Transition Metal Ion Directed Supramolecular Assembly of One- and Two-Dimensional Polyrotaxanes Incorporating Cucurbituril

Ki-Min Park, Dongmok Whang, Eunsung Lee, Jungseok Heo, and Kimoon Kim*[a]

Abstract: This paper reports a synthetic strategy to construct one- and two-dimensional (1D and 2D) polyrotaxanes, in which a number of rings are threaded onto a coordination polymer, by the combination of self-assembly and coordination chemistry. Our approach to construct polyrotaxanes with high structural regularity involves threading a cucurbituril (CB) "bead" with a short "string" to form a stable pseudorotaxane, followed by linking the pseudorotaxanes with metal ions as "linkers" to organize into a 1D or 2D polyrotaxane. A 4- or 3-pyridylmethyl group is attached to each end of 1,4-diaminobutane or 1,5-diaminopentane to produce the short "strings", which then react with the cucurbituril "bead" to form stable pseudorotaxanes. The reaction of the pseudorotaxanes with various transition metal ions including Cu^{II}, Co^{II}, Ni^{II}, Ag^{I}, and Cd^{II} produces 1D or 2D polyrotaxanes, in which many molecular "beads" are threaded onto 1D or 2D coordination polymers as confirmed by X-ray crystallography. 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 beads in the pseudorotaxane, and the size and coordination ability of the counteranion.

Keywords: coordination modes • rotaxanes • solid-state structures • supramolecular chemistry • transition metals

Introduction

Mechanically interlocked molecules[1] such as rotaxanes, catenanes, and knots have intrigued synthetic chemists not only because of their aesthetic appeal but also because of their potential applications. For example, [2]rotaxanes, which are composed of a ring threaded on a linear chain terminated by bulky stoppers, 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 molecular-scale information processing. To realize molecular electronic devices, however, such molecular machines need to be organized into an array to behave coherently. Solid-state supramolecular assembly of rotaxane units may be a promising approach toward organizing such rotaxane-based molecular machines into two-dimensional (2D) and three-dimensional (3D) arrays in a controlled manner. Therefore, we decided to explore organizing rotaxanes (or pseudorotaxanes) by self-assembly into 1D and 2D polyrotaxanes with well-defined structures in the solid state.

Previously, most 1D polyrotaxanes have been synthesized by threading molecular "beads", particularly cyclodextrins (CDs), onto organic polymers.[3–6] However, these systems in general lack structural regularity as the molecular "beads" are often not threaded in all the available recognition sites of the polymer chains. It is mainly due to the fact that affinity of the ring components (CDs or crown ether-type macrocycles) toward the recognition sites in the polymers is not high enough to ensure complete threading. Furthermore, the bucket-shaped CDs generate many possible orientational isomers of the resulting CD-containing polyrotaxanes. Therefore, no polyrotaxane of this type could be isolated in a single-crystal form suitable for X-ray crystallography.[7] These results suggest that molecular beads should have a highly symmetrical structure and high affinity towards the recognition sites to organize (pseudo)rotaxanes into 1D and 2D polyrotaxanes with highly ordered structures in the solid state, which can be characterized by single-crystal X-ray crystallography. These requirements for molecular "beads" seem to be met with cucurbituril.

