M_3L_2$  and  $M_6L_8$  coordination cages with moderately flexible ligands and that of  $M_6L_8$  coordination cages by less flexible ligands encourage us to explore a more flexible ligand, tris(isonicotinoylmethyl)ethane (tnme), which is so flexible that it can adopt various conformations to satisfy the construction of different metallogages. Compared with tpst, the self-assembly of tnme with linear coordinated Ag(I) metal ions in the presence of  $ClO_4^-$  or  $BF_4^-$  ions affords  $M_6L_4$  type coordination cage instead (Figure 1c).<sup>22</sup> The ligand exhibits an L-shaped conformation in which two arms of tnme hang in the same direction whereas the third one extends along the direction almost perpendicular to the former two. The angles between three coordinated pyridines in tnme are about 30°, 81°, and 102°, respectively. This unique conformation, which is quite different from those found in the propeller shaped



**Figure 2.** (a) The shuttlecock-like metal<sub>4</sub>-BTC4A building block possessing four points of extension, (b) graphical representation of the self-assembly of the coordination cage through a [6 + 12] condensation, and (c) the extremely large metal cage based on Co<sub>4</sub>-BTC4A building blocks with inner cavity and outer pockets.

tripodal ligands tpst and tppa, contributes to the formation of the Ag<sub>6</sub>(tnme)<sub>4</sub> metal cage. This cage unit has a 20 × 16 × 4 Å<sup>3</sup> cavity with the ClO<sub>4</sub><sup>-</sup> ions near the two-coordinated Ag(I) to stabilize it.

In the above Ag<sub>6</sub>(tnme)<sub>4</sub> cage unit, Ag(I) ions are two-coordinated with tnme ligand, leaving potential interaction sites that may be further linked into a larger metal cage unit. When ClO<sub>4</sub><sup>-</sup> ions are replaced by PF<sub>6</sub><sup>-</sup> anions as a larger counteranion, self-assembly of tnme and Ag(I) gives rise to a Ag<sub>12</sub>(tnme)<sub>8</sub> metal cage instead.<sup>22</sup> In this case, two Ag<sub>6</sub>(tnme)<sub>4</sub> units are linked by Ag...Ag interactions to form a larger Ag<sub>12</sub>(tnme)<sub>8</sub> metal cage unit with the inducement of PF<sub>6</sub><sup>-</sup> anion (Figure 1c). Here tnme presents another conformation with the angles between three coordinated pyridines being about 34°, 101°, and 111°, respectively. The Ag<sub>12</sub>(tnme)<sub>8</sub> metal cage unit can be viewed as the dimer of the Ag<sub>6</sub>(tnme)<sub>4</sub> unit whose cavity is up to 22 × 17 × 10 Å<sup>3</sup>.

