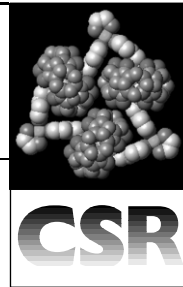


Mechanically interlocked molecules incorporating cucurbituril and their supramolecular assemblies



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Mechanically interlocked molecules incorporating cucurbituril (CB[6]) as a molecular 'bead' and their supramolecular assemblies are described. An efficient synthesis of 1D, 2D and 3D polyrotaxanes with high structural regularity and molecular necklaces has been achieved by a combination of self-assembly and coordination chemistry. The functional aspects of these interlocked molecules and their supramolecular assemblies, including molecular machines and switches based on [2]rotaxanes, a 2D polyrotaxane with large cavities and channels, pseudorotaxane-terminated dendrimers, and interaction of pseudorotaxanes containing polyamines and CB[6] with DNA are also described.

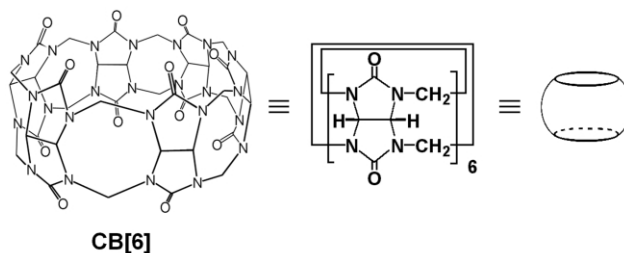
1 Introduction

One of the most significant developments in supramolecular chemistry during the past two decades has been the efficient synthesis of mechanically interlocked molecules¹ such as catenanes and rotaxanes, which have attracted considerable attention arising from not only their aesthetic appeal but also their potential applications such as molecular machines or switches.^{2,3} The introduction of various template strategies pioneered by Sauvage,⁴ Stoddart⁵ and others⁶ has made the

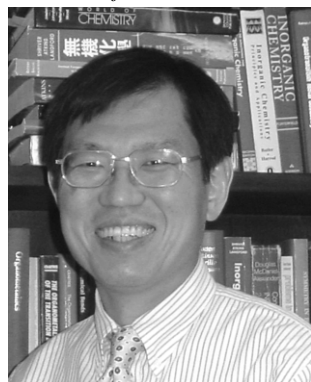
preparation of such topologically intriguing molecules much more feasible than before.

Cyclodextrins (CDs), cyclic oligosaccharides comprising six or more α -1,4-linked D-glucopyranose rings have played a significant role in the development of this field.⁷ The well-documented ability to form stable host-guest complexes with many different types of guests in aqueous solutions makes these readily available, bucket-shaped molecules one of the most attractive of building blocks (as ring components) in the template synthesis of interlocked structures, in particular rotaxanes and polyrotaxanes. In 1981, for example, Ogino reported the seminal work on [2]rotaxanes incorporating a cyclodextrin as a ring component, which were synthesized by threading an α - or β -CD with a long diaminoalkane to form an inclusion complex followed by the attachment of a metal complex at each amine terminal as a stopper.⁸ During the 1990s, a number of polyrotaxanes containing CDs were also synthesized.^{9–12} Harada and coworkers reported a polyrotaxane in which a number of CD 'beads' are threaded on a long poly(ethyleneglycol) chain.⁹ Independently, Wenz also synthesized polyrotaxanes incorporating α -CDs using several different approaches.¹⁰ Although rare, catenanes incorporating CDs are described in the literature, the first one being reported by Stoddart and coworkers.¹³

Cucurbituril (CB[6]) is a hexameric macrocyclic compound self-assembled from an acid-catalyzed condensation reaction of



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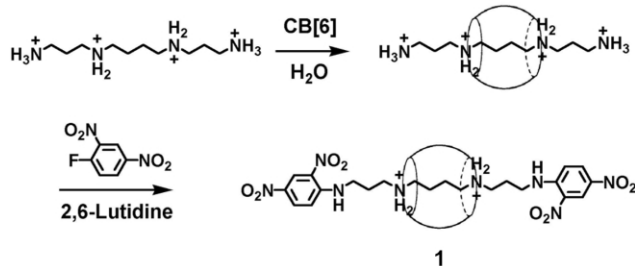
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glycoluril and formaldehyde.¹⁴ It has a cavity of ~ 5.7 Å diameter, accessible from the exterior by two carbonyl laced portals of ~ 4 Å diameter. Although the size of the cavity is similar to that of α -CD, the highly symmetrical structure with two identical openings distinguishes it from α -CD. In a similar way to CDs, the hydrophobic interior of CB[6] provides a potential site for inclusion of hydrocarbon molecules. Unlike CDs, however, the polar carbonyl groups at the portals allow CB[6] to bind ions and molecules through charge-dipole and hydrogen bonding interactions. For example, CB[6] forms very stable 1:1 host-guest complexes with protonated diaminoalkanes, particularly diaminobutane and diaminopentane ($K = \sim 10^5$ – 10^6), which is attributed to the strong charge-dipole as well

as hydrogen bonding interactions between the protonated amine groups and the portal carbonyl groups of CB[6], and hydrophobic interaction between the internal methylene units and the inside wall of the cavity. The inclusion properties of CB[6] as a synthetic receptor have been investigated extensively by Mock and coworkers. They also observed that CB[6] mediates 1,3-dipolar cycloaddition between azide and alkyne inside the cavity of the host with a large rate acceleration. The easy synthesis, highly symmetric structure and ability to form very stable inclusion complexes with protonated aminoalkanes, particularly diaminoalkanes, make CB[6] attractive as a building block for construction of interlocked molecules, in particular rotaxanes and polyrotaxanes. Nevertheless, when we initiated our study on interlocked molecules in the early 1990s, few rotaxane or catenane containing CB[6] compounds had been reported.¹⁵ In this review, I will describe interlocked molecules incorporating CB[6] and their supramolecular assemblies mostly based on our work.

2 Simple rotaxanes

The first simple rotaxane containing CB[6] as a molecular bead was synthesized by threading CB[6] with spermine to form a pseudorotaxane (a rotaxane without bulky stoppers to prevent dethreading) and then attaching dinitrophenyl groups to both ends of the spermine unit to prevent dethreading (Scheme 1).¹⁶



Spermine was chosen as 'string' in this synthesis because it has not only high affinity ($K = \sim 10^7$) toward CB[6], but also terminal amine groups to each of which a bulky substituents can be introduced. Interestingly, CB[6] itself is sparingly soluble in water, but the resulting pseudorotaxane is quite soluble in water. The drastically improved solubility upon formation of the pseudorotaxane allows the one-pot, high yield synthesis of rotaxane **1**.

In the ¹H NMR spectrum of **1**, the proton signals of the internal methylene units of the spermine chain, which are now placed inside the CB[6] cavity, are shifted upfield upon formation of the rotaxane because of the strong shielding effect of CB[6]. The upfield-shifted signals are a signature of successful threading, and are useful in the characterization of interlocked molecules containing CB[6] by ¹H NMR spectroscopy. The X-ray crystal structure of **1** reveals a CB[6] molecular 'bead' held tightly at the middle of the string by strong hydrogen bonding between the two inside protonated amine nitrogen atoms and the oxygen atoms at the CB[6] portals. Recently, Buschmann *et al.* have also reported [2]rotaxanes containing CB[6] threaded on spermine, but with different stoppers.¹⁷

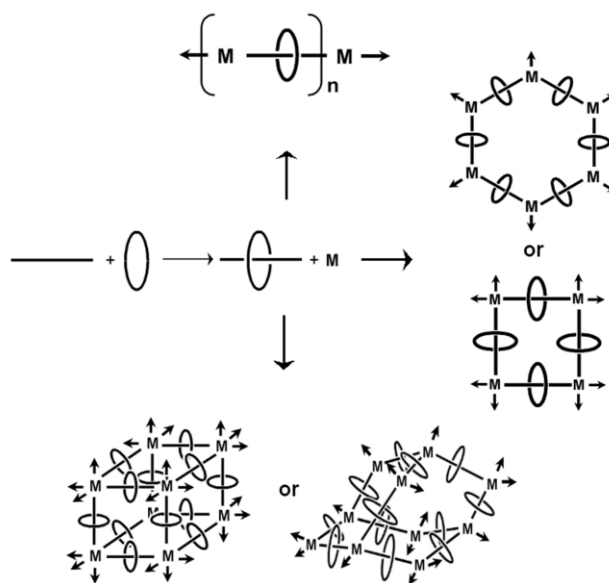
3 Metal-directed self-assembly of polyrotaxanes containing CB[6]

When we initiated our program on interlocked molecules containing CB[6], the polyrotaxanes reported up until that time contained molecular "beads" such as CDs threaded on organic

polymers. As they generally lacked high structural regularity none of these polyrotaxanes had yet been characterized by single crystal X-ray crystallography. Furthermore, neither polyrotaxanes containing molecular 'beads' on coordination polymers nor higher dimensional polyrotaxanes such as 2D or 3D polyrotaxanes had been reported. In the construction of polyrotaxanes, therefore, we decided to employ transition metal ions which have proven to be very useful in the construction of supramolecular architectures^{18–20} arising from their capability of forming relatively strong bonds with preferred coordination geometries.

