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# Coordination Assemblies of Metallacyclic, Prismatic and Tubular Molecular Architectures Based on the Non-rigid Ligands

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**Keywords:** Metallacycle / Coordination prism / Coordination tube / Non-rigid ligand / Molecular architecture

This microreview covers recent advances in the assembly of coordination molecular architectures showing cyclic, prismatic and tubular structures based on the semi-rigid or flexible ligands. Four assembly routes are outlined depending on the symmetry interactions between specific ligands and metal ions.

## 1. Introduction

During the past decades, great attentions have been paid to control the self-assembly of metallasupramolecular species, and numerous discrete molecular architectures with different shapes and functionalities have been synthesized in an effort to approach the ambitious goal: rational prediction and design.[1] Usually, the coordination assemblies can be classified into two main branches: infinite coordination

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polymers and discrete molecular architectures. The field of coordination polymers continues to expand exponentially because of their potential applications in the areas of catalysis, chirality, conductivity, luminescence, magnetism, spin-transition (spin-crossover), non-linear optics (NLO) and porosity or zeolitic behaviors. On the other hand, interests in the design and construction of discrete molecular architectures have also experienced extraordinary progress not only because of their intrinsic aesthetic appeals but also due to their various potentials for being used as sensors, probes, catalysts, containers and in basic host-guest chemistry.

On the base of some well-documented strategies, such as Molecular Library Model,[1a,1b] Symmetry Interaction Model,[1c,1d] Directional-Bonding Approach,[1a] Weak-Link Synthetic Approach,[1e] and so on, various discrete molecular architectures with desired shapes and concomitant properties have been synthesized. However, most of these approaches relate to high symmetric molecules, such as polygons and polyhedra. The ligands therein used are usually rigid or specifically multifunctional, and the coordination geometry of metal center sometimes needs protecting. In contrast, using of non-rigid (semi-rigid or flexible) ligands to construct well-shaped molecular architectures is far less common, partly due to the less predictable assembly process. However, the incorporation of flexible components may endow the molecular architectures with potential advantages, for example, a "breathing" ability in the solid state and adaptive recognition properties as a functional of coexisting guest or counterions. Furthermore, flexibility of the non-rigid ligand can afford a good opportunity to investigate the details of the self-assembly process and provide more information for the directional synthesis of target supramolecular complexes. For instance, the flexibility of the ligand can lead to the formation of both discrete macrocycles and infinite polymeric structures on the basis of the conformational freedom of the connecting fragment, and the conversion between these two types of structures could be related by the concept of ring-opening isomerism.[2] Most important, deliberate design of non-rigid ditopic ligands can afford organic "molecular clips" which make it easy to construct relatively lower-symmetric molecular architectures of rectangular or prismatic shapes following a ligand-directed symmetry-interaction approach.[3]

We have long been involving in the synthesis of cyclic, tubular or cage-like metallasupramolecules through design of the specified semi-rigid or flexible ligands with benzimidazolyl or quinolyl as terminal groups and rigid arenes or flexible alkenes as spacers. Given the availability of different coordination modes provided by the designed ligands, we have synthesized a diverse array of discrete structures ranging from simple binuclear cyclic $M_2L_2$, prismatic $M_3L_2$, $M_2L_3$ or $M_2L_4$, to tubular $M_4L_4$ molecular architectures. The present microreview will mainly concentrate on recent progress in the assembly of the prismatic coordination structures by using of the non-rigid ligands, involving some related examples of macrocyclic and tubular molecules on the basis of the results from our and other groups, but avoid covering comprehensive literature examples.

## 2. Design Approaches

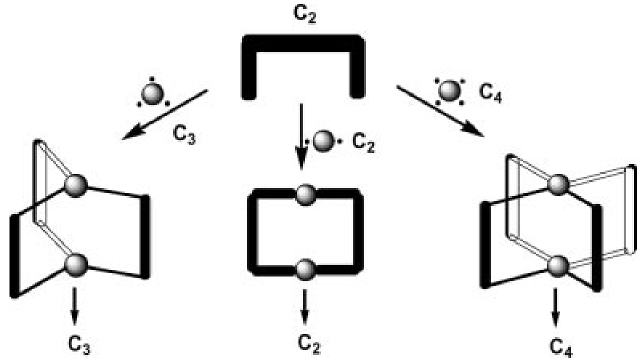
Several general strategies have been developed for construction of the discrete coordination molecular architectures.[1] The directional-bonding or molecular library approaches[1a,1e] are efficient for building up molecular polygons or polyhedra based on rigid ligands, the symmetry-interaction approach[1a–1d] is a powerful tool to elegant shapes and architectures like helicates, tetrahedral and adamantoid structures through multibranched chelating ligands, the molecular paneling approach is used by Fujita et al.[1b] to assemble large 3D assemblies, and the weak-link approach is mainly developed by Mirkin et al.[1e] to prepare supramolecular architectures from flexible ligands. However, none of above strategies are characteristic of prismatic structures.

In contrast to the highest symmetric polyhedral structures which possessing multiple $n$-fold rotation axes, the right prisms are composed of two regular $n$-gons perpendicular to a sole $n$-fold rotation axis, such as trigonal and tetragonal prisms, therefore, showing relatively lower symmetry. The even lower symmetric oblique prisms only contain two polygonal bases in parallel and several lateral parallelograms without actual $n$-fold rotation axis. On the other hand, a lot of dimeric cage structures possessing apparent $D_{nh}$ symmetry also show prismatic shape without the strict lateral parallelograms. The common feature of these structures is the absence of multiple $n$-fold rotation ($n \geq 3$) symmetry but having two parallel $n$-gons. If such structures are open ended (two bases of the prisms are not closed), tubular structures are formed. Similar symmetry relationship between the polyhedral and prismatic structures can also be found between polygonal and rectangular structures.

To achieve convergent assembly of molecular prisms by preventing appearance of more than one $n$-fold axes during the self-assembly process, more deliberate predesign and judicious choice of the components are required. One of constructive approaches proposed by Stang and co-workers is to design a "molecular clip": two parallel coordination sites are facing in the same direction, which allows for the assembly e.g. of a molecular rectangle by using rigid bipyridyl bridging ligands[4a,4b] or of trigonal prisms by using tritopic ligands with pyridyl subunits.[4c] Taking advantages of such a design principle, we have proposed a ligand-directed symmetry-interaction approach,[3] relying on synthesis of shape-defined "organic molecular clips" which display a coordination directing mode similar to Stang's organometallic clips, thereby facilitate modular assembly of prismatic architectures. On the basis of known examples from our and other groups, the following routes for assembly of coordination prismatic cages and related structures could be outlined:

### 2.1 Molcular Clips + Metal Ions of $C_n$ Symmetry

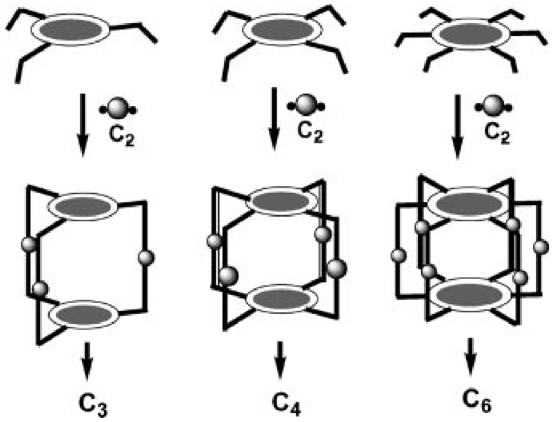
As shown in Scheme 1 a molecular clip can be a ditopic semi-rigid ligand possessing two coordinating arms which must take the *cis* conformation. Because the molecular clip has a symmetry no higher than 2-fold, combination of the molecular clips with two axial centers will give rise to rectangle or *n*-gonal prisms determined by *n*-fold symmetry of the axial centers ($C_n$). That is, two linearly coordinating metal ions will connect two clips to form a rectangular-shaped structure, while two triangularly coordinating metal ions can lead to the formation of a trigonal prism, and further, a tetragonal prism may be generated by using two metal ions which prefer a square-planar coordination environment. The shape and size of the assembled molecules are determined by the size of the ligands and preferred coordination of the metal ions.



Scheme 1. Assembly of rectangular or prismatic structures from molecular clips and metal ions of $C_n$ symmetry.