## 2.2. Discrete Metal Cages Based on Metal Clusters

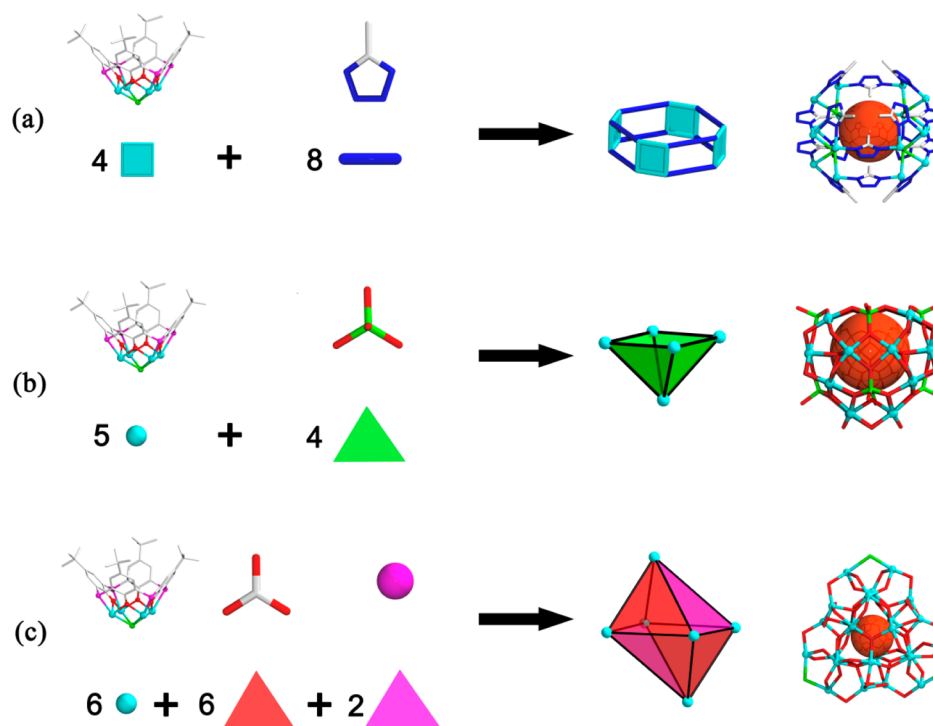
As mentioned above, tuning the metal ions with different coordination numbers and geometries is an efficient approach to modulate the final structures of the cages. A wide variety of metal-organic supramolecular ensembles can be obtained by us by virtue of different coordination spheres of metal ions, including linear, square-planar, and octahedral geometries. Variation of metal ions offers compositional and functional diversity since they are inherently modular in their nature. However, the categories of metal species, coordination modes, and geometries are limited; therefore, an alternative approach is developed with the replacement of single metal ions by metal clusters for the achievement of molecular diversity and complexity. There are two clear-cut advantages of this strategy: (1) metal clusters are much bigger than single metal ions, which helps to construct and stabilize metal cages with larger size, especially nanosized cages; (2) metal clusters can generate diverse assembly modes that could not be achieved with single metal ions, thus obtaining unprecedented supramolecular

metal cages. Followed by this strategy, the size, symmetry, components, and directionality of metal cluster building units may provide a novel means for the rational synthesis of new coordination cages.

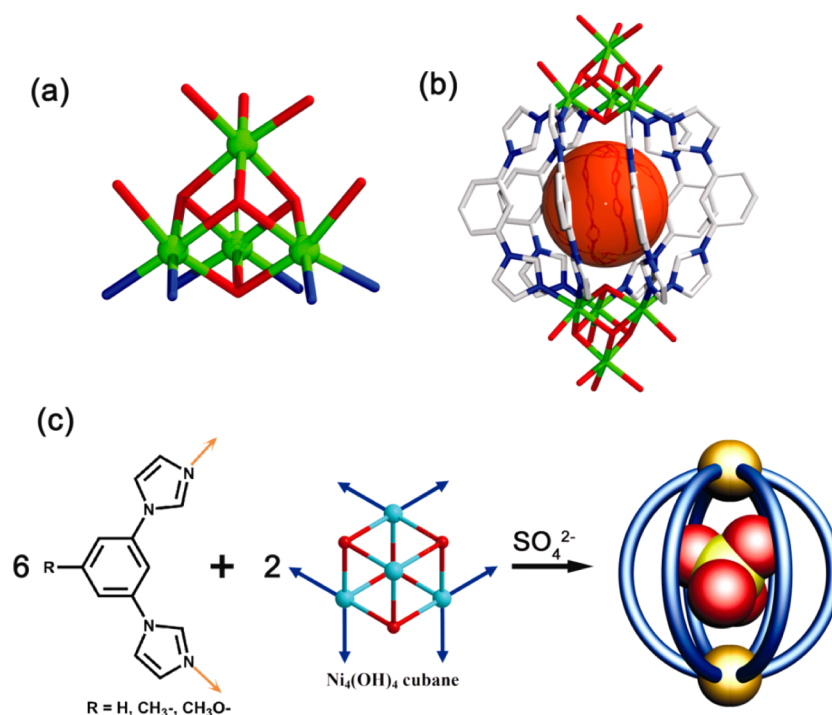
Metal carboxyl clusters are demonstrated as versatile nodes for the construction of metal cages. In 2001, Yaghi and co-workers introduced a famous dinuclear paddle-wheel unit, M<sub>2</sub>(COO)<sub>4</sub>, to produce a 25 Å cuboctahedron.<sup>23</sup> Fe<sub>3</sub>O(CO<sub>2</sub>)<sub>3</sub> is another metal cluster that can be utilized to construct a tetrahedral metal cage by capping three cofacial sites of this triangular prismatic cluster.<sup>24</sup> Recently, Yuan and co-workers reported a C<sub>3</sub>-symmetric trinuclear zirconocene cluster, with which a family of coordination zirconocene tetrahedra have been synthesized.<sup>25</sup> Besides metal carboxyl clusters, polyoxometalates can also be employed. In the example of polyoxometalate-based coordination cage reported by Yang and co-workers,<sup>26</sup> the predesigned three-connected Ni<sub>6</sub>PW<sub>9</sub> clusters served as the vertexes of a large cubic coordination cage.