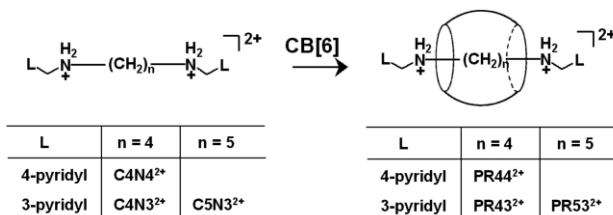
3.1 Synthetic strategy of polyrotaxanes using metal ion linkers

Our synthetic strategy for the construction of polyrotaxanes works in tandem, as illustrated in Scheme 2.²¹ It involves



threading a CB[6] 'bead' with a short 'string' to form a stable pseudorotaxane, followed by joining the pseudorotaxanes with metal ions as 'linkers' to organize into a 1D, 2D or 3D polyrotaxane. In principle, the overall topology and structure of the polyrotaxane can be controlled by the coordination number and geometry of the metal linker and the structure of the pseudorotaxane

With this idea in mind we designed short 'strings' such that they not only formed stable inclusion complexes with CB[6], but also bound metal ions using the donor atoms strategically placed at the terminals. A 3- or 4-pyridylmethyl group was attached at both *N*-terminals of diaminobutane or diaminopentane to produce the short 'strings' (C4N4²⁺, C4N3²⁺, C5N3²⁺, see Scheme 3) which were then allowed to form very



Scheme 3

stable pseudorotaxanes with CB[6] (PR44²⁺, PR43²⁺, PR53²⁺, respectively; Scheme 3). Despite the poor solubility of CB[6]

itself in water, the resulting pseudorotaxanes readily dissolve in water because of their overall +2 charge. Various transition metal ions with different preferred coordination numbers and geometries along with several different counterions were then allowed to react with the pseudorotaxanes to organize them into polyrotaxanes in the solid state.

3.2 One-dimensional polyrotaxanes

Slow reaction of $M(\text{NO}_3)_2$ ($M = \text{Cu}^{2+}$, Ni^{2+} , and Co^{2+}) with pseudorotaxane **PR44**²⁺ produces 1D polyrotaxanes in the solid state. The X-ray crystal structure of Cu-1D-polyrotaxane (**2**) (Fig. 1a) revealed CB[6] 'beads' threaded on a coordination polymer, the chain of which comprises alternating Cu^{2+} and **PR44**²⁺.²² The CB[6] 'beads' are held tightly on the polymer backbone by strong hydrogen bonds between the protonated amine nitrogen atoms of the 'string' and the CB[6] oxygen atoms as seen in the above simple rotaxane structure. The coordination geometry of the copper ion is square pyramidal with two adjacent basal positions occupied by two pyridine units of two pseudorotaxanes and the remaining basal and apical positions by three water molecules. The *cis* coordination of the two pyridine units to the metal center makes the polymer chain run in a zigzag fashion (Fig. 1a). On the other hand, reaction of $M(\text{NO}_3)_2$ ($M = \text{Co}^{2+}$ and Ni^{2+}) with **PR44**²⁺ produces the 1D polyrotaxanes (**3**, and **4**, respectively), which are isostructural. In **3**, two pseudorotaxane units are linked by a metal ion in a pseudo-octahedral coordination geometry with the axial sites occupied by two pyridyl nitrogens from **PR44**²⁺ and the equatorial positions by four water molecules. The sigmoidal shape of the pseudorotaxane and the *trans* coordination of the terminal pyridyl units to the metal centers result in a square-wave-shaped polymer chain (Fig. 1b). The major structural difference between the two 1D polyrotaxanes **3** and **2** is that the two pyridyl units are coordinated to the metal center in a *trans* geometry in **3** whereas they are bound in a *cis* geometry in **2**. As a result, the former has a square-wave-shaped polymer chain, whereas the latter exhibits a zigzag-shaped polymer chain (Fig. 1a vs 1b). Silver(I) ion with high propensity to form two-coordinate, linear complexes also works as a linker to produce 1D polyrotaxanes; reaction of silver tosylate with **PR44**²⁺ produces a 1D polyrotaxane (**5**) (Fig. 1c) in which the two terminal

pyridyl units of **PR44**²⁺ are coordinated to the metal ion in a *trans* geometry to yield a straight-chain polymer.

Another important factor affecting the solid state structures of polyrotaxanes is the 'string' or pseudorotaxane itself. Upon switching from **PR44**(NO_3)₂ to **PR43**(NO_3)₂, the reaction of the pseudorotaxane with $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ yields zigzag-shaped 1D polyrotaxanes (**6** and **7**, respectively), which are also isostructural with each other. In contrast to **3** and **4**, the crystal structures of **6** and **7** reveal that the metal ions are in octahedral geometries with two *cis* sites occupied by two pyridyl nitrogens from **PR43**²⁺. The *cis* coordination of the terminal pyridyl units to the metal centers results in a zigzag-shaped polymer chain similar to that in **2** (Fig. 1d).

It would be interesting to study solution properties of these polyrotaxanes. However, attempts to measure solution properties of these polyrotaxanes have been hampered by their extremely poor solubility in any solvents. Under forcing conditions they lose their integrity to fall apart into their components.

3.3 Helical one-dimensional polyrotaxanes

Helical 1D polyrotaxanes can be obtained with the pseudorotaxane **PR53**²⁺ where the 'string' is longer as well as more flexible compared to that in **PR44**²⁺. The reaction of AgNO_3 with **PR53**(NO_3)₂ yields the helical 1D polyrotaxane **8** (Fig. 1e and 2a).²² The helix, in which two **PR53**²⁺ and two silver ions constitute one turn, is extended along the *b* axis of the crystal with a pitch of 17.9 Å. Each silver ion is coordinated by two **PR53**²⁺ in a linear fashion.

When $\text{Cd}(\text{NO}_3)_2$ instead of $\text{Ag}(\text{NO}_3)_2$ is allowed to react with **PR53**²⁺ a different type of helical 1D polyrotaxane (**9**) is formed. In **9**, each turn of the helix comprises four units of **PR53**²⁺ and two different types of $\text{Cd}(\text{II})$ ions with each type containing two ions, leading to a helical pitch of 50.5 Å (Fig. 2b). While one type ($\text{Cd}(1)$) of the cadmium ions is coordinated by two pyridyl units of **PR53**²⁺ at *trans* positions of its octahedral coordination sphere, the other type ($\text{Cd}(2)$) is coordinated by two pyridyl units of **PR53**²⁺ at *cis* positions.

The crystals of **8** and **9** are racemic mixtures containing equal amounts of right-handed and left-handed helices in the same crystal. Construction of only one enantiomer, either right-