## 2.2 Multipodal Ligands + Metal Ions of $C_2$ Symmetry

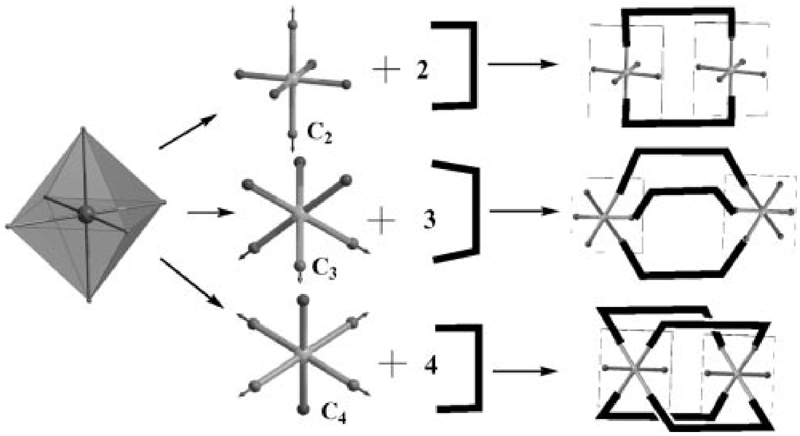
A complementary approach to construct compositionally different but topologically identical prismatic molecules compared to route 2.1 is shown in Scheme 2. In this route, a multipodal ligand which contains more than two legs connecting with the basal core and pointing in the same direction (*cis* conformation) is used to determine the *n*-fold rotation axis. In combination of the metal ions with $C_2$ symmetry, *n*-gonal prismatic structures are readily available depending on the size and shape of the ligands. One of the advantages of this route is that assembly of the coordination prisms with higher $C_n$ symmetry ($n \geq 5$) become feasible. This is hard for route 2.1 due to absence of metal ions with coordination geometry having $C_5$ or higher rotation symmetry.



Scheme 2. Assembly of prismatic structures from multipodal ligands and metal ions of $C_2$ symmetry.

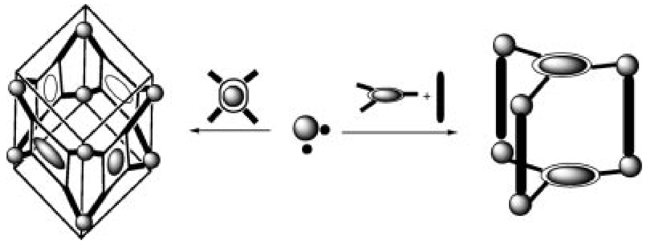
## 2.3 Molcular Clips + Protected Metal Ions of Restrained $C_n$ Symmetry

Another route to construct rectangular and prismatic molecular architectures is to use selected symmetry of metal ions with protected coordination geometry. For example, the octahedral metal ions are known to provide versatile coordination symmetry, however, it is a surprise that their potential application in construction of molecular prisms has so far been mainly realized in tetragonal prisms. As depicted in Scheme 3, the utilization of four equatorial sites can afford a $C_4$ tetragonal node, while a $C_3$ trigonal node can be produced if three *fac*-coordination sites are blocked. Even further, if only two opposite coordination sites are kept free while all other occupied, a linear node of $C_2$ symmetry is obvious. Such symmetry restrained metal ions interact with the appropriate molecular clips can lead to formation of tetragonal prism, dicapped trigonal prisms and molecular rectangles, respectively. Therefore, octahedral metal ions could become an abundant source to construct



Scheme 3. Assembly of rectangular or prismatic structures from molecular clips and blocked octahedral metal ions.

rectangular or prismatic molecular architectures following the ligand-directed symmetry-interaction approach if their $C_n$ symmetry can be properly retained.[5] Similarly, the metal ions of square pyramidal geometry could provide $C_4$ symmetry if the apical site is blocked, and the trigonal bipyramidal geometry could give rise to $C_3$ symmetry if two axial sites are protected.



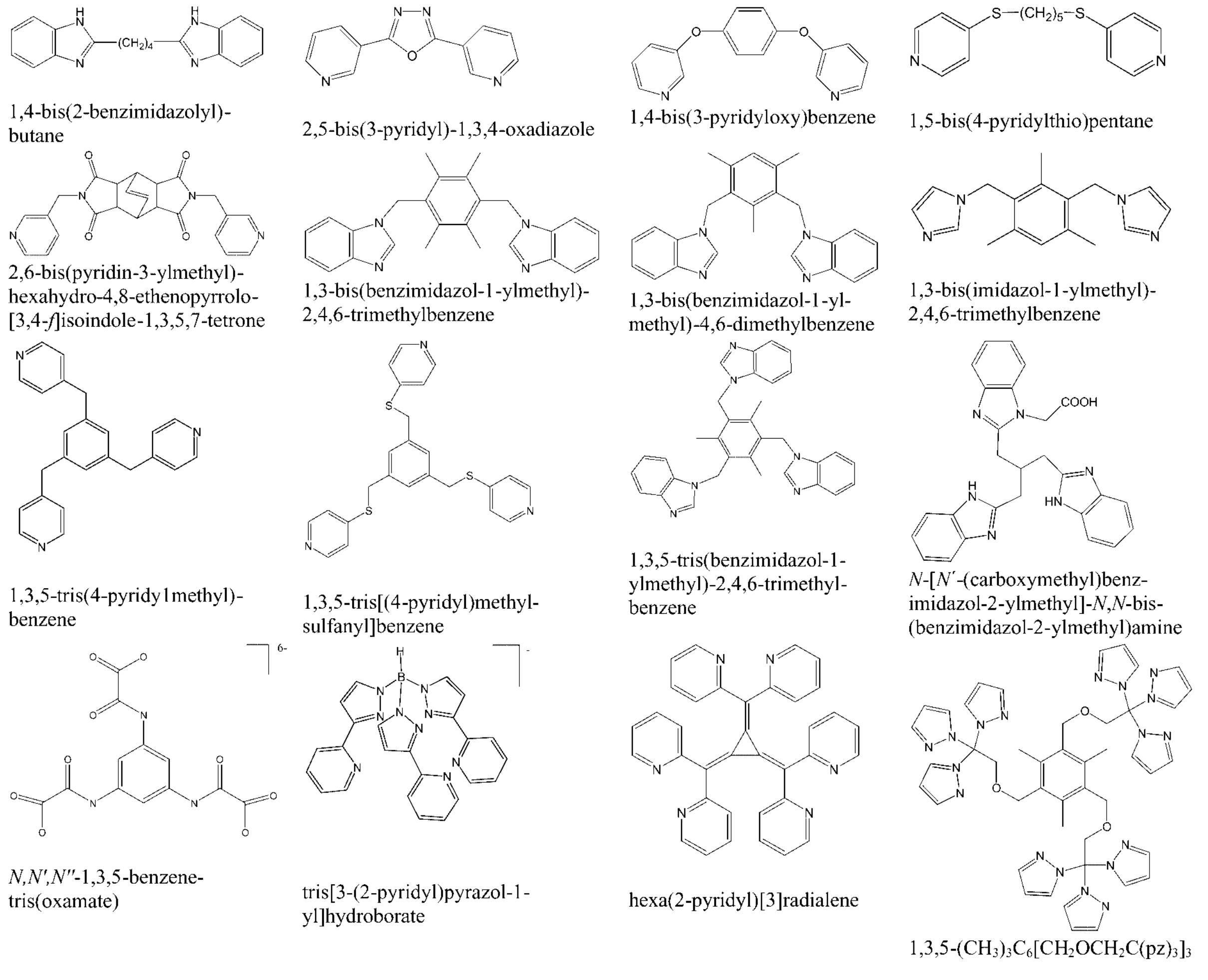
Scheme 4. Representative of multicomponent assembly of a molecular tube or a trigonal prism.

### 2.4 Multicomponent Self-Assembly

By contrast to above approaches for construction of discrete molecular architectures based on $C_n$ symmetry, deliberate design of prismatic architecture has long been achieved from multiple components self-assembly as depicted in Scheme 4.