In our group, a tetranuclear metal entity that is constructed by one *p*-*tert*-butylthiacalix[4]arene (H<sub>4</sub>BTC4A) ligand binding to four metal ions is used as a promising molecular building block to build new metal cages. This cationic shuttlecock-like C<sub>4</sub>-symmetric metal<sub>4</sub>-BTC4A subunit, showing further coordination ability from four directions as Figure 2a shown, can be utilized as a large vertex of coordination polyhedra in the presence of linear, bent, or facial ligands. Self-organization of six Co<sub>4</sub>-BTC4A building blocks with 12 linear ligands, 1,4-benzenedicarboxy acid (H<sub>2</sub>BDC), brings about an extremely large truncated octahedral coordination cage<sup>27</sup> as shown in Figure 2b, where Co<sub>4</sub>-BTC4A molecular aggregates occupy six vertices while BDC<sup>2-</sup> ligands act as the 12 edges of the truncated octahedron (Figure 2c). This truncated octahedron possesses eight trigonal windows with edge length ca. 10.83 Å at its eight faces. This nanoscopic cage with around 3.2 nm in diameter has a cavity volume of ca. 700 Å<sup>3</sup>. The permanent





**Figure 3.**  $M_4L_8$  wheel-like cage (a),  $M_5L_8$  open helmetlike cage (b), and  $M_6L_8$  octahedral cage (c) based on  $metal_4$ -BTC4A building blocks.

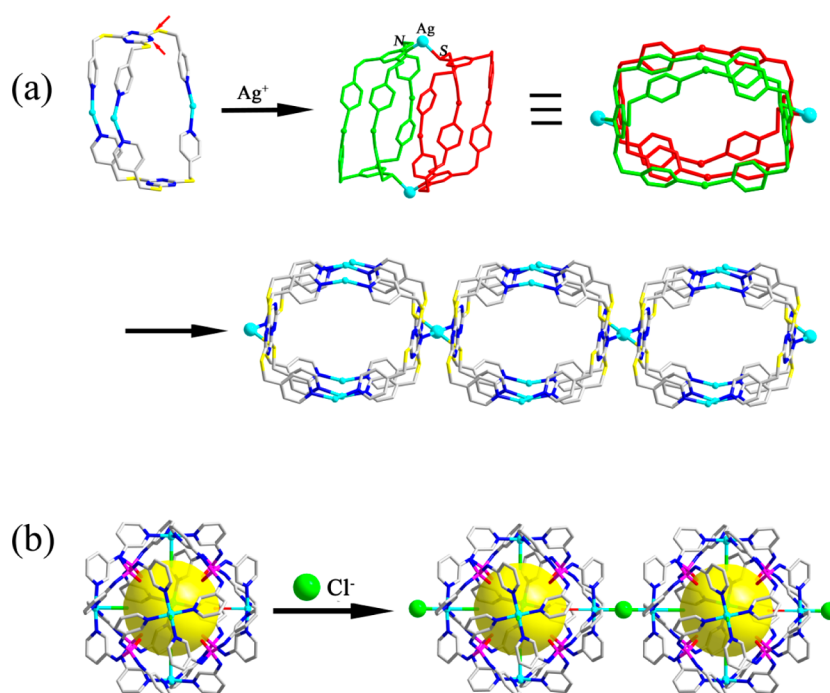


**Figure 4.** (a)  $Ni_4(\mu-OH)_4$  metal cluster possessing six points of extension, (b) the discrete hexagonal-prismatic cage based on  $Ni_4(\mu-OH)_4$  metal clusters, (c) graphical representation of the self-assembly of the coordination cage through a [6 + 2] condensation.

porosity of this cage is confirmed by gas adsorption experiments.