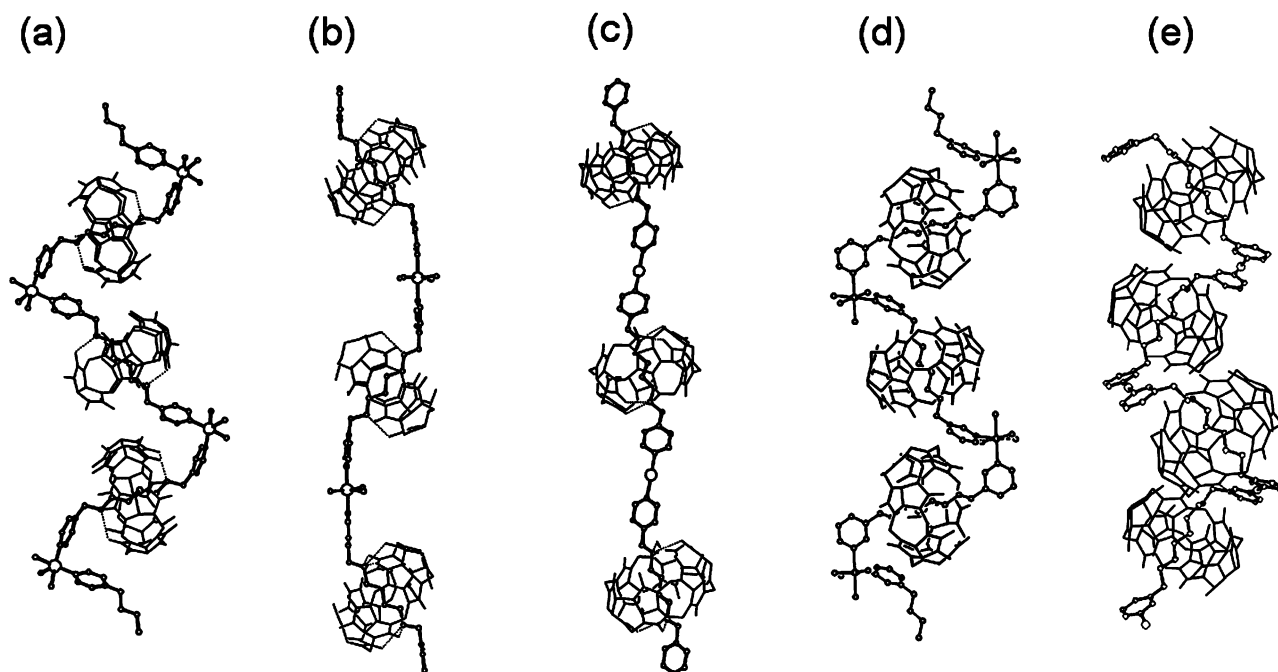


Fig. 1 X-ray crystal structures for (a) zigzag shaped 1D polyrotaxane (**2**), (b) square-wave shaped 1D polyrotaxane (**3** and **4**), (c) straight-chain 1D polyrotaxane (**5**), (d) zigzag shaped 1D polyrotaxane (**6** and **7**), and (e) helical 1D polyrotaxane (**8**).

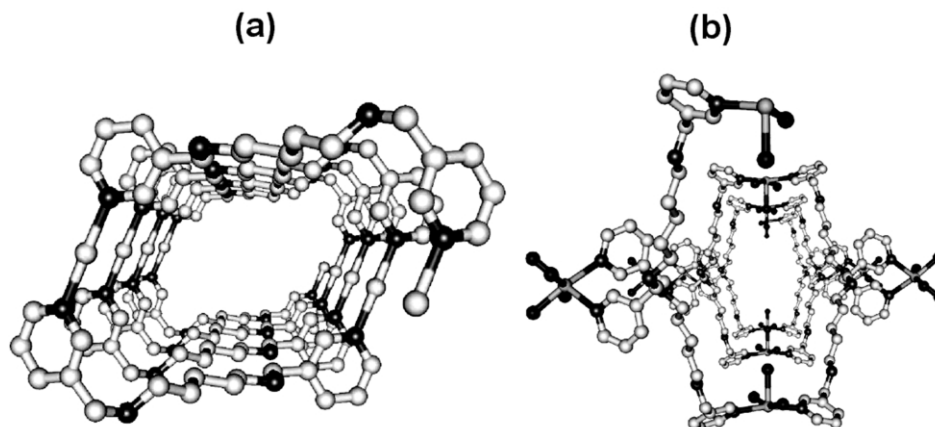


Fig. 2 Helical structures of the polymer backbones in (a) **8** and (b) **9**. CB[6] 'beads' are omitted for clarity.

handed or left-handed polyrotaxane helix, remains to be achieved. Such homochiral helical polyrotaxanes may have interesting applications.

3.4 Two-dimensional polyrotaxanes

So far I have demonstrated that metal ions and pseudorotaxanes play an important role in determining the solid state structures of polyrotaxanes. Of course, they are not the only important factors. Counter anions also play an important role in determining the solid state structures. As described above, the reaction of silver tosylate with **PR44**²⁺ produces a 1D polyrotaxane. However, when the counter anion is switched to nitrate ion, the same procedure yields a 2D polyrotaxane (**10**) in which CB[6] 'beads' are threaded onto a 2D coordination polymer network (Fig. 3a).²³

The 2D network consists of large edge-sharing chair-shaped hexagons with a Ag(I) ion at each corner and a molecule of **PR44**²⁺ at each edge connecting two Ag(I) ions. The edge of the hexagon is ~21 Å and the separation of the opposite corners is ~38 Å. Each silver ion is coordinated by three **PR44**²⁺ and a nitrate ion in a distorted tetrahedral geometry. In the solid, two independent 2D networks interpenetrate with full interlocking of the hexagons to form a polycatenated 2D polyrotaxane net.²³

Switching the pseudorotaxane from **PR44**²⁺ to **PR43**²⁺ in the same procedure produces another 2D polyrotaxane. Reaction of Ag(CF₃SO₃) with **PR43**(CF₃SO₃)₂ yields **11** (Fig. 3b) in which CB[6] 'beads' are threaded onto a square-meshed 2D coordination polymer network. Although the coordination geometry of the silver ion is slightly distorted tetrahedral, the polyrotaxane

network has a layer structure in which the 2D networks are stacked along the *c* axis with a mean interplanar separation of ~12.7 Å. In contrast to **10**, no catenation of the 2D network is observed in this structure with disordered triflate anions filling the space inside the square grid.

From the topological viewpoint, the 2D coordination polymer nets in **10** and **11** are classified as (6,3)- and (4,4)-nets, respectively.²⁴ After our result on the first 2D polyrotaxane was published, two different types of 2D polyrotaxane polymers were reported by Robson and coworkers.^{25,26}

3.5 Three-dimensional polyrotaxanes

The successful construction of 2D polyrotaxanes encouraged us to pursue 3D polyrotaxanes using the same approach, but all attempts failed to produce 3D polyrotaxanes using transition metal ions and pseudorotaxanes with pyridyl terminal groups. Finally, we decided to use lanthanide metal ions as linkers since they have larger ionic radii, and higher coordination numbers compared to transition metal ions. Considering their tendency to form stable complexes with carboxylates we also decided to use pseudorotaxanes with carboxylate terminal groups, which can be generated *in situ* from those with cyano terminal groups under hydrothermal conditions.

Reaction of **PCN43**²⁺ with Tb(NO₃)₃ under hydrothermal condition produces a 3D polyrotaxane (**12**) (Scheme 4).²⁷ The basic building unit of the 3D polyrotaxane framework consists of a binuclear Tb³⁺ center and six pseudorotaxane units, **PCA43**²⁺, each of which contains 3-phenylcarboxylate groups at the terminals. Under the hydrothermal conditions **PCN43**²⁺ with cyano groups at the terminals was first converted to

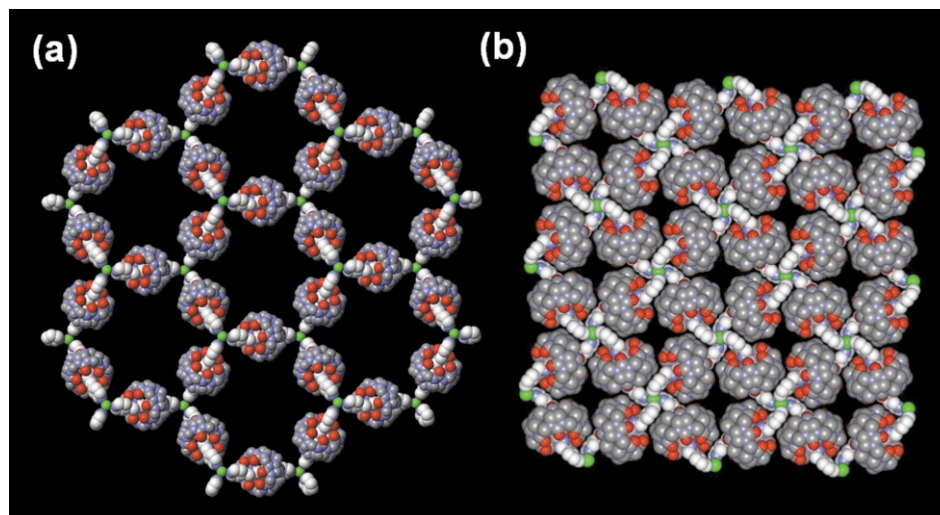
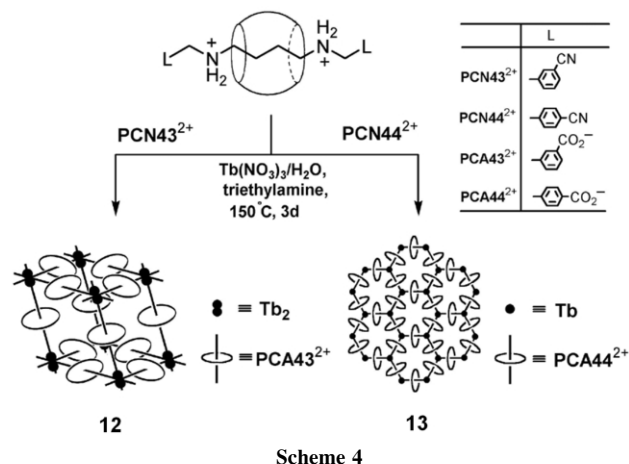


Fig. 3 Space filling representations for (a) hexagonal 2D polyrotaxane net in **10**,²³ and (b) square-grid shaped 2D polyrotaxane net in **11**.