This approach is mainly characteristic of the rigid ligands. The pioneering work in this field includes Lehn's cylindrical structures[6] assembled from tetrapyridine and hexaphenylhexaazatriphenylene derivatived multidentate compounds involving two triangular ligands and three ditopic linear ligands. However, the flexible tetrapyridine ligand containing the $CH_2CH_2$ spacer was found to be able to result in the similar trigonal structure.[6c] Fujita and co-workers have reported a series of prismatic architectures based on the self-assembly of tridentate panel-like ligand, bidentate pillar ligand and *cis*-capped $Pd^{II}$ or $Pt^{II}$ ions.[7a–7c] Because the ligands are normally "self-select",[7a,7c] the template has been found necessary for the formation of such prismatic structures. Moreover, thus constructed molecular architectures are usually kinetically stable once formed and remain stable to a certain extent even after the template was removed.

It is interesting that formation of tubular structures sometimes takes benefit from such a multicomponent assemble process.[7d] As shown in Scheme 4, if the ligands oc-



Scheme 5. Part of the mentioned ligands.

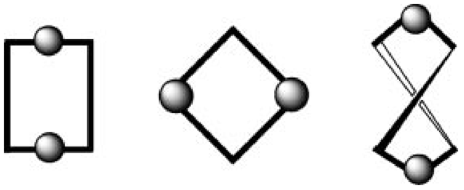
cupying the bases of the prisms are absent, the prismatic structure becomes open-ended, thus turning into tubular architectures keeping the shape of the prisms.

It should be noticed that there are other routes besides above four have also appeared in the literature. On the other hand, these approaches sometimes may also result in formation of helical structures, such as double-stranded, triple-stranded and even quadruple-stranded helicates,[1d,8] which sometimes become ambiguous to be distinguishable from the prismatic structures. However, for the molecular architectures having well-shaped structure or even possessing apparent $C_{n\mathrm{h}}$ or $D_{n\mathrm{h}}$ symmetry which incompatible with the helical sense, it is inappropriate to describe them as helicates. In this microreview, we mainly focus on apparently regular molecular architectures. A few obvious helicates are only mentioned selectively. In many cases, the structures may not possess the exact crystallographically imposed $C_n$ symmetry thus deviating from the right prisms, or only keeping the overall prismatic shapes. Part of organic ligands mentioned in the following discussion are listed in Scheme 5.

## 3. Cyclic Molecular Architectures

### 3.1 $M_2L_2$ Metallacycles and Rectangles Based on Non-Rigid Ligands

Design and synthesis of cyclic molecular architecture has attracted extensive interests in several research fields, including materials chemistry and molecular nanotechnology. Dinuclear metallacycles may represent the most productive cyclic molecular architectures, partly owing to the fact that the closed $M_2L_2$ motif is the smallest metallacyclic species hence the most thermodynamically favored one predominant over other larger species in solution. As early examples of such structures, flexible long-chain diphosphanes $Ph_2P(CH_2)_nPPh_2$ ($n \geq 3$) have been shown to generally give rise to dinuclear ring structures on reaction with equivalent amounts of silver(I) or copper(I) salts, containing terminal or bridging anions.[9] Depending on the different conformations of the non-rigid ligands, $M_2L_2$ cyclic molecules can display varied shapes like molecular rectangles, molecular rhombus and dinuclear helicates as shown in Scheme 6. Usually, when the non-rigid ligand contains two terminal coordinating arms which adopt a *cis* conformation and point to the same direction, the ligand can act as a "molecular clip" to react with metal ions to form $M_2L_2$ rectangles. While the angular ligand turning in the middle can react with two metal ions to assemble an $M_2L_2$ molecule showing rhombic structure. On the contrary, if the conformation of the non-rigid ligand is changed from *cis* to *trans*, the ligand can twist along two metal axes to form dinuclear helicate. For example, Hannon et al. designed a series of bis(pyridylimine) Schiff-base ligands from methyldianiline, which offer sufficient flexibility for two strands to wrap around the two metal centers while impose the same stereochemistry at both centers. Reaction of these ligands with $Cu^I$ or $Ag^I$ ions afforded various dinuclear helicates.[10]



Scheme 6. Schematic view of the rectangular, rhombic or dinuclear helical $M_2L_2$ metallacycles.

Compared to the well developed higher symmetric $M_4L_4$ square, molecular rectangles may be able to exhibit improved selectivity and sensitivity with respect to molecular recognition and separation.[4] However, preparation of molecular rectangles based on the rigid ligands is still challengeable, because simply mixing two ligands of different lengths and *cis*-protected metal corners usually forms two types of molecular squares instead of molecular rectangles due to the enthalpic reason.[11] Alternatively, Stang and coworkers creatively designed an organometallic "clip" which anchors two metal corners on each side of a rigid ligand and opens two labile coordination sites in a nearly parallel fashion ready for connecting the second rod-like dipotic ligand.[4a] Similarly, clever design of semi-rigid ligand possessing two co-facial directing coordination groups could provide analogous "organic molecular clips" which facilitate a ligand-directed symmetry-interaction approach[3] for fabrication of rectangular structures as demonstrated in route 2.1 and 2.3.

Early examples matching such design approach can be found in a series of cofacial dinuclear complexes formed from bis(β-diketone) and bis(β-ketoenamine) ligands.[12a–12d] The well-defined size and shape of these complexes show inner cavity where small guest molecules are able to be hosted. Latter examples include Mirkin's neutral $Re^I$ macrocycles of the phosphanylthioether ligands,[12e] Cotton's molecular loops composed of two dimetal *cis*-$Mo_2(DAniF)_2^{2+}$ units (DAniF = *N*,*N′*-di-*p*-anisylformamidinate) linked by two dicarboxylate dianions,[12f] Chung's $Ag^I$ metallosupramolecules of the flexible 2-pyridyl ligands,[12g] and Fujita's rhombic structure consisting of two angular dipyridyl ligands and *cis*-protected metal ions.[12h]

We designed a series of semi-rigid and flexible ligands containing two (benz)imidazolyl or quinolyl terminal coordinating groups.[13] The flexibility of the methylene $-CH_2-$ groups endow the ligands conformational freedom and, when induced by the symmetry interaction from properly selected metal ions, they behavior as molecular "clips" to assemble dinuclear metallocycles showing the rectangular structures. The shape and size of these molecular rectangles could be adjusted by modifying the structures of the ligands, thereby imposing distinguishable nature of the cavity and ability of hosting small molecules or counterions (Figure 1).[3] In addition, many dinuclear macrocycles based on the non-rigid ligands have good solubility, thus giving a chance to investigate their solution dynamics and the potential mechanism of self-assembly by means of NMR and ESI-MS techniques. For example, in complexes

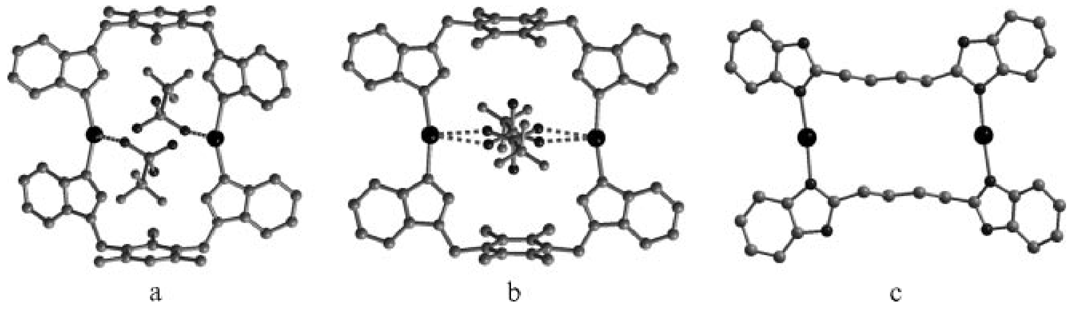
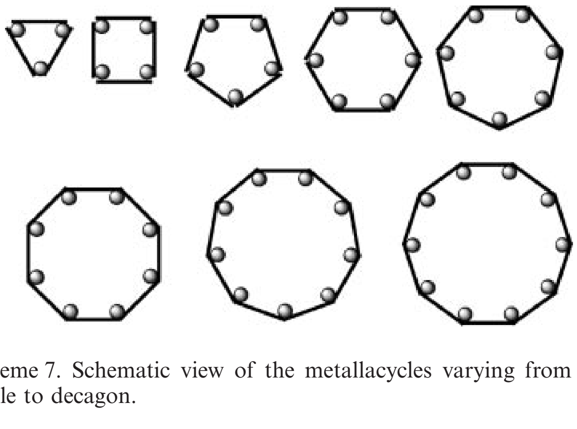