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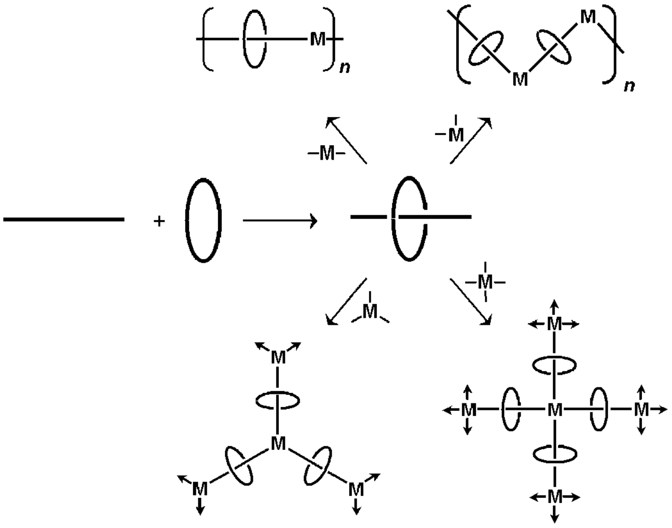
Cucurbituril (CB) is a macrocyclic cavitand with an internal cavity of ≈5.5 Å diameter that is accessible from the exterior by two carbonyl laced portals of ≈4 Å diameter.[8–10] It resembles CDs, particularly α-CD, in terms of the cavity size. However, unlike CDs, it has a highly symmetrical structure with two identical openings. One of the remarkable properties of CB is its ability to form very stable 1:1 host–guest complexes with protonated diaminoalkanes, particularly diaminobutane and diaminopentane.[11] The high stability of the inclusion complexes is due to the strong ion dipole as well as hydrogen-bonding interactions between the protonated amine groups of the guests and the carbonyl groups of the host. The highly symmetric structure and the ability to form very stable inclusion complexes with protonated diaminoalkanes make CB quite attractive as a building block for interlocked structures, in particular rotaxanes, as demonstrated by one-pot, high-yield synthesis of a [2]rotaxane using CB as a "bead".[12]

In organizing rotaxanes (or pseudorotaxanes) into 1D and 2D polyrotaxanes with highly ordered structures, we decided to employ coordination bonding with transition metal ions, which have proven to be very useful in the construction of supramolecular architectures[13–19] as a result of their capabilities to form relatively strong bonds with preferred coordination geometries.

Taking these together, we have now developed a general strategy to organize pseudorotaxanes into polyrotaxanes with high structural regularity in the solid state. In this article, we describe transition metal ion directed supramolecular assembly of 1D and 2D polyrotaxanes incorporating CB as the cyclic component. Preliminary results were communicated earlier.[20]

Results

Strategy: Our synthetic strategy for the construction of polyrotaxanes with high structural regularity works in tandem as illustrated in Scheme 1. It involves threading a cucurbituril "bead" with a short "string" to form a stable pseudorotaxane, followed by linking the pseudorotaxanes with metal ions as "linkers" for the organization into a 1D or 2D 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.