PCA43²⁺ with carboxylate terminals, which then reacted with Tb³⁺ to form **12**. The 3D polyrotaxane has an inclined α -polonium topology with the binuclear terbium centers behaving as six-connected nodes.²⁴ The unit cell of the α -polonium-like net is depicted in Fig. 4.

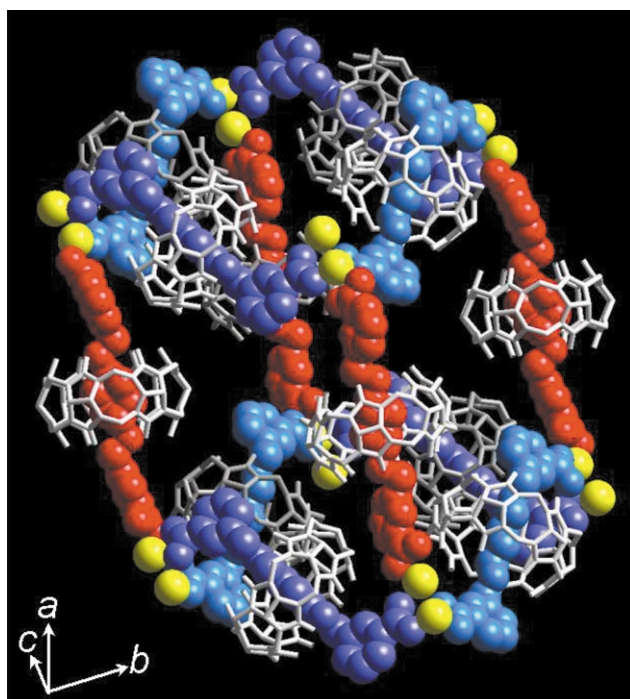


Fig. 4 Unit cell of the α -polonium-like net in 3D polyrotaxane **12**.²⁷

Here again, a small change in the building block results in a totally different solid state structure. Under the same conditions, for example, the reaction of Tb(NO₃)₃ with the isomeric pseudorotaxane PCN44²⁺ that has 4-cyanophenyl terminal groups, produces a polycatenated 2D polyrotaxane (**13**) (Scheme 4), whose structure is similar to that of **10**. Here again PCN44²⁺ is first converted to PCA44²⁺ with carboxylate terminals under hydrothermal conditions before coordination to Tb metal ions to form **13**. Each Tb metal center in **13**, coordinated by three PCA44²⁺, behaves as a three-connected node.

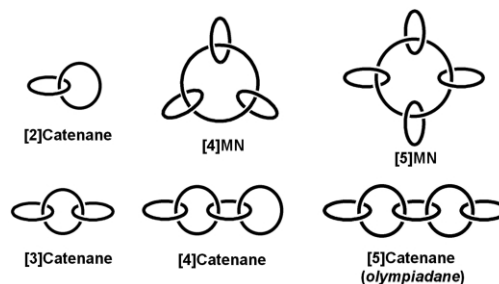
3.6 General comments on the metal-directed assembly of polyrotaxanes

In this section, I present a general strategy to organize pseudorotaxanes into 1D, 2D and 3D polyrotaxanes with high structural regularity in the solid state by utilizing the principles

of self-assembly and coordination chemistry. A key to the success of this approach is the highly symmetric structure of CB[6] and its tendency to form exceptionally stable pseudorotaxanes, which ensures complete threading of all the recognition sites of polyrotaxanes. The overall structure of a polyrotaxane is the result of interplay among various factors that include the coordination preferences of the metal ion, spatial disposition of the donor atoms with respect to the CB[6] 'beads' in the pseudorotaxane and the size and coordination ability of the counter anion. Other factors such as reaction conditions, various supramolecular interactions in the solid state as well as packing efficiency also act as the final determinants of the overall structure. In this approach, therefore, judicious choice of metal ions, counter ions, 'strings' and reaction conditions is important to construct polyrotaxanes with desired solid state structures. The present strategy can be extended to the synthesis of discrete interlocked molecules such as molecular necklaces, described in the following section.

4 Molecular necklaces

Molecular necklaces are interlocked molecules in which a number of small rings are threaded onto a large ring. From the topological point of view, they constitute a subset of catenanes. For a given number of rings, a molecular necklace is uniquely defined. A molecular necklace consisting of $(n - 1)$ rings threaded on a large ring (total n rings) is denoted as $[n]$ MN, which is a topological stereoisomer of classical $[n]$ catenane where n rings are mechanically interlocked each other one in a linear fashion (Scheme 5). For example, a molecular necklace



Scheme 5

[5]MN and 'olympiadane'²⁸ ([5]catenane) synthesized by Stoddart are topological stereoisomers. The minimal molecular necklace is [4]MN; the smaller molecular necklaces [2]MN and [3]MN are equivalent to [2]catenane and [3]catenane, respectively.

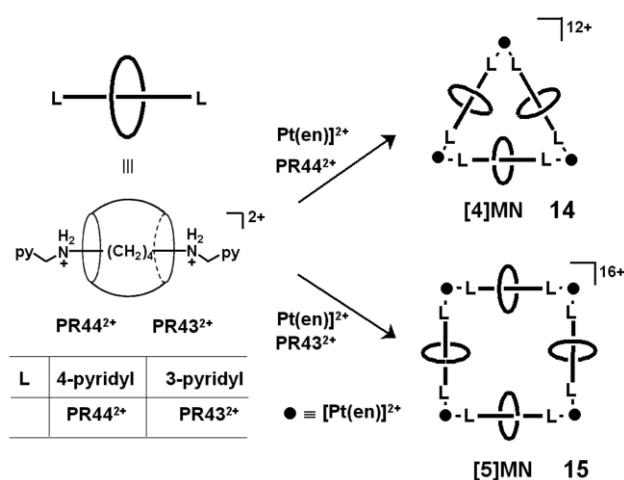
The first molecular necklaces were discovered by accident. In an elegant synthesis of [3]catenanes, Sauvage and coworkers observed unexpected formation of a mixture of $[n]$ MN ($n = 4-7$), some of which were isolated and characterized by electrospray (ESI) mass spectrometry.²⁹ Stoddart and coworkers also isolated and characterized a [4]MN in the synthesis of oligocatenanes.²⁸ However, these syntheses were generally carried out under kinetic control, which normally leads to a mixture of products. Therefore, efficient synthesis of molecular necklaces remained challenging.

4.1 Molecular necklaces [4]MN and [5]MN

Our strategy for the construction of molecular necklaces [4]MN and [5]MN is similar to that for polyrotaxanes. In the synthesis of molecular necklaces, however, we use a metal complex with *cis* 'vacant' coordination sites such as Pt(en)(NO₃)₂ (en = ethylenediamine), instead of simple metal salt, as a '90 degree angle connector'. Metal complexes with *cis* vacant coordination

sites have been used as ‘angle connectors’ in the synthesis of molecular squares and cages by Fujita,¹⁸ and Stang.¹⁹

Reaction of **PR44**(NO₃)₂ with Pt(en)(NO₃)₂ in refluxing water for 24 h produces **14** (Scheme 6) in near quantitative yield



Scheme 6

(by NMR).³⁰ The same product can be obtained from an equimolar mixture of CB[6], **C4N4**(NO₃)₂, and Pt(en)(NO₃)₂ under the similar reaction conditions. The very simple ¹H NMR spectrum of **14** indicates that it has a highly symmetric structure. However, these spectroscopic data did not tell us unequivocally whether it is a [4]MN, a [5]MN or an even higher homologue [n]MN. The structure of **14** was finally determined by X-ray crystallography after over a year trial of crystallization. Somewhat surprisingly, the X-ray crystal structure of **14** (Fig. 5a) reveals that three CB[6] molecular ‘beads’ are threaded on a molecular triangle.³⁰ Each corner of the triangle is occupied by a Pt(en) moiety and each side by a sigmoidal shaped pseudorotaxane unit **PR44**²⁺, which links the two Pt moieties with a Pt...Pt separation of ~19.5 Å. The three CB[6] molecules in **14** are arranged in such a way that almost no vacant space exists inside the molecular triangle, indicating that the hydrophobic interactions between the three CB[6] rings may assist in the efficient formation of the necklace.