Figure 1. Rectangular structures formed in complexes (a) $[Ag_2\mathbf{L^1}_2](CF_3SO_3)_2$ [$\mathbf{L^1}$ = 1,3-bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene],[3] (b) $[Ag_2\mathbf{L^2}_2](CF_3SO_3)_2$ [$\mathbf{L^2}$ = 1,4-bis(benzimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene][3] and (c) $[Ag_2(C4BIm)_2](CF_3CO_2)_2$.[13a]

$[Ag_2(C4BIm)_2](CF_3CO_2)_2$ [C4BIm = 1,4-bis(2-benzimidazolyl)butane][13a] as shown in Figure 1, c, the solution dynamics study showed that equilibria among the $[Ag_2(C4BIm)_2]^{2+}$ dication and other potential oligomers were established via a solvent-assisted dissociative exchange mechanism. The calculated metal–ligand exchange barrier from VT-$^1$H NMR results was comparable with the energy of a strong hydrogen bond, which accounts for the reason that why the formation of $Ag^I$ complexes are very unpredictable and can be easily affected by various subtle factors and why astonishingly diversified structures and topologies could be obtained from $Ag^I$ and quite similar ligands, namely, supramolecular isomerism.[13a]

### 3.2 $M_nL_n$ ($n \geq 3$) Metallacycles Based on Non-Rigid Ligands

The directional-bonding approach has been usually used to predetermine the larger cyclic molecules, and various structures with a wide range of sizes, shapes and desirable physical properties have been obtained through careful selection of the metal starting material, coordinatively inert directing ligands or bridging ligands.[1] Theoretically, multinuclear cyclic molecular architectures can be synthesized via the systematic combination of ditopic building blocks and metals conforming to required angles as shown in Scheme 7, in which the regular models of polygons, such as triangles, squares, pentagon, hexagons an so on, could be developed.



Scheme 7. Schematic view of the metallacycles varying from triangle to decagon.

However, there are many subtle factors which can influence the final formation of the cyclic molecules based on the non-rigid ligands, so precise control of the polygonal shape and size is often difficult. Nevertheless, Puddephatt et al.[14a] reported a cationic molecular triangle $[\{Pt(Bu_2\text{-}bipy)[\mu\text{-}4\text{-}NC_5H_4C(NO)NH\text{-}4\text{-}C_5H_4N]\}_3]^{6+}$ which was assembled from the *cis*-blocked platinum(II) unit $(Bu_2\text{-}bipy)Pt^{2+}$ and the unsymmetrical bis(pyridine) ligand $4\text{-}NC_5H_4C(NO)NH\text{-}4\text{-}C_5H_4N$ (Figure 2, a), while a neutral molecular triangle $[cis\text{-}Mo_2(DAniF)_2]_3(trans\text{-}1,4\text{-}O_2CC_6H_{10}CO_2)_3$ (DAniF = *N*,*N′*-di-*p*-anisylformamidinate) containing metal–metal bound units derived from paddlewheel complexes was obtained by Cotton et al.[14b] The square $M_4L_4$ molecules are rather common for the rigid ligands, but still remain rare for the non-rigid ligands. One example can be found in a nickel(II)-based cationic molecular square $[Ni(HL)]_4^{4+}$ which was achieved via self-assembly from a pentadentate N4S ligand bis[phenyl(2-pyridyl)methanone] thiocarbazone ($H_2L$).[14c] The ligand was believed to be "conformationally rigid" and its multidentate character made it possible to use the octahedral metal ion for formation of square structure. A similar example is a zinc(II)-based square complex assembled from a linear-spacer-bridged bis(pyrrol-2-ylmethyleneamine) ligand. The structure possesses a $D_4$ geometry with two pyrrol-2-ylmethyleneamine units adopt a *trans* arrangement resulting in inner dimensions of 8.7 × 8.7 Å[14d] as shown in Figure 2, b.

It is usually believed that, for the $M_nL_n$ macrocyclic structures, when the value *n* becomes larger, the discrete macrocycles becomes more thermodynamically disfavored in solution. However, the flexibility of the ligands sometimes may facilitate formation of multinuclear macrocyclic $M_nL_n$ ($n \geq 4$) with the aid of template guest. Known examples may be found from a series of $M_6L_6$ assemblies,[15] such as the chiral $Ag_6L_6$ from a completely stereospecific self-assembly of a semi-rigid bipyridine derivative with fused pinene group,[15a] neutral molecular $Pd_6L_6$ hexagons by using of flexible carboxylic acid modified ditertiary phosphanes $\kappa^3$-$P_2O$-terdentate ligands,[15b] $Fe_6L_6$ hexameric ferric wheels from reaction of various *N*-substituted diethanolamines.[15c] Even larger metallacycles[16] include [30]-metallacrown-10 compounds $[Mn(C_{14}H_9N_2O_3)(CH_3OH)]_{10}\cdot 5CH_2Cl_2\cdot 16CH_3OH\cdot H_2O$ and $[Fe(C_{14}H_9N_2O_3)(CH_3OH)]_{10}\cdot$

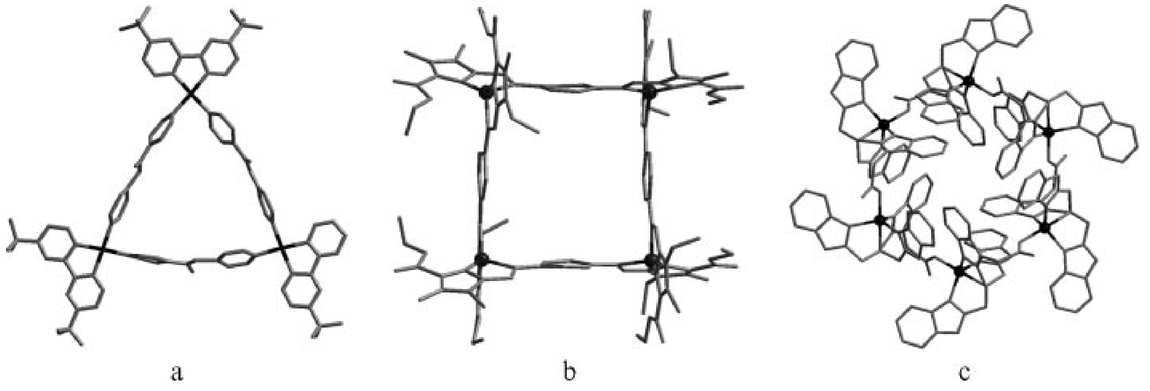


Figure 2. (a) A cationic molecular triangle [{Pt(Bu$_2$-bipy)[μ-4-NC$_5$H$_4$C(NO)NH-4-C$_5$H$_4$N]}$_3$]$^{6+}$,[14a] (b) a zinc(II)-based square complex assembled from a bis(pyrrol-2-ylmethyleneamine) ligand,[14d] and (c) a hexanuclear cationic metallamacrocycle [Cu$_6$(Acntb)$_6$]-(ClO$_4$)$_6$·6H$_2$O.[15d]

3CH$_2$C$_{12}$·12.5CH$_3$OH·5H$_2$O with a pentadentate ligand *N*-phenylsalicylhydrazidate,[16a] [36]metallacrown-12 Ni$^{II}$ compound [Ni(C$_{13}$H$_9$N$_3$O$_2$)(CH$_3$OH)]$_{12}$ from a pentadentate Schiff-base ligand salicylaldehyde 2-pyridinecarboxylhydrazone,[16b] 36-membered dodecanuclear Mn$^{II}$ metalladiazamacrocycle [Mn$_{12}$(tpeshz)$_{12}$(dmf)$_{12}$] (H3tpeshz = *N-trans*-2-pentenoylsalicylhydrazide)[16c] and [Mn$_{12}$(chxshz)$_{12}$(MeOH)$_{12}$] (H3chxshz = *N*-cyclohexanoylsalicylhydrazide),[16d] and a chiral luminescent Au$_{16}$ ring [(dppm)$_2$Au$_4$(pipzdtc)]$_4$(PF$_6$)$_8$ assembled from achiral components dppm [bis(diphenylphosphanyl)methane] and K$_2$(pipzdtc) (piperazine-1,4-dicarbodithiolate).[16e]

We have modified a versatile *C*$_3$-symmetric ligand, tris(2-benzimidazolylmethyl)amine (ntb), by introducing one acetic acid group to get a new unsymmetric tripodal ligand *N*-[*N*′-(carboxymethyl)benzimidazol-2-ylmethyl]-*N*,*N*-bis(benzimidazol-2-ylmethyl)amine (HAcntb). Reaction of this ligand with Cu(ClO$_4$)$_2$ afforded a nanometer-sized hexanuclear cationic metallamacrocycle [Cu$_6$(Acntb)$_6$](ClO$_4$)$_6$·6H$_2$O as shown in Figure 2, c.[15d] Each Cu$^{II}$ ion is coordinated by three imino-nitrogen atoms and the apical amino-nitrogen atom form the same ligand, and one oxygen atom of the branching methylenecarboxylate group from another ligand, thus linking six Cu$^{II}$ ions to a hexameric structure possessing a crystallographically imposed –3 symmetry.