Such shuttlecock-like  $metal_4$ -BTC4A has proven to be a versatile four-coordinated node for the construction of metalocages with different shapes. A  $M_4L_8$  wheel-like entity (M in this paragraph represents the shuttlecock-like molecular building unit) can be produced using eight 5-methyl tetrazolate ligands as double bridging linkers (Figure 3a).<sup>28</sup> When

phosphate anions are introduced, five  $Co_4$ -BTC4A subunits can be linked into an open helmetlike  $M_5L_8$  nanocage through a [5 + 8] condensation (Figure 3b). This unprecedented  $Co_{20}$  metalocage, with a large 16-membered ring in its opening cavity, presents the first example of pentameric calixarene coordination cages.<sup>29</sup> Furthermore, the self-assembly of six shuttlecock-like  $Mn_4$ -BTC4A building blocks and eight facial anions leads to a distorted octahedral  $Mn_{24}$  metalocage



**Figure 5.** (a) A 1D coordination polymer based on nanosized tube units composed of  $\text{Ag}_3(\text{tpst})_2$  metallocages and (b) the transformation from discrete  $\text{M}_6(\text{tpa})_8$  metallocages to 1D cage-based coordination polymer.

through a  $\text{M}_6\text{L}_8$  condensation (Figure 3c).<sup>30</sup> Liao and co-workers also reported a series of nanoscale coordination cages with tripodal rigid ligands via a face-directed strategy based on similar  $\text{metal}_4\text{-BTC4A}$  subunits.<sup>31</sup> It needs to be emphasized that, different from the traditional coordination polyhedra, such  $\text{metal}_4\text{-BTC4A}$  based metallocages incorporate two kinds of host shells, that is, inner cavity of the coordination polyhedron and outer pocket constructed by the bowl-shaped calix[4]arene ligand. This unusual characteristic might make them potential candidates as bifunctional hosts.

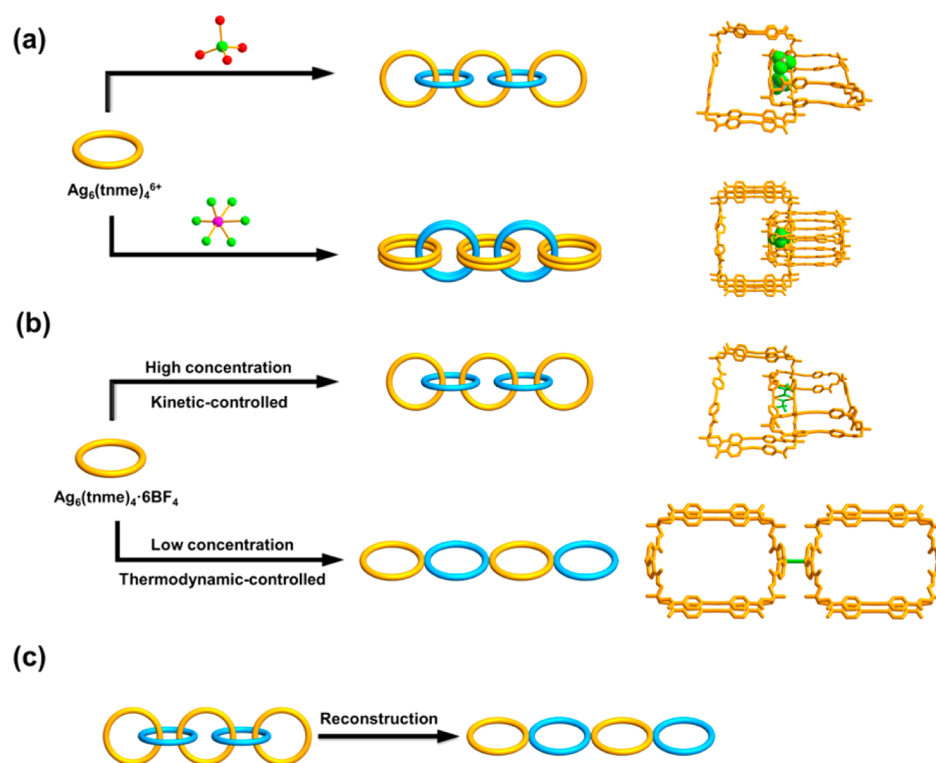
The multigonal prismatic cages, such as pentagonal and hexagonal cages, are rarely reported. One of the reasons is that for a single metal ion it is impossible to offer the  $C_n$  ( $n \geq 5$ ) symmetry coordination sites limited by the coordination number and coordination geometry. An alternate method of obtaining high-symmetry coordination sites may be the use of a metal cluster instead of a single metal ion. Recently, we reported an unusual cubane-like hydroxyl metal cluster,  $\text{Ni}_4(\mu\text{-OH})_4$ , in which four Ni(II) ions and four  $\mu\text{-OH}^-$  groups occupy eight corners of the cube alternately (Figure 4a).<sup>32</sup> Such  $\text{Ni}_4(\mu\text{-OH})_4$  metal clusters can be further connected from various directions, resulting in a theoretically high-symmetry metal cluster SBU (secondary building unit). Self-assembly of  $\text{Ni}_4(\mu\text{-OH})_4$  cubanes with clip-like organic ligands (1,3-bis(1-imidazolyl)benzene, 1,1'-(5-methyl-1,3-phenylene)bis(1*H*-imidazole), and 1,1'-(5-methoxy-1,3-phenylene)bis(1*H*-imidazole)) can generate a family of hexagonal-prismatic cages with a slight difference (Figure 4b). In this case, most of the coordination sites of octahedral Ni(II) ions are occupied by oxygen atoms, leaving six unsaturated coordination sites from three Ni(II) ions, which are further linked by six clip-like ligands to form a hexagonal-prismatic cage with the help of  $\text{SO}_4^{2-}$  templates (Figure 4c). This investigation may provide a new strategy toward the construction of the high  $C_n$  ( $n > 5$ ) symmetric metallocages.