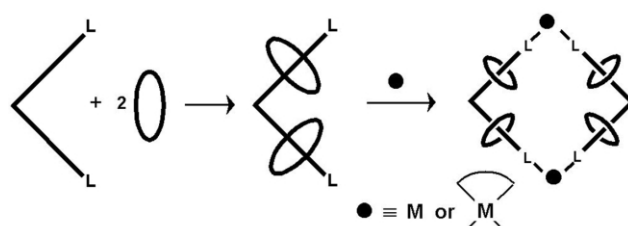
We can also construct square-shaped molecular necklaces [5]MN using the same approach. Simply changing the position of the nitrogen atom on the pyridyl group from 4 to 3 produces a [5]MN (**15**) as a major product (Scheme 6). In the X-ray crystal structure of **15**, four molecular ‘beads’ are threaded on a square framework whose corners are occupied by the Pt(en) units (Fig. 5b) with an average nearest neighbor Pt...Pt distance

of ~17.7 Å. Actually, the square framework has a butterfly structure with a bent angle of 77.7° and a distance between the two Pt wingtips of ~22 Å.

We recently discovered an interesting temperature effect on the necklace formation. While reaction of **PR44**(NO₃)₂ with Pt(en)(NO₃)₂ under refluxing condition produces a [4]MN exclusively, as described above, the same reaction at room temperature for 70 h yields a ~1:1 mixture of [4]MN and [5]MN as confirmed by ¹H NMR spectroscopy and ESI mass spectrometry. These results indicate that under refluxing conditions, the entropic effects can overcome the enthalpic cost associated with the sterically congested and strained [4]MN structure. However, the strain free [5]MN and entropically favored [4]MN coexist at a lower room temperature, where the enthalpic and entropic factors compete with each other. Thermal or entropic effects, therefore, strongly affect the equilibrium in this thermodynamically controlled self-assembly reaction.

4.2 Molecular necklace [5]MN via a 2 + 2 approach

As described above, this approach generates both triangular necklaces and square necklaces. We therefore decided to take another approach to square necklaces with four molecular ‘beads’, which we now call a 2 + 2 approach.³¹ In this approach, we use an L-shaped preorganized pseudorotaxane in which two molecular ‘beads’ are already in place, and using metal ions or metal complexes as a ‘glue’ we can construct the molecular necklace [5]MN containing 4 molecular ‘beads’ (Scheme 7).



Scheme 7

L-Shaped ‘strings’ that we designed have either a benzene or phenanthroline core with two arms, each of which contains a diaminobutane unit and a pyridyl unit. Threading 2 equiv. of CB with the L-shaped ‘strings’ to form pseudorotaxanes **LB44**⁴⁺ and **LP44**⁴⁺, respectively, which are then allowed to react with metal salts such as Cu(NO₃)₂ or metal complexes such as Pt(en)(NO₃)₂ produces molecular necklaces [5]MN (Scheme 8). For example, reaction of **LP44**⁴⁺ and Cu(NO-

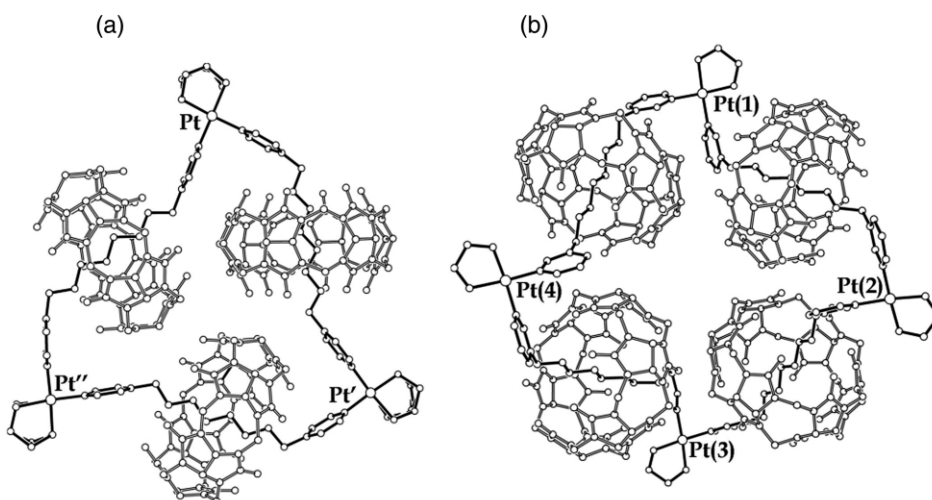
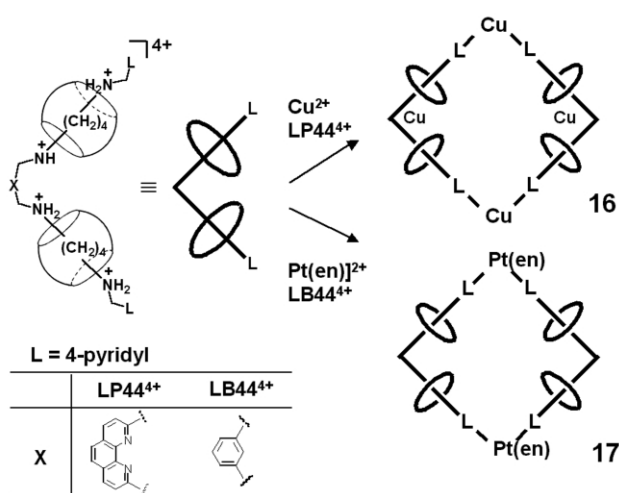


Fig. 5 X-ray crystal structures of (a) [4]MN **14** and (b) [5]MN **15**.



Scheme 8

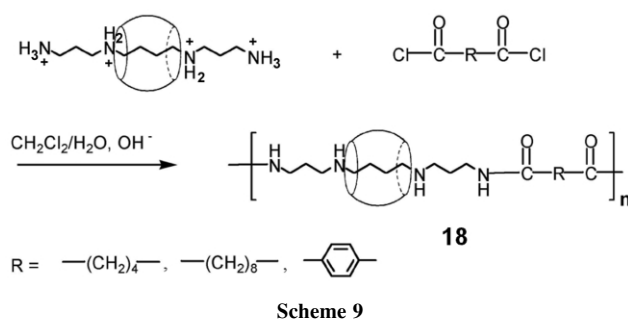
$3)_2$ produces **16**, the X-ray crystal structure of which reveals that two copper ions (Cu(1) and Cu(3)) link two **LP44⁴⁺** units to form a molecular necklace MN[5] (Fig. 6a). There are two additional copper ions (Cu(2) and Cu(4)) bound inside the phenanthroline corners. Each of these copper ions is coordinated by two phenanthroline nitrogen atoms, a secondary amine nitrogen atom and two oxygen atoms of CB[6]. Coordination of the amine nitrogen atoms to the copper ions makes two sides of the molecular square considerably shorter than the other two; therefore, the necklace framework is better described as a rectangle with a dimension of $\sim 19.3 \times 17.0$ Å. Likewise, reaction of **LB44⁴⁺** with Pt(en)(NO₃)₂ produces [5]MN **17**, the X-ray crystal structure of which shows a diamond shaped framework with a Pt...Pt distance of 26.4 Å (Fig. 6b).

5 (Pseudo)polyrotaxanes containing CB[6] threaded on organic polymers

5.1 Main chain (pseudo)polyrotaxanes containing CB[6]

While our work on polyrotaxanes containing CB[6] threaded on coordination polymers was in progress, we also synthesized (pseudo)polyrotaxanes containing CB[6] threaded on organic polymers in collaboration with Professor Do of Suncheon National University. The (pseudo)polyrotaxanes (**18**) were synthesized by interfacial polymerization of CB[6]–spermine

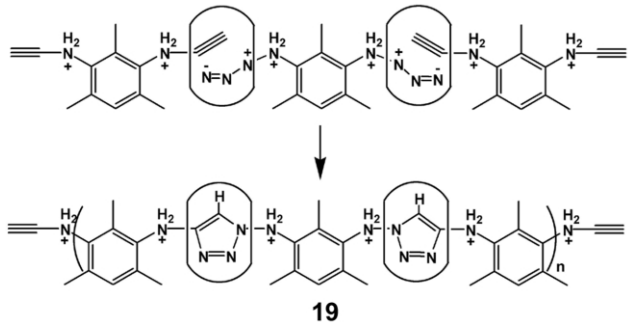
pseudorotaxane with various diacid chlorides such as 1,6-hexanedioyl chloride (adipoyl chloride) and terephthaloyl chloride (Scheme 9). The IR, DSC, and TGA data supported the



Scheme 9

formation of (pseudo)polyrotaxanes, but their poor solubility in common solvents hampered further characterization of the novel polymers.³² Buschmann and coworkers also prepared similar (pseudo)polyrotaxanes of polyamides and CB[6].³³ Interfacial polymerization of adipoyl chloride and the complexes of CB[6]–1,6-diaminohexane (protonated) in several different molar ratios produces pseudopolyrotaxanes containing various amounts of CB[6] threaded on polyamide. The thermal behavior of the pseudopolyrotaxanes was studied. Here again further characterization was hampered by their poor solubility; they dissolve only in concentrated sulfuric acid.