As mentioned above, one of the disadvantages by using non-rigid ligand is the difficulty of the controlling the size of the target macrocycles. A typical example is the assembly of a series of chiral molecular polygons, ranging from triangle to octagon, with [*cis*-(PEt$_3$)$_2$PtCl$_2$] and the same enantiopure 6,6′-bis(alkynyl)-1,1′-binaphthalene.[17] The limited conformational flexibility of the bridging ligand is believed the key to the facile one-pot self-assembly of six polygons of different size, which were able to be purified by silica gel column chromatography in varied yield. Another problem by using non-rigid ligand is the difficulty of determining the shape of the molecules. In many cases, so called circular helicates were obtained. For example, Steel et al. obtained an M$_3$L$_3$ trinuclear metallacycles[18a] by exploiting a semi-rigid ligand 1,3-bis(8-quinolyloxymethyl)-benzene to react with AgCF$_3$SO$_3$, and Hannon et al. reported a Cu$^I$ trinuclear helicate[18b] by utilizing semi-rigid bis(pyridylimine) Schiff-base ligands based on 4,4′-methylenebis(2,6-dimethylaniline). Moreover, different polygons can interconvert into each other by guest- or counterion-induced interactions which favor one over another during the assembly process. For example, Stang et al.[19a] reported an equilibrium mixture of triangular and square assemblies which was established in solution when the flexible, ditopic donor unit, *trans*-bis(4-pyridyl)ethylene, was treated with the ditopic acceptor unit, *cis*-(Me$_3$P)$_2$Pt(OTf)$_2$, in a 1:1 ratio. Such equilibrium is dependent on water and anions, and selective crystallization of either of the two species can be accomplished via the appropriate choice of solvents and ratio of anions. Similarly, Lehn and co-workers demonstrated that a linear trinuclear triple helicate could be converted to a pentagonal M$_5$L$_5$ in the presence of a template chloride anion while hexagonal M$_6$L$_6$ in the presence of a sulfate anion.[19b]

## 4. Prismatic Molecular Architectures

Design and assembly of prismatic molecular architectures, especially for those possessing an internal cavity capable of entrapping guest molecules, has been receiving great interests in recent years because of the prospective applications in host-guest chemistry, molecular recognition, catalysis, biology (drug delivery), and materials science (molecular devices). This section will give some examples according to the *n*-gonal bases of the prismatic structures.

### 4.1 Trigonal Prismatic Cages

### *4.1.1 Assembled via Route 2.1*

Two three-connected metal ions locating at two bases and three ditopic ligands acting as lateral edges are required by this approach. The Ag$^I$ ion is a good candidate which is well known to display flexible coordination geometry vary-

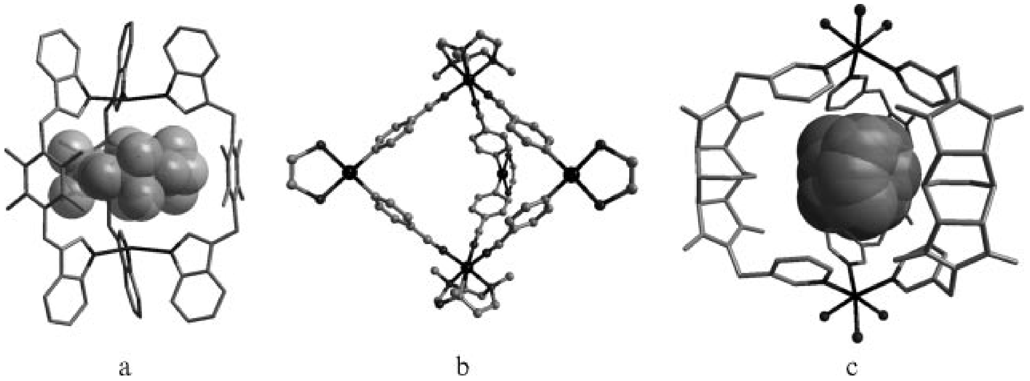


Figure 3. (a) Trigonal prismatic structures in complex $[Ag_2\mathbf{L}^2{}_3](CF_3SO_3)_2$,[21a] (b) trigonal-bipyramidal cage in complex $[[(Me_3tacn)Rh(CCPy)_3]_2[(DCPE)Pt]_3]$[22b] and (c) dicapped trigonal prismatic cage in complex $[Zn_2\mathbf{L}^3{}_3(H_2O)_6]\cdot(CF_3SO_3)_4\cdot CHCl_3$.[5] Guest molecules are shown in space-filling mode.

ing from two-coordinate linear to six-coordinate octahedral geometry.[20] When taking the triangular coordination geometry, $Ag^I$ ion can be utilized as trigonal node to assemble trigonal prisms in combination with three clip-like bis(monodentate) ligands. For example, we have prepared a ligand 1,4-bis(benzimidazol-1-ylmethyl)2,3,5,6-tetramethylbenzene (**L**$^2$) which reacts with $AgCF_3SO_3$ in a 2:3 ratio to afforded a trigonal prismatic cage $[Ag_2\mathbf{L}^2{}_3](CF_3SO_3)_2$ as shown in Figure 3, a.[21a] The three ligands adopted the *cis* conformations with the nitrogen donor atoms from the benzimidazole rings pointing to the same direction, thus behaving as molecular "clip". The entire cationic prism exhibits an unusual $S_3$ symmetry. Steel et al.[21b] reported a similar structure which was described as a helicate. Another example of trigonal prism with trigonal geometric metal ions at the bases has been synthesized by Johnson and coworkers.[21c] In this case they used three dithiol ligands and two $As^{III}$ metal ions and the trigonal prism was close to a $C_{3h}$ symmetry.

### *4.1.2 Assembled via Route 2.3*

If metal ions of higher coordination numbers are used for such a purpose, the metal centers have to be protected to degrade the symmetry to $C_n$ according to the route 2.3. For instance, when the metal ions take the tetrahedral coordination geometry, one of four coordination sites has to be occupied by a monodentate anion or auxiliary ligand. By utilizing diphosphane ligand 1,2-bis(diphenylphosphanyl)acetylene (dppa) to react with $Ag^I$ ions in a 2:3 ratio, a trigonal prism with tetrahedral geometric $Ag^I$ atoms at bases was obtained by James et al., in which the fourth coordination sites was taken by oxygen from anion $CF_3SO_3^-$ or $NO_3^-$, and the three P atoms from diphosphane ligands took the other three coordination sites.[22a] Another interesting example is the trigonal-bipyramidal supramolecular cage constructed by Youngs et al.[22b] where they used the well protected octahedral $Rh^{II}$ and square $Pt^{II}$ ions as shown in Figure 3, b. The reaction of 4-ethynyl-pyridine with the facially protected $(Me_3tacn)RhCl_3$ in the presence of *tert*-butyllithium afforded the octahedral complex $(Me_3tacn)Rh(CCPy)_3$, further reaction of this unit with three corner restricted *cis*-$(DCPE)Pt(NO_3)_2$ resulted in the mixed-metal-containing trigonal bipyramidal $[[(Me_3tacn)Rh(CCPy)_3]_2((DCPE)Pt)_3]$. From another point of view, this structure can be described as an assembly of three angular metal-containing ligands with two facially protected octahedral metal ions, showing a shape analogous to the trigonal prism.