Metal clusters can bring diverse assembly modes that cannot be achieved by single metal ions. Utilization of metal clusters instead of single metal ions as vertexes affords two obvious advantages that not only can enlarge the size but also can enrich shapes and functionalities of metallocages, greatly widening the world of the discrete metallocages.

### 3. COORDINATION-DRIVEN SELF-ASSEMBLY OF INFINITE FRAMEWORKS BASED ON DISCRETE METALLOCAGES

As discussed above, by modulation of coordination modes of metal ions or metal clusters, a variety of supramolecular cages can be constructed when suitable ligands are employed. These discrete supramolecular cages, exhibiting large inner cavities, plentiful shapes, and adjustable windows, may have promising applications in many fields. However, investigation merely on the assembly of discrete cages may have limitations not only in exploring structural diversity and performance enhancement of the metallocages but also in further understanding of self-assembly processes. Due to the large cavities in these discrete supramolecular cages or potential unsaturated coordination sites on their surfaces, these cages may be further assembled into infinite frameworks with more complexity if suitable conditions are provided. Different from the self-assembly of discrete cages described previously, such further assembly mainly focuses on the relationships between the discrete cages including their interactions, connections, and transformations.

We have introduced several types of metallocages above. In fact, these discrete metallocages may be further assembled into more complicated ensembles under suitable assembly conditions. Direct linking their unsaturated coordination sites and interlocking their cavities are the two strategies to assemble discrete metallocages into infinite frameworks.



**Figure 6.** Self-assembly system based on the Ag<sub>6</sub>(tnme)<sub>4</sub> metallocage.

### 3.1. Infinite Cage-Based Frameworks Linked by Coordination Bonds

The tpst ligand possesses rich coordination sites. Besides three pyridine groups, N and S atoms of the trithiocyanuric group have potential coordination ability. The redundant coordination atoms may further assemble the cage based on tpst into a more complicated ensemble by linking these free donor atoms. As Figure 5a shows, with the help of one N and one S atom from the trithiocyanuric group, two triangular prism Ag<sub>3</sub>(tpst)<sub>2</sub> metallocages are linked by an additional Ag(I) atom to form a basic nanosized tube unit with the dimensions of 1.34 × 0.96 × 0.89 nm<sup>3</sup>. Because the coordination geometry of this additional Ag(I) atom is still incomplete, an infinite chain thus is generated by sharing Ag atoms with neighboring tube units (Figure 5a).<sup>19</sup> This structure represents a unique chain structural motif in supramolecular coordination chemistry.