Steinke³⁴ reported a novel way (Scheme 10) to produce polyrotaxanes utilizing 1,3-dipolar cycloaddition between azide and alkyne inside the cavity of CB[6], which was first discovered by Mock. The average molecular weight of **19** estimated by GPC, MALDI-TOF mass and ¹H NMR spectroscopy is close to 10,000. Very recently, Steinke also reported



Scheme 10

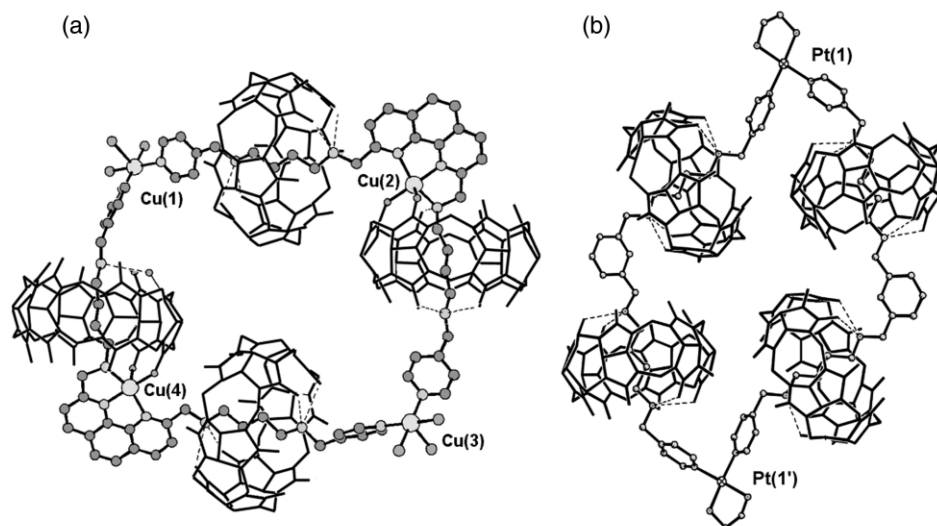
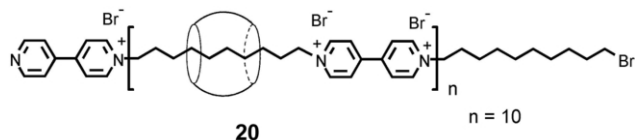


Fig. 6 X-ray crystal structures of (a) [5]MN **16** and (b) [5]MN **17**.

new main chain pseudopolyrotaxanes by threading CB[6] onto poly(iminohexamethylene chloride) ($M_w = 52,000$ by GPC) which was obtained by reduction of nylon 66 with BH_3-Me_2S .³⁵ The threading occurs through strong host-guest interaction between CB[6] and the protonated diiminohexamethylene unit. However, the threading process is quite slow even when excess CB[6] is used; equilibrium was reached after about 400 h at 90 °C. When excess CB[6] is used, the degree of threading reaches almost 50%, which indicates that threaded and unthreaded repeat units of the polymer alternate.

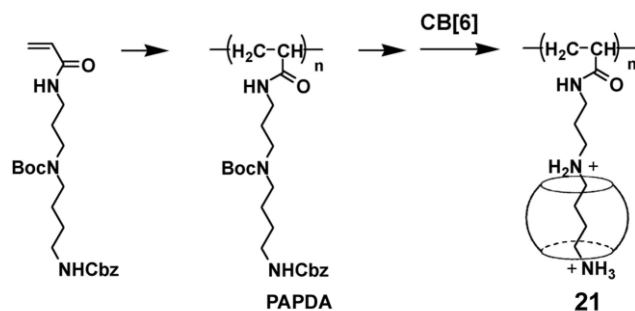
Recently we also synthesized a water-soluble main chain pseudopolyrotaxane (**20**) containing CB[6] ‘beads’ threaded on



a polyviologen polymer where approximately 10 bipyridinium units are linked by decamethylene units in between.³⁶ The degree of threading can be controlled between 0.1 and 1.0. ¹H NMR data support that CB[6] ‘beads’ reside on decamethylene units. The charge-dipole interaction between the bipyridinium unit and the CB[6] portal oxygen atoms and hydrophobic interaction between the decamethylene unit and the CB[6] cavity interior appear to be responsible for the threading. The hydrodynamic radius of the polymer estimated by NMR spectroscopy increases from 56 to 62 Å upon complete threading of CB[6]. Although the intrinsic viscosity of the pseudopolyrotaxane is higher than that of parent polyviologen polymer, the Huggins constant for the former is smaller than that for the latter.

5.2 Side-chain (pseudo)polyrotaxanes containing CB[6]

Side-chain polyrotaxanes containing macrocycles threaded on side chains have been reported. For example, Ritter *et al.* synthesized a polyrotaxane containing CD threaded on side chains of poly(ether sulfone).¹² We synthesized new side-chain pseudopolyrotaxanes containing CB[6] threaded on side chains. The polymer PAPDA, each repeating unit of which contains a protected diaminobutane unit as a side-chain, was first synthesized (Scheme 11). The molecular weight of the polymer



Scheme 11

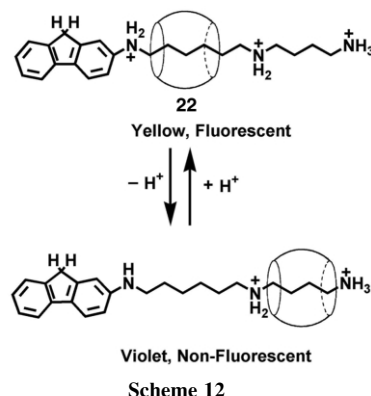
estimated by GPC is 8700 (M_w ; $M_w/M_n = 1.18$), which corresponds to a degree of polymerization of ~ 30 . Deprotection of the diaminobutane units followed by threading of CB[6] on the side-chains results in the desired side-chain pseudopolyrotaxane (**21**).³⁷ Complete threading of ‘beads’ on all the side chains is evidenced by ¹H NMR spectroscopy. Several other side-chain pseudopolyrotaxanes having different polymer backbones but essentially the same side chains have also been synthesized.

6 Functional aspects of interlocked systems incorporating CB[6]

6.1 Molecular machines and switches based on rotaxanes containing CB[6]

One of the motivations to study mechanically interlocked molecules is that they are potentially useful in constructing molecular-scale devices such as molecular machines and molecular switches, as Stoddart and others have elegantly demonstrated recently.^{2,3} [2]Rotaxanes have been successfully employed in the construction of molecular machines.² Here, translocation of the ring along the linear component can be achieved by external chemical, electrochemical or photochemical stimuli. In appropriately designed systems, such mechanical movements can be made to occur between two different well-defined states, and if such movements are signaled by an observable change in the property of the system, they can behave as switches for sensor and molecular-scale information processing.

In 1990, Mock reported a (pseudo)rotaxane-based molecular switch consisting of a CB[6] ‘bead’ and a triamine ‘string’, $PhNH(CH_2)_6NH(CH_2)_4NH_2$.¹⁵ When all the nitrogen atoms of the ‘string’ are protonated at low pH, the ‘bead’ resides at the protonated diaminohexane site, because CB[6] forms a more stable complex with diprotonated diaminohexane than with diprotonated diaminobutane. Upon deprotonation of the aniline nitrogen ($pK_a = 6.7$), however, the ‘bead’ migrates to the diprotonated diaminobutane site because binding with the monoprotonated diaminohexane is weaker. Based on this elegant work, we designed a fluorescent molecular switch **22** (Scheme 12), which can signal the change in the ‘bead’ position

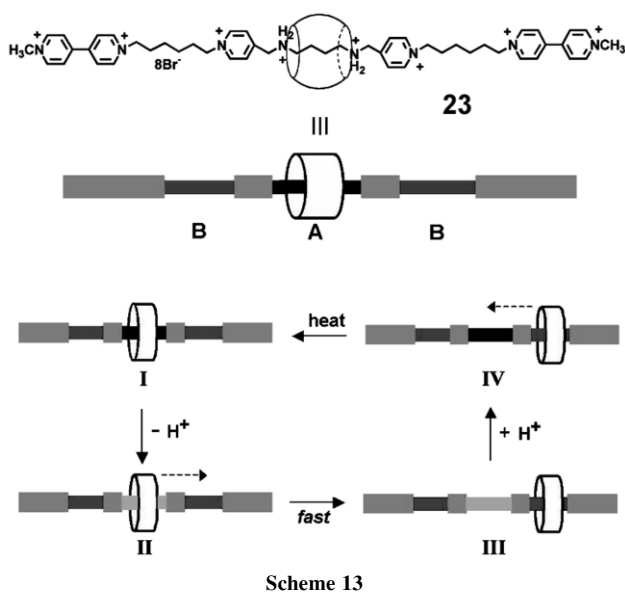


Violet, Non-Fluorescent
Scheme 12

by color and fluorescence changes.³⁸ NMR studies revealed that the molecular bead in **22** resides predominantly at the (diprotonated) diaminohexane site at a pH lower than its pK_a (5.7), but translocates to (diprotonated) diaminobutane site when the pH of the solution becomes higher than the pK_a . Most importantly, the switching of CB[6] from one site to the other in **22** is easily detected by change in color and fluorescence. The color of the aqueous solution of **22** at pH 1.0 is yellow, which changes slowly with increasing pH and becomes violet at pH 7.0. Furthermore, the solution of **22** at pH 1.0 is highly fluorescent with an emission maximum at 308 nm. The fluorescence intensity decreases with increasing pH due to the deprotonation of the aromatic nitrogen. The fluorescence is almost completely quenched at pH 7.0.