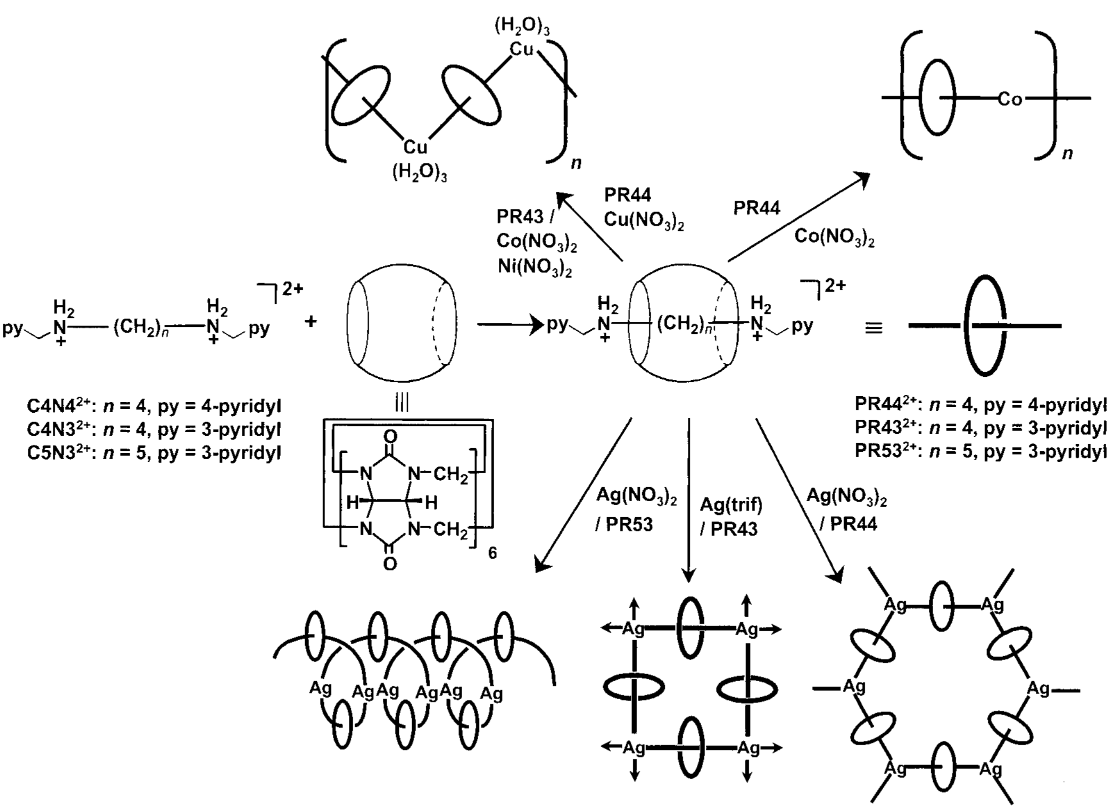


Scheme 1. Synthetic strategy to one- and two-dimensional polyrotaxanes.

With this idea in mind we designed short "strings" such that they not only form stable inclusion complexes with CB, but also bind metal ions using the donor atoms strategically placed at the terminals. A pyridylmethyl group with different pyridyl nitrogen positions was attached at the terminals of diaminobutane or diaminopentane to produce the short "strings" (**C4N4**$^{2+}$, **C4N3**$^{2+}$, **C5N3**$^{2+}$, see Scheme 2). Indeed, these "strings" form very stable pseudorotaxanes with CB (**PR44**$^{2+}$, **PR43**$^{2+}$, **PR53**$^{2+}$, respectively, Scheme 2). It is interesting to note that although CB itself is sparingly soluble in water, the resulting pseudorotaxanes are readily soluble in water because of their overall +2 charge. Various transition metal ions such as Cu^{II}, Ni^{II}, Co^{II}, Ag^{I}, and Cd^{II} were then allowed to react with the pseudorotaxanes to organize them into polyrotaxanes.

1D Polyrotaxanes: The 1D polyrotaxane **1** is formed when a solution of $Cu(NO_3)_2$ in methanol is allowed to diffuse slowly into an aqueous solution of the pseudorotaxane **PR44**$(NO_3)_2$.[20a] The X-ray crystal structure of **1**, as expected, reveals CB "molecular beads" threaded on the coordination polymer, the chain of which is composed of alternating copper ions and **PR44**$^{2+}$ (Figure 1a). A CB "bead" is held tightly at the middle of each repeating unit by strong hydrogen bonds between the protonated amine nitrogen atoms of the "string" (**C4N4**$^{2+}$) and the oxygen atoms of CB. The coordination geometry around each copper ion is square pyramidal (Figure S1): two pyridine units of **PR44**$^{2+}$ occupy the two adjacent basal positions while three H_2O molecules occupy the remaining basal and apical positions. The *cis* coordination of the two pyridine units to the metal makes the polymer chain change its direction abruptly at the metal center. As a result, the polymer chain is forced to adopt a zigzag shape. In the crystal, the coordination polymer chain runs along the [−111] direction with a repeating unit of 11.93 Å. Hydrogen-bonding interactions exist between the water molecules bound to the copper ions of one chain and the oxygen atoms of CB "beads" of the adjacent chains further reinforcing the overall structure in the crystal (Figure S2). Four nitrate counterions and fourteen water molecules for each repeating unit fill the remaining space while forming an extensive hydrogen-bonding network in the lattice.