It has been speculated that the unsaturated coordination site is an impetus to construct infinite cage-based frameworks in self-assembly process; however, the direct evidence is lacking. Single-crystal-to-single-crystal (SCSC) transformation from a discrete cage to an infinite cage-based coordination polymer may witness this process. Immersing single crystals of the aforementioned Cu<sub>6</sub>(tppa)<sub>8</sub> cage in NaCl solution at room temperature affords a 1D cage-based chain.<sup>20</sup> Here, the Cl<sup>-</sup> anions exchange with ClO<sub>4</sub><sup>-</sup> anions outside the cages and coordinated H<sub>2</sub>O molecules at Cu(II) sites; then a 1D cationic chain of coordination cages is formed through bridging of the newly formed cage units by Cl<sup>-</sup> ions (Figure 5b). After the transformation, the unsaturated coordination sites of five-coordinated Cu(II) centers are occupied by Cl<sup>-</sup> ions, and their coordination modes change to six-coordination. Most of the SCSC cases involve the dimerization or polymerization of unsaturated molecules or guest exchange of porous materials, while such local structural changes of discrete molecular cages

induced by anion exchange have rarely been observed so far. This kind of SCSC transformation can also be viewed as a stepwise assembly of cage-based coordination polymers. Recently, Zhou and co-workers presented a reversible transformation between discrete nanocages and a chain of nanocages induced by the hydrophobicity/hydrophilicity of the solvent mixture.<sup>33</sup>

Besides 1D infinite cage-based coordination polymers, their 3D analogs were successfully constructed from discrete metallocages.<sup>34–37</sup> Most of them were synthesized through in situ assembly of metal ions and bridging ligands, which we do not emphasize here. A stepwise construction of a MOF using a molecular polyhedron precursor was first obtained in 2009.<sup>38</sup> In this case, the terminal ligands of an octahedral nanocage are displaced by bridging ligands thus linking the cages to a 3D pcu-a network. Then, using the classical nanocage MOP-15 as the precursor, Su and co-workers reported a step-by-step assembly of a series of fcu topological MOFs by a similar strategy.<sup>39,40</sup> In this example, the labile peripheral terminal coordinated water molecules of MOP-15 are fully substituted by different linear bridging ligands. These infinite cage-based MOFs can be applied in drug delivery as well as adsorption and separation of dyes.

To sum up, there are two routes to acquire cage-based coordination polymers. An explicit one is to introduce a linker to fill the unsaturated coordination sites on the surface of a metallocage. Because such unsaturated metallocages are quite limited, the other way is to replace the liable terminal ligands on a metallocage with bridging ligands by tuning the coordination conditions around the cage. From discrete metallocages to cage-based coordination polymers, the structural complexity and stability are always achieved, enriching and favoring the practical applications of metallocages.

### 3.2. Infinite Cage-Based Frameworks Linked by Mechanical Bonds

Aside from coordination interactions, mechanical bonds such as interlocking and interpenetrating, which play a crucial role in the assembly of biomacromolecules and molecular machines, can also help to construct extended frameworks; however, it is rarely realized in metallocages.<sup>41</sup> Infinite cage-based polycatenanes were not documented until very recently. The first example of an infinite cage-based polycatenane was reported by Lu and co-workers,<sup>42</sup> in which, an infinite three-dimensional metal–organic framework by sextuple intercatenation of discrete adamantane-like cages was presented. Later, Dehnen and co-workers reported a strand-like polycatenane constructed by icosahedral cages.<sup>43</sup> More recently, Lu and co-workers obtained two polycatenanes with different dimensions (1D and 3D) based on discrete tetrahedral cages.<sup>44</sup> The dynamic pores of the latter were proven by PXRD and adsorption investigation. The compound also displays size-dependent adsorption/desorption behaviors of alcohols.