We have prepared a semi-rigid conformational adaptive ligand, 2,6-bis(pyridin-3-ylmethyl)hexahydro-4,8-ethenopyrrolo[3,4-*f*]isoindole-1,3,5,7-tetrone (**L**$^3$), which can react with the octahedral $Zn^{II}$ ion to afford a complex $[Zn_2\mathbf{L}^3{}_3(H_2O)_6]\cdot(CF_3SO_3)_4\cdot CHCl_3$[5] as shown in Figure 3, c. Two $Zn^{II}$ ions in this complex are coordinated by three different ligands and three water molecules, resulting in a N3O3 environment where three N and three O atoms are arranged in a *fac*-conformation allowing of a *3*-fold rotation symmetry $C_3$, thus the $[M_2\mathbf{L}^3{}_3]^{4+}$ cationic motif displays a dicapped trigonal prismatic structure (Figure 3, c) containing a trigonal cage in which a disordered $CHCl_3$ guest molecule is hosted. The molecule possesses an exact $C_{3h}$ point symmetry with a $C_3$ rotation axis passing through two $Zn^{II}$ atoms and a mirror plan bisecting the molecule.[5]

It should be noted that routes 2.1 and 2.3 are also applicable to rigid ligands providing the ligands are ditopic and exhibit the molecular clip character. For instance, Du et al.[23a] obtained a trigonal prism $[Cu_2(\mathbf{L}^4)_3(CH_3CN)_2](ClO_4)_2$ [**L**$^4$ = 2,5-bis(3-pyridyl)-1,3,4-oxadiazole] in which one coordination site of each distorted tetrahedral $Cu^I$ center is occupied by N atom of an acetonitrile solvent, and the other three coordination sites join three different ligands acting as a 3-connecting node. Each trigonal prismatic cation hosts one water guest inside the cavity. Moreover, the bases of the trigonal prism can also be provided by different metal ions. Catalano et al. reported two mixed-metal trigonal prisms $[AuPdTl(P_2phen)_3](PF_6)_2$ and $[AuPtTl(P_2phen)_3](PF_6)_2$, where one basal site was taken by $Au^I$, and the other by $Pd^0$ or $Pt^0$. One $Tl^I$ ion was encapsulated inside via metal–metal interactions.[23b]

A combination of two six-coordinate metal ions and three flexible bis(bidentate) ligands can also follows route 2.1 to give $M_2L_3$ molecular architecture, however, in most cases the ligands are twisted and the structures are actually dinuclear triple-stranded helicates[24] which fall out the scope of this review.

### *4.1.3 Assembled via Route 2.2*

Alternatively, the two bases of the trigonal prism can also be provided by non-metal planes. As shown in Scheme 3, tripodal ligands can be exploited in the assembly of trigonal prism following route 2.2, where the trigonal prism is generated in combination with three bridging metal ions. The tripodal ligands could be based on an aromatic ring, macrocycle, or even B atomic core having three *cis,cis,cis* conformational coordinating legs.

### *4.1.3.1 From Tri(monodentate) Tripodal Ligands Based on Aromatic Core*

By using of the inherent $C_3$ symmetry of benzene ring, Fujita and co-workers designed one semi-rigid tripodal ligand 1,3,5-tris(4-pyridylmethyl)benzene and firstly described the formation of a trigonal prismatic structure having $M_3L_2$ components with two tripodal ligands bridged by three palladium atoms.[25] By changing the donor group 4-pyridyl to 1-imidazolyl, Sun and co-workers synthesized some new types of tripodal ligands and obtained a series of $M_3L_2$ trigonal prisms composed of two tripodal ligands and three bridging tetrahedral geometric zinc ions[25b] or linear coordinated silver ions.[25c–25e] Their results indicated that the frameworks of these prisms were mainly determined by the nature of the tripodal ligand and geometric need of the metal ions, independent of the anions and the solvents. A similar trigonal prism was also reported by Lindoy et al.,[25f] where they combine a flexible tripodal ligand 1,3,5-tris[(4-pyridyl)methylsulfanyl]benzene with three silver(I) ions affording an $M_3L_2$ prismatic structure.

Similarly, based on the inherent $C_3$ symmetry of mesitylene core, we have designed a semi-rigid tri(monodentate) tripodal ligand 1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene with 1-benzimidazolyl as coordination donor groups. Reaction of this tripodal ligand with $AgBF_4$, $AgClO_4$ or CuI resulted in a series of $M_3L_2$ trigonal prismatic cages which comprising two *syn*-conformational tripodal ligands jointed by three linearly coordinated metal ions with six benzimidazolyl legs nearly perpendicular to the central mesitylene cores (Figure 4, a).[3,26a] It was found that the assembly processes were not significantly affected by the counteranions, metal-to-ligand ratio or the solvent used, and the guest molecules encapsulated inside the cages showed diversified shapes and sizes varying from the spherical anion $BF_4^-$, $ClO_4^-$ to the planar $Cu_2I_4^{2-}$ coordination motif. To enlarge the inner cavity, the three legs of such tri(monodentate) tripodal ligand can be elongated. Ahn et al. have prepared a ligand containing three extended 4-pyridine legs with mesitylene or 1,3,5-triethylbenzene as cores. Two homochiral trigonal prisms were obtained from two tripodal ligands bridged by three $Pd^{II}$ ions. Since these prisms had internal binding sites, the authors believed that these cages could recognize organoammonium ions, or even chiral guests.[26b]

### *4.1.3.2 From Tri(bidentate) or Tri(tridentate) Tripodal Ligands Based on Aromatic Core*

To assemble the trigonal prismatic structures by using the tri(monodentate) tripodal ligands, three metal ions with only two free coordination sites are required, such as linear coordinated $Ag^I$ or $Cu^I$ ions. The metal ion of higher coordination number needs proper blocking. Such restriction can be released by using tri(bidentate) or tri(tridentate) tripodal ligands. Journaux et al.[27a] designed a tripodal ligands *N,N′,N′′*-1,3,5-benzenetris(oxamate) with oxamate group as coordination donor. Two ligands adopted a tris(*N*,O-bidentate) coordination mode to generate a trigonal prism in which each $Cu^{II}$ ions was coordinated by two nitrogen atoms and two oxygen atoms in the equatorial plane. Similarly, Reger et al.[27b] designed a tri(tridentate) tripodal ligand $1,3,5\text{-}(CH_3)_3C_6[CH_2OCH_2C(pz)_3]_3$ (pz = pyrazolyl ring). Since each arm of this flexible tripodal ligand has three potential coordination donors, so many metal ions with different coordination geometry can be used to assembly $M_3L_2$ trigonal prism. Reaction of this ligand with $AgBF_4$ gave rise to a trigonal prismatic cage of composition $\{[Ag_3L_2(CH_3CN)](BF_4)_3\}\cdot(CH_3CN)_4$, in which all arms take a bidentate coordination mode to join three four coordinating $Ag^I$ ions. One $CH_3CN$ guest molecule was encapsulated inside the trigonal prism (Figure 4, b).

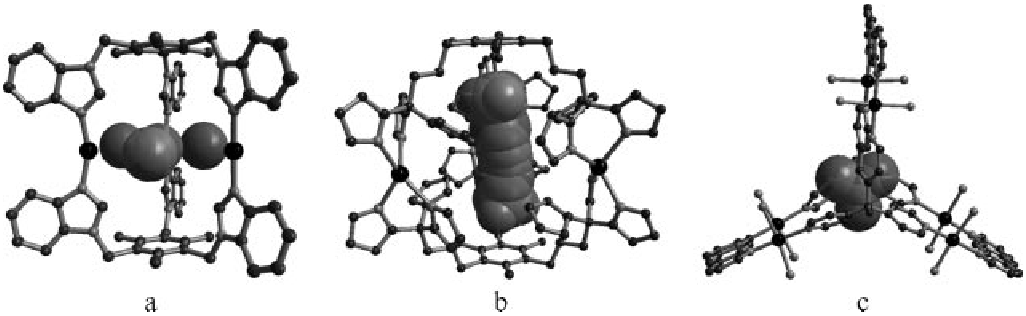


Figure 4. Representative trigonal prismatic structures assembled from (a) a tri(monodentate) tripodal ligand,[3] (b) a tri(tridentate) tripodal ligand[27b] and (c) an sp$^3$ C atom based tripodal ligand.[28d]