Recently we reported another bistable [2]rotaxane containing CB[6] that behaves as a kinetically controlled switch.³⁹ While the stabilities of CB[6]-diaminoalkane complexes strongly depend on pH, the complex formation between CB[6] and 1,6-di(pyridinium)hexane is little affected by the pH of the solution. Taking these inclusion properties of CB[6] into account, we designed a bistable [2]rotaxane (**23**) consisting of

CB[6] as a ‘bead’, one protonated diaminobutane unit as a station (A), two pyridinium groups as linkers, two hexamethylene units as further stations (B), and two terminal viologen groups (Scheme 13).

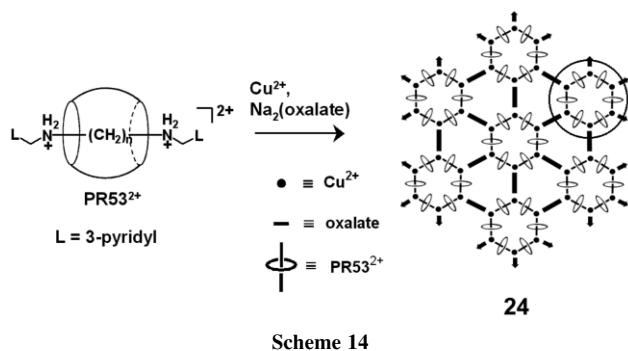


While the CB[6] ‘bead’ in **23** resides exclusively at station A at a neutral pH, (state I, Scheme 13), deprotonation of the protonated diaminobutane unit in **23** by addition of a base promotes the movement of CB[6] from station A to station B (state III). Although addition of a suitable acid at this state causes re-protonation of the diaminobutane unit, it does not promote the immediate translocation of the CB[6] ‘bead’ back to station A (state IV). In fact, the reverse process initiated by addition of an acid is too slow to be observed at room temperature due to a high activation barrier ($\Delta G^\ddagger = 26$ kcal); however, at 80 °C, the CB[6] ‘bead’ shuttles back quickly and completely to station A. Therefore, this bistable [2]rotaxane behaves as a kinetically controlled molecular switch in which the kinetically stable new state is maintained at room temperature after removal of an applied stimulus. The switching of the molecular ‘bead’ from one site to the other site is driven by pH change, but the reverse process requires pH change plus thermal activation. This novel switching system may thus provide useful insights in designing ‘safeguarded’ molecular switches.

6.2 Polyrotaxanes as open-framework materials

The building principle of the polyrotaxanes described in Section 3 can be applied to the construction of metal-organic open-framework materials, which is a subject of current intense investigation.⁴⁰ For example, the large hexagonal 2D polyrotaxane net described in Section 3.4 suggests that such pseudorotaxanes can be used as large, rigid *supramolecular* building blocks for the construction of metal-organic open-frameworks. Along this line, we recently reported a novel 2D polyrotaxane network with large cavities and channels, which demonstrates that this is indeed a viable approach to modular porous solids.

Reaction of pseudorotaxane **PR53**²⁺ with $\text{Cu}(\text{NO}_3)_2$ in the presence of oxalate ions produces 2D polyrotaxane **24** (Scheme 14).⁴¹ A close inspection of the structure reveals that a hexagonal, seven-membered molecular necklaces [7]MN composed of six copper ions and six pseudorotaxanes behaves as a secondary building unit⁴⁰ of the 2D polyrotaxane (Scheme 14). Each corner of the supramolecular hexagon is occupied by a copper ion with a $\text{Cu}\cdots\text{Cu}$ distance of ~ 13.9 Å for the side and



~ 27.8 Å for the diagonal. The molecular necklaces are connected to each other through coordination of oxalate to the copper corners to form a large 2D hexagonal array. The 2D layers in turn stack along the *c* axis with a mean interlayer separation of 12.9 Å, in such a way that the cavities are aligned vertically to form 1D channels along the *c* axis. The 1D channel has a small aperture with an effective diameter of ~ 5 Å and a long cylindrical void with a dimension of $\sim 14 \times \sim 20$ Å (Fig. 7). The 1D channels are interconnected to form a 3D channel network.

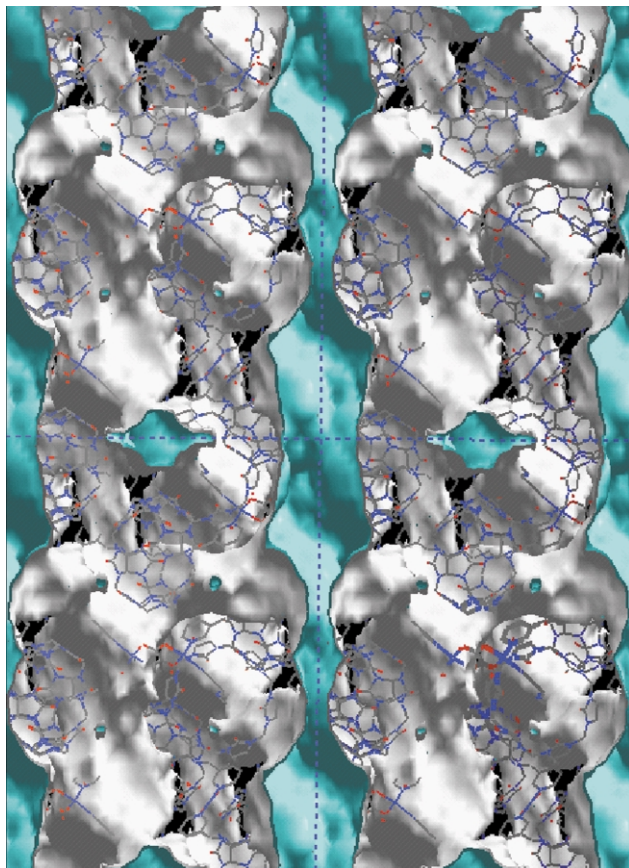


Fig. 7 Cross-sectional views of **24** on the *ac* plane showing the channels (in blue).⁴¹

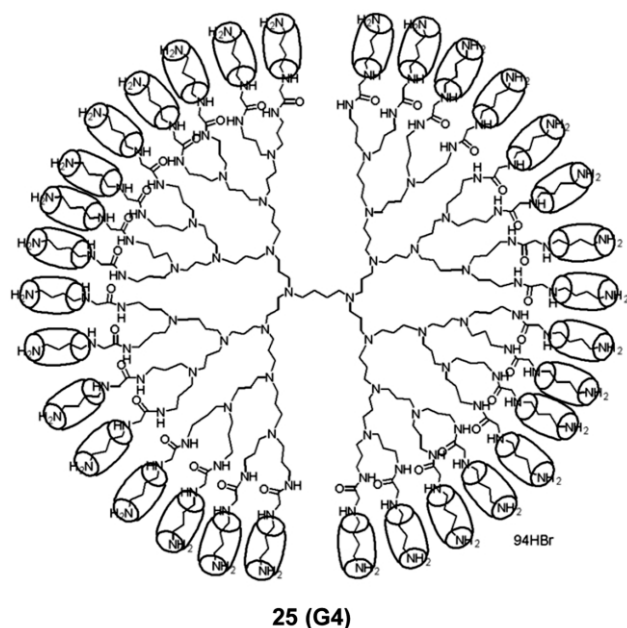
Size-selective exchange of anion as well as coordinated ligand in **24** has been observed. The exchangeable aqua ligands suggest the metal centers in **24** may be used for recognition, binding and activation of specific substrates. This work demonstrates a new synthetic strategy to modular porous solids, which utilizes large, rigid, interlocked supermolecules as primary or secondary building blocks.