Our group presented another example of an infinite polycatenane based on the extension of discrete metallocages. As shown in Figure 6a, the neighboring discrete  $\text{Ag}_6(\text{tnme})_4$  or  $\text{Ag}_{12}(\text{tnme})_8$  metallocages are interlocked with each other to form an infinite polycatenane.<sup>22</sup> Since the interlocking process is an entropically unfavorable process, achievement of such cage-based polycatenanes requires three key points: first, the size of window and cavity is large enough to permit interlocking; second, suitable metal–donor joints that can quickly associate and disassociate are needed as key intermediates for interlocking; finally, the final polycatenane assembly can be further stabilized by weak interactions such as  $\pi\cdots\pi$ , hydrogen bonding, and electrostatic interactions. In our case, the cavities of  $\text{Ag}_6(\text{tnme})_4$  and  $\text{Ag}_{12}(\text{tnme})_8$  cages are  $20 \times 16 \times 4 \text{ \AA}^3$  and  $22 \times 17 \times 10 \text{ \AA}^3$ , respectively, providing a large space for interlocking. The driving force of the interlocking comes from the  $\pi\cdots\pi$  interactions between the ligands and the strong charge–charge interactions further stabilize the interlocking. Moreover, the key intermediate  $\text{Ag}_5(\text{tnme})_4$  was first observed by us, based on which a possible interlocking process is suggested. Since strong electrostatic interactions play an important role in stabilizing the final polycatenane, electro-negative anions with different sizes,  $\text{ClO}_4^-$  and  $\text{PF}_6^-$ , thus lead to different polycatenanes based on  $\text{Ag}_6(\text{tnme})_4$  and  $\text{Ag}_{12}(\text{tnme})_8$ , respectively.

In the above interlocking system, suitable anions such as  $\text{ClO}_4^-$  can induce  $\text{Ag}(\text{I})$  and ligand  $\text{tnme}$  to assemble into the  $\text{Ag}_6(\text{tnme})_4$  cage quickly (about 5 min), which inspires us to develop a more mild self-assembly system that can efficiently construct discrete metallocages into infinite polycatenanes. Further investigation shows that  $\text{Ag}_6(\text{tnme})_4(\text{BF}_4)_6$  metallocages can effectively be assembled into a new 1D polycatenane in their supersaturated  $\text{MeOH}/\text{CHCl}_3$  solution at  $30^\circ\text{C}$  within 24 h,<sup>45</sup> which represents the most effective construction of multiple mechanical bonds based on discrete cages. More interestingly, when the concentration of the metallocages in the solution is unsaturated, the  $\text{Ag}_6(\text{tnme})_4(\text{BF}_4)_6$  metallocages prefer to assemble into a 1D polycage instead in which the interactions between neighboring cage units are stronger metal–metal interactions (Figure 6b).

The high concentration of  $\text{Ag}_6(\text{tnme})_4(\text{BF}_4)_6$  cages tends to form a less stable polycatenane quickly, and the low concentration of  $\text{Ag}_6(\text{tnme})_4(\text{BF}_4)_6$  cages tends to afford a more stable polycage slowly, which demonstrates that the

polycatenane is a kinetic product while the polycage is a thermodynamic product. So the kinetic product polycatenane could be reconstructed into the thermodynamic product smoothly under suitable conditions. Finally, we find that the polycatenane can entirely transform into the polycage at  $30^\circ\text{C}$  in  $\text{MeOH}/\text{CHCl}_3$  solution (Figure 6c). As far as we know, no other assembly systems can provide the kinetic products and thermodynamic products selectively through changing the concentration of substrates and transform kinetic products into thermodynamic products smoothly, which are all realized in this novel assembly system.

### 4. CONCLUDING REMARKS

In retrospect, discrete metallocages and infinite cage-based frameworks can be controllably obtained by coordination-driven self-assembly. Metal vertexes play a pivotal role in such self-assembly process: by utilization of different geometry of metal ions coordinated with suitable ligands, a variety of discrete metallocages can be rationally designed and synthesized; replacement of single metal ions with metal clusters offers various opportunities for the preparation of nanoscopic supramolecular ensembles, giving access to both structural diversity and functional modulation; when unsaturated coordination sites exist on the surfaces of the cage, high-dimensional cage-based frameworks will be achieved.

In the past few years, many efforts have been devoted to the chemistry of discrete metallocages for their charming structures and promising applications. Extending the exploration from discrete cages to infinite cage-based frameworks brings a new world to this field since (1) structural complexity and functional improvement can be synchronously achieved in infinite cage-based systems and (2) the study of relationships between cages provides us a pathway to a deep understanding of self-assembly processes. Investigation on metallocages as well as cage-based frameworks is so fascinating that it warrant devoting more effort to this blossoming field in the future.

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