### *4.1.3.3 From Tripodal Ligands Based on Non-Aromatic Core*

Alternatively, tripodal ligand could also contains a non-aromatic core, such as cavitand moiety, $sp^3$ C or B atoms etc.[28] Shinkai et al. obtained a trigonal prism via $Pd^{II}$-pyridine interactions when they used the tripodal ligand based on homooxacalix[3] as starting material, in which the [60] fullerene can be encapsulated inside the cavity.[28a] A variety of tripodal organic ligands or metal-containing ligands with $sp^3$ C, adamantane, Si or P=O as central cores have been synthesized by Stang and co-workers. Reaction of these ligands with predesigned metal-containing "clip" or organic "clip" afforded various trigonal structures (Figure 4, c).[28b–28d] Ward et al. synthesized an $M_3L_2$ structure by using tri-chelating hexadentate ligand tris[3-(2-pyridyl)-pyrazol-1-yl]hydroborate based on B center, in which each $Cu^I$ ion is four coordinated by two *N*,*N′*-bidentate arms from two ligands.[25e] Torres et al. also reported an $M_3L_2$ trigonal cage based on subphthalocyanine which is a 14 π-electron aromatic macrocycle combining three *N*-fused diiminoisoindole units around a boron atom.[25f]

## 4.2 Tetragonal Prismatic Cages

### *4.2.1 Assembled via Route 2.1*

Metal ions preferring square-planar coordination geometry can be utilized to assemble tetragonal prisms through route 2.1 when the four coordination sites in the same plane are taken by four bis(monodentate) ligands with *cis* conformation.[29] The $Pd^{II}$ and $Pt^{II}$ ions are the mostly used square-planar geometric metal ions in the literature, and the coordination flexible $Cu^{II}$ ion sometimes is also used in the construction of tetragonal prism when it adopts square-planar coordination geometry. One of the earliest papers in this area is reported by Steel and co-workers,[29a] where they synthesized a coordinatively saturated tetragonal cage by using the ligand 1,4-bis(3-pyridyloxy)benzene and $Pd^{II}$ ion. One hexafluorophosphate anion was encapsulated inside the cage acting as a bridging ligand via the weak Pd···F interactions. However, this structure exhibits the helical sense and described by authors as the quadruply stranded helicate. A more regular trigonal prism was fabricated by Fujita et al.[29b] when they used a rigid bis(pyridyl) ligand to react with $Pd(NO_3)_2$ at a ratio of 2:1, in which each tetragonal prismatic cage encapsulated a nitrate ion inside its cavity. An isomorphous tetragonal structure based on $Pt^{II}$ ion was reported by Chand et al. in modified reaction conditions.[29c] Similar tetragonal prism based square-planar $Pd^{II}$ ions was also assembled from a semi-rigid ligand 1,3-bis(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (bitmb), in which the two square planar geometric $Pd^{II}$ ions were bridged by four bitmb ligands in *cis*-conformation.[29d] By exploiting some bis(amidopyridine) ligands to react with $[PdCl_2(PhCN)_2]$, Puddephatt at al. obtained a series of dipalladium(II) tetragonal prisms (Figure 5, a), these prismatic complexes exhibited remarkable host–guest chemistry. The encapsulated guest molecules could vary from anions, neutral molecules to cations, depending on the conformation of the bis(amidopyridine) ligands.[30]

### *4.2.2 Assembled via Route 2.3*

The metal ions adopting the square-pyramidal or octahedral coordination geometries can be used to assemble tetragonal prisms if the apical positions were blocked by auxiliary ligands or counterions. In this route, the metal ions usually involve $Co^{II}$, $Zn^{II}$, $Ni^{II}$, $Cu^{II}$ and so on.[31] One of the early tetragonal prisms constructed following this way is the $Cu^{II}$ prism synthesized by Atwood and co-workers,[31a] in which the two octahedral $Cu^{II}$ ions are bridged by four semi-rigid bis(monodentate) ligands and two coordinated water molecules occupy the axial positions. Later they reported an isomorphous tetragonal structure by using six-coordinate $Co^{II}$ ion instead of $Cu^{II}$.[31b] From the reaction of a semi-rigid ligand 3,5-bis(benzimidazol-1-ylmethyl)-1,4-dimethoxyl-2,6-dimethylbenzene with $Co(BF_4)_2 \cdot 6H_2O$ in the presence of solvent $CH_3CN$, Amouri et al.[31c] obtained a coordinatively unsaturated cobalt-based $M_2L_4$ cage, in which each $Co^{II}$ ion adopted a square-pyramidal coordination geometry. The four equatorial positions were occupied by four benzimidazolyl arms and the solvent molecule $CH_3CN$ coordinated to $Co^{II}$ ions at the axial position. The anion $BF_4^-$ was encapsulated inside through weak interactions with the metal centers. Similar tetragonal prisms have also been synthesized by Bu et al.[31d] when they used a flexible ligand 1,5-bis(4-pyridylthio)pentane to react with $Co(ClO_4)_2 \cdot 6H_2O$ or $Zn(ClO_4)_2 \cdot 6H_2O$.

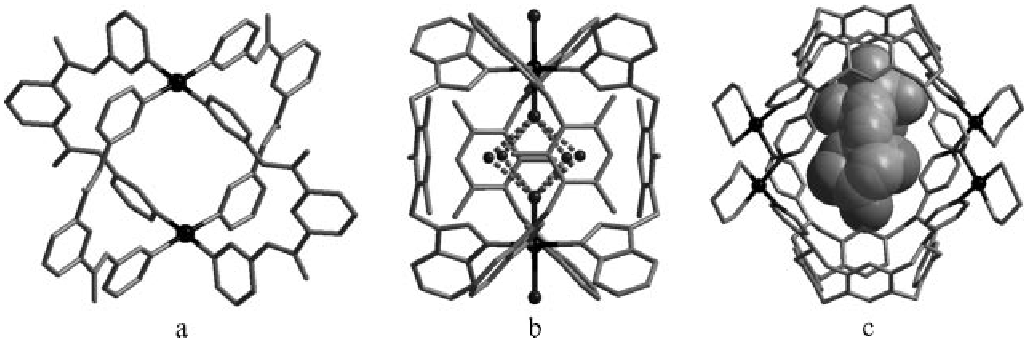


Figure 5. Representative tetragonal prismatic structures assembled with (a) square planar $Pd^{II}$ ion,[30a] (b) octahedral $Ni^{II}$ ion[3] and (c) cavitand-based tetrapodal ligand[33c] (phenyl groups are omitted).

We have prepared a semi-rigid ligand 1,3-bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene (bbimms) which reacted with $Cu(ClO_4)_2$ to afford a right prismatic cage complex.[3,21a] Four ligands take *cis* conformation to bridge two copper(II) ions to form the prism within which resides an axially disordered perchlorate anion. There is crystallographically imposed $C_4$ axis passing through the two $Cu^{II}$ atoms and a $\sigma_h$ mirror across the center of the molecule, resulting in an $S_4$ symmetry of the box. Along the $C_4$ axis the perchlorate anions are arranged alternately inside and outside the box to generate a one-dimensional multicompartmental column. Moreover, we found that metal halide compounds like $NiCl_2$ and $CoCl_2$ were good candidates for providing four open equatorial sites. The halide atoms are usually retained after metal ions coordinate with the bis(monodentate) ligands, so metal halide can be ideally used to assembly tetragonal prisms. From the reaction of mbbimb ligand with $NiCl_2 \cdot 6H_2O$, we obtained a neutral $S_4$ symmetric tetragonal prismatic cage as shown in Figure 5, b. In this complex, the two $Ni^{II}$ ions are held by the benzimidazolyl arms from four $C_4$-symmetrically arranged ligands via four equivalent Ni–N bonds with the octahedral coordination geometry completed by two axial chloride ions. There are four *4*-fold symmetrically arranged water molecules was hosted inside the cage via weak O–H···Cl hydrogen bonds. Similar tetragonal prismatic cages based on metal halide were also reported by Hong et al.[31e] when they used a flexible ligand 1,3-bis(pyrid-4-ylthio)propan-2-one to react with $CoCl_2 \cdot 6H_2O$ or $CoBr_2 \cdot 6H_2O$, where only one halide anion ligated to metal ions at the apical position to complete a distorted square-pyramidal coordination geometry.

### *4.2.3 Assembled via Route 2.2*

Similar to trigonal prisms described above, tetragonal prismatic structures can also be assembled from two tetrapodal ligands and four bridging metal ions through route 2.2. Four legs of the tetrapodal ligand could be monodentate, bidentate or tridentate. As a consequence, four metal ions with two, four or six coordination sites available are required, respectively.