6.3 Rotaxane dendrimers containing CB[6]

As many of the applications exploit functional groups at the periphery, modification of terminal groups of dendrimers is of

enormous current interest. While most of these modifications have been achieved by covalent bond formation with the terminal groups, modifications using noncovalent bonds/interactions may be more attractive as they offer many advantages including reversibility. Therefore, we decided to explore formation of pseudorotaxanes at terminals of dendrimers, which may offer an interesting way of modifying the dendrimer exterior by noncovalent interaction.

Using commercially available polypropylimine (PPI) dendrimers (G1 – G5) as starting materials, we attached diaminobutane units at the terminals and then threaded CB[6] onto the terminals to produce pseudorotaxane-terminated dendrimers (**25**).⁴² The G5 pseudorotaxane-terminated dendrimer contains



64 'beads' threaded at the periphery of the dendrimer with molecular weight of ~94,500. An atomic force microscopy image of the G5 dendrimer on a mica surface reveals a flattened sphere with a diameter of ~15 nm and a height of ~1 nm.

One of the advantages of non-covalent modifications is *reversibility*: in this case, you can easily change the structure and properties of a dendrimer reversibly by threading and dethreading of molecular 'beads'. According to molecular dynamics study, for example, the overall size of the G3 dendrimer increases from 40~41 to 44~49 Å upon threading of CB[6] (Fig. 8). Upon threading molecular 'beads', furthermore, the large terminal pseudorotaxane units form a rigid

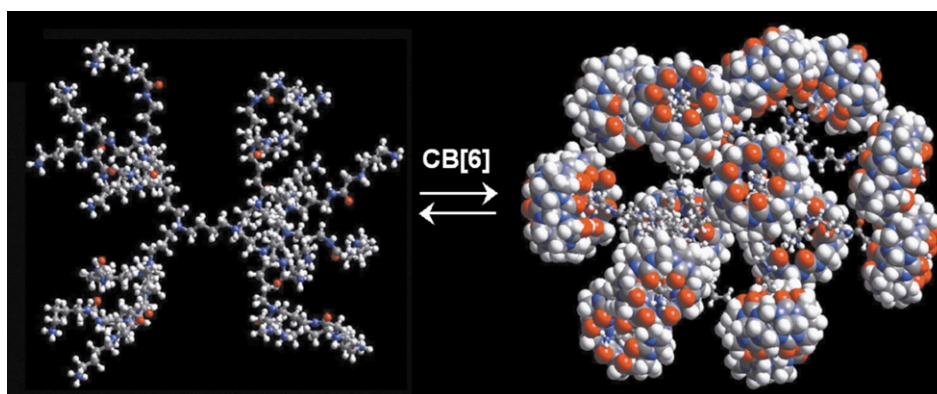
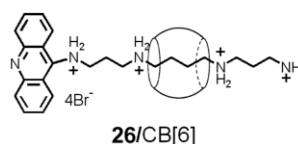
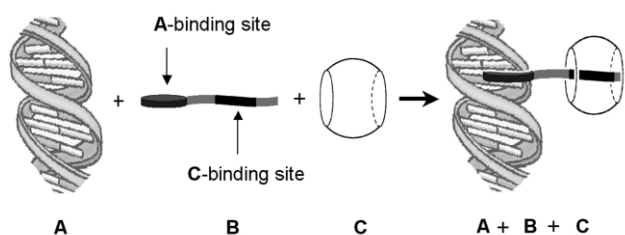


Fig. 8 Structural change of **25** (G3) upon threading and dethreading of CB[6] obtained by molecular dynamic simulation.⁴²

shell at the exterior of the dendrimer, as demonstrated by molecular dynamic simulation and NMR experiments. The terminal pseudorotaxane units therefore can potentially inhibit escape of guest(s) trapped in the interior. Furthermore, all or a part of the molecular 'beads' of these dendrimers are dethreaded upon treatment with a base. Therefore, this threading and dethreading of molecular 'beads' at the terminals may provide these novel dendrimers with a mechanism for reversible encapsulation and release of guest molecules, which may find useful applications including drug delivery.

6.4 Interaction of polyamine–CB[6] pseudorotaxanes with biomolecules

In collaboration with Professor Nakamura of Tokyo University we have been investigating interaction of (pseudo)rotaxanes containing CB[6] with biomolecules such as DNA. In developing a rational method to deliver a molecule to a target site of a biomolecule we considered a modular strategy relying on non-covalent assembly of molecules. As a part of this work we recently reported a chemical prototype of the modular targeting strategy in delivering a small molecule (C) to DNA (A) with the aid of a linker molecule (B) that can bind both A and C at different sites by noncovalent interactions as illustrated in Scheme 15.⁴³



Scheme 15

The bifunctional linker molecule **26** (Scheme 15) is composed of a spermine attached covalently to an acridine unit; the acridine binds to DNA through intercalation while the spermine unit binds to CB[6] to form a pseudorotaxane by threading. The

binding ability of the pseudorotaxane **26**–CB[6] to DNA was assessed by ethidium bromide competition experiments, gel mobility shift assay and nuclease inhibition experiments. All the results support the idea that the acridine–spermine linker module can effectively deliver CB[6] to the target DNA through a ternary supramolecule as illustrated in Scheme 15.

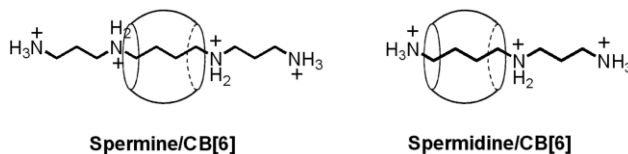
Nakamura also discovered that the activities of polyamines such as spermine and spermidine, which are known to bind DNA and to accelerate transcription and nuclease activities, are greatly affected by their formation of pseudorotaxanes with CB[6]. For example, spermidine–CB[6] pseudorotaxane is much more effective than spermidine itself in accelerating topoisomerase activity.⁴⁴ In fact, only 1/10 of spermidine–CB[6] pseudorotaxane compared to conventional TaKaRa protocol is required to activate topoisomerase. Furthermore, while spermine upon forming pseudorotaxane by threading CB[6] increases restriction enzyme activity, the role of spermine in increasing the nuclease activity is substantially reduced. Although the origin of the changes in the polyamine activities upon threading CB[6] remains to be established, these results demonstrate that the biological activities of such molecules can be altered by noncovalent modification.

7 Summary and outlook

In this review, I describe interlocked molecules incorporating CB[6] as a molecular ‘bead’ and their supramolecular assemblies mostly based on our work. As a molecular ‘bead’, CB[6] has several advantages over CDs including a highly symmetrical structure with two identical portals and high affinity toward protonated diaminoalkanes, which allowed us efficient synthesis of a number of intriguing interlocked compounds incorporating CB[6]. In particular, combining principles of self-assembly and coordination chemistry we were able to construct 1D, 2D and 3D polyrotaxanes with high structural regularity, where judicious choice of metal ions, counter ions, ‘strings’ and reaction conditions is important to obtain the polyrotaxanes with desired solid state structures. The same strategy can be extended to the efficient synthesis of discrete interlocked molecules such as molecular necklaces, which would be extremely difficult to synthesize by conventional covalent synthesis.

The functional aspects of these interlocked molecules and their supramolecular assemblies are being actively studied. Simple molecular machines and switches based on movement of CB[6] have been synthesized. Based on this work, we may be able to design and construct sophisticated molecular switches that serve as a key component of molecular electronic devices. To realize molecular electronic devices, however, such molecular switches need to be organized into an array to behave coherently. The work described in Section 3 may provide insights into the construction of well-defined 1D, 2D or 3D organization of such molecular switches. Besides, 2D and 3D polyrotaxane networks with large cavities and channels may find interesting applications in separation, catalysis and as sensors. The formation of pseudorotaxanes at the terminals of a dendrimer with CB[6] offers an interesting way of modifying the dendrimer exterior by noncovalent interaction, which may find useful applications such as in drug delivery. Such noncovalent modification may be important for other biological applications as the biological activities of polyamines are significantly altered upon formation of pseudorotaxanes with CB[6].

Very recently, new cucurbituril homologues CB[5], CB[7] and CB[8], which contain five, seven and eight glycoluril units, respectively, were reported.⁴⁵ The chemistry of the higher



homologues CB[7] and CB[8], which are equivalent to β - and γ -CDs, respectively, in terms of the cavity size, is being actively explored.⁴⁶ With these new building blocks exciting interlocked systems with novel structures, properties and functions are yet to be created!

8 Acknowledgements

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