Although various tetrapodal ligands based on the aromatic ring are available in literature, successful application of route 2.2 to assembly of tetragonal prismatic structure is still rare.[32] However, Brisbois et al.[32] obtained one organometallic tetragonal complex when they used tetradentate ligand based on cyclobutadienyl core to react with ethylenediamine palladium(II) nitrate, in which the two organometallic tetrapodal ligands CpCo-tetrakis(3-pyridyl)cyclobutadiene were bridged by four *cis*-protected $Pd^{II}$ ions. On the other hand, Shinkai and co-workers[32b] have exploited porphyrin-based tetrapodal ligands containing four pyridyl donor groups to react with the *cis*-protected $Pd^{II}$ ions, leading to formation of dimeric capsules. The $^1H$ NMR spectral studies indicate that such self-assembled molecular capsules have a highly symmetrical $D_{4h}$ structure as well as a large inside cavity.

Even more tetrapodal ligands have been synthesized on the basis of cavitand or calix[4]arene moieties with substituted pyridyl or cyano groups as coordination donors.[33] The first tetragonal cage based on cavitand ligand was reported by Dalcanale et al.,[33a] in which the two tetracyanocavitand derivatives were connected by four square-planar $Pd^{II}$ or $Pt^{II}$ ions. Afterwards, a series of similar enlarged prismatic cages have been reported by them or others through design of related deepened cavitand precursors via introduction of an appropriate coordinating group on the resorcinarene skeleton (Figure 5, c).[33b–33e] Hong et al.[33f] designed cavitand ligand via introduction of four flexible 4-pyridylmethyl groups at the upper rims and assembled $Pd^{II}$ and $Pt^{II}$ cages, while Harrison et al.[33g] synthesized similar prisms by using cavitand ligand with four flexible methyliminodiacetic acids attached to its upper rims. The cage was formed from two ligands connected by four six-coordinate $Co^{II}$ ions.

### 4.3. Multigonal Prismatic Cages

The coordination prismatic structures with two bases of *n*-gons ($n \geq 5$) are heretofore rather rare. One of the reasons is that the metal ions with $C_n$ ($n \geq 5$) symmetric coordination sites locating in the same plane remain very unusual, so the routes 2.1 and 2.3 are not applicable for such a purpose. The routes 2.3 and 2.4 are potentially practicable for construction of e.g. pentagonal or hexagonal-prismatic structures, however, it was found difficult to maintain $C_n$ ($n \geq 5$) symmetry during self-assembly process. For example, pentapodal[34a] and hexapodal[27b] ligands have been prepared to react with the two-connecting metal ions, nevertheless, assembly of pentagonal or hexagonal prismatic structures were not successful due to failure to prevent intramolecular metal chelation or conformational isomerization.

One example close to a hexagonal-prismatic structure was reported by Steel and co-workers.[34b] They synthesized an $M_6L_2$ cage by using the ligand hexa(2-pyridyl)[3]radialene ($\mathbf{L^5}$) to react with silver tetrafluoroborate. In this complex, two ligands both adopt a hexapodal hexadentate coordination mode, connected by six bridging $Ag^I$ ions to result in a hexapodal prismatic metallosupramolecule with an encapsulated $\mu_3$-fluorido anion (Figure 6).

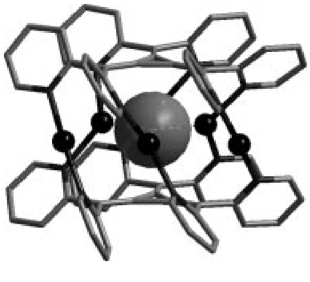


Figure 6. A representative hexagonal prismatic structure assembled with a hexapodal ligand $\mathbf{L^5}$.[34b]

## 5. Tubular Molecular Architectures

In contrast to the well-developed inorganic nanotubes and organic nanotubular molecular architectures, the field of inorganic-organic hybrid coordination nanotubes remains largely unexplored in spite of the fast moving developments in the area of inorganic-organic hybrid materials. Recently, designing and constructing of tubular structures by utilizing coordination chemistry has been realized to be a useful approach, and a number of coordination polymers containing tubular channels have been synthesized.[35] However, the discrete coordination tubular molecular architectures remain rather uncommon. Depending on the deliberately protected angular coordination environments displayed by metal atoms and the judicious choice of the multidentate ligands, construction of coordination tubes via multicomponent assembly route 2.4 is feasible in the aid of template effect of the guest molecules. Initial work in this topic was reported by Fujita and co-workers.[36] They synthesized one discrete coordination tube by using rigid oligo(3,5-pyridine)s ligand and *cis*-protected Pd$^{II}$ ions, in which the four ligands were bridged by Pd$^{II}$ ions to encircle into tube, and the rod-like guests was the essential template of the formation of such coordination nanotubes (Figure 7, a). The tube dissociated into its components by the removal of the guest molecule and again re-associated by the addition of guest molecule.[36a] The length of thus formed tubes could be controlled just by elongating the ligand with increasing the numbers of pyridine nuclei.[36b] However, the solubility of the ligand became poorer when the ligand had more rigid rings, therefore they further introduced methylene ($CH_2$) groups to design flexible long tape-shape ligand, and successfully extended the length of similar coordination nanotube to 3.5 nm.[36c] Another longer coordination tube based on Pd$^{II}$ was also reported by them when they used one semi-rigid tetrapodal ligand having four terpyridines arms to react with Pd$^{II}$ ions, in which the two tetrapodal ligands were circled into a 3.0 nm open tube as a result of the coordination of terpyridines with Pd$^{II}$ ions.[36d]

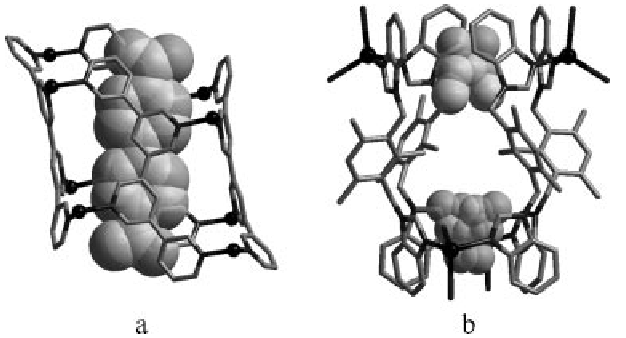


Figure 7. Tubular structures assembled with (a) a tetrakis(3,5-pyridine) ligand[36b] and (b) a *trans*-conformational ditopic semi-rigid ligand.[36e]

Based on the fact that the ditopic semi-rigid ligand is able to display either *cis*- or *trans*-conformation depending on the orientation of the two coordinating arms, we synthesized a discrete tubular tetramers $[Hg_4Cl_8(bbimms)_4]$ [bbimms = 1,3-bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene] when we reacted the semi-rigid ligand bbimms with $HgCl_2$ which favors bent coordination geometry. The neutral molecular tube was generated by self-cyclization of four $[HgCl_2(bbimms)]$ subunits whose orientation alternates successively up and down (Figure 7, b), and the guest molecules DMSO or DMF played an important role in the formation and stabilization of the tubular structures. The interior cavity of the tube was approximately 4.6 × 8.6 × 16.8 Å after consideration of the van der Waals radii. Furthermore, the neutral tubes were aligned to resemble a pipeline and that these pipelines were arranged into a three-dimensional columnar architecture.[36e]

## Concluding Remarks

In summary, well-shaped discrete molecular architectures are able to be constructed by using non-rigid ligands in contrast to the usually favored rigid ligands. Appropriate design and control of the donor groups and conformations of the semi-rigid or flexible ligands facilitate formation of relatively lower symmetric metallacyclic, prismatic and tubular structures in comparison to the higher symmetric polygonal or polyhedral structures. According to the distinguished nature of the non-rigid ligands and symmetry modification of metal ions, four assembly routes are available to direct formation of rectangular, prismatic and tubular architectures which are inherently related through the rotation symmetry. However, it should be noticed that the non-rigid ligands often display conformation freedom, for example, facile conversion between *cis* conformation and *trans* conformation of the ditopic semi-rigid ligands, which make it possible to generate coordination polymers instead of discrete molecular architectures. Therefore, vast effort is still needed to fully understand various subtle factors that influence the formation of closed molecular architectures as well as the shape stability and cavity size.

## Acknowledgments

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