This success prompted us to explore other metal ions as "linkers" to organize the pseudorotaxane units into polyrotaxanes. Indeed, 1D polyrotaxanes can be synthesized with other metal ions that normally prefer octahedral geometry. For example, slow reaction of $Co(NO_3)_2$ and $Ni(NO_3)_2$ with **PR44**$(NO_3)_2$ in aqueous solution yields 1D polyrotaxanes **2** and **3**, respectively, which are isostructural with each other.[21] In the crystal structure of **2** (Figure 1b), the coordination geometry around each Co^{II} ion is pseudooctahedral with the axial sites occupied by two pyridyl nitrogens from **PR44**$^{2+}$; the



Scheme 2. Synthetic scheme of pseudorotaxanes and one- and two-dimensional polyrotaxanes.

equitorial positions are occupied by four water molecules (Figure S3). 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 (Figure 1b). In the crystal, the coordination polymer chain extends along the [201] direction with a repeating unit of 18.81 Å. As in **1**, the metal-bound water molecules take part in hydrogen bonding with carbonyl oxygen atoms of CB on the adjacent polyrotaxane chains (Figure S5a). Besides, the nitrate counterions along with several water molecules make an extensive H-bonding network in the lattice contributing to the overall solid-state structure.

The major structural difference between the two 1D polyrotaxanes **1** and **2** is that the two pyridyl units are coordinated to the metal center in a *trans* geometry in **2** whereas they are bound in a *cis* geometry in **1**. As a result, the former has a square-wave-shaped polymer chain, whereas the latter exhibits a zigzag-shaped polymer chain (Figure 1a and b).

However, if we switch pseudorotaxane from **PR44**$(NO_3)_2$ to **PR43**$(NO_3)_2$, its reaction with Co^{II} and Ni^{II} yields zigzag-shaped 1D polyrotaxanes **4** and **5**, respectively, which are also isostructural with each other. In contrast to **2** and **3**, the crystal structures of **4** and **5** reveal that the metal ions are in

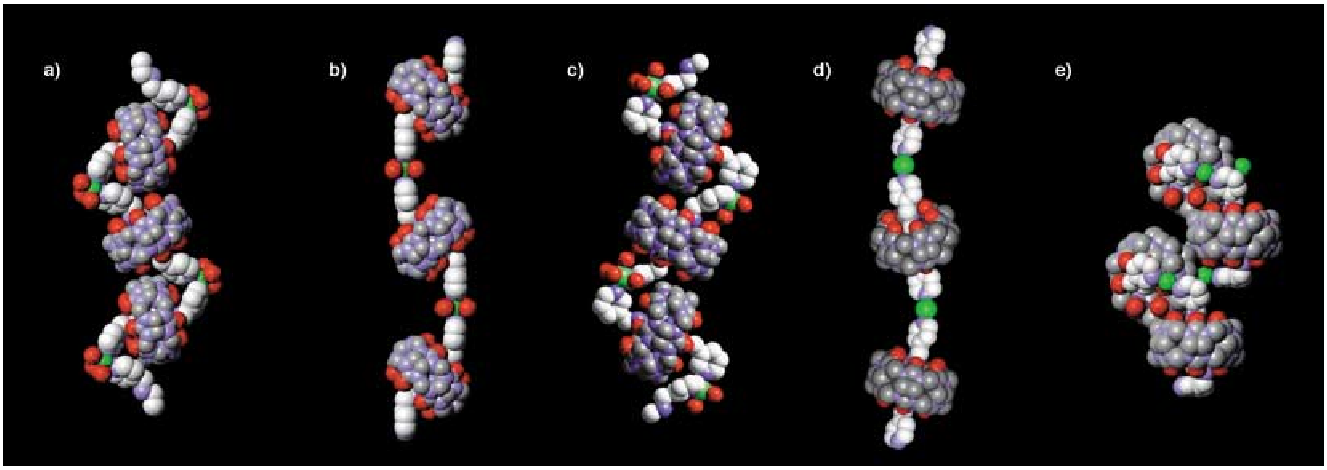


Figure 1. Space-filling representations for a) zig-zag-shaped 1D polyrotaxane **1**; b) square-wave-shaped 1D polyrotaxane **2**; c) zig-zag-shaped 1D polyrotaxane **4**; d) linear chain 1D polyrotaxane **6**; e) helical 1D polyrotaxane **7**. Hydrogen atoms are omitted for clarity. Color codes: carbon (organic strings), gray; carbon (CB beads), dark gray; nitrogen, purple; oxygen, red; metal ion, green.

octahedral geometries with two *cis* sites occupied by two pyridyl nitrogens from **PR43**$^{2+}$; the remaining positions are occupied by four water molecules (Figure S6 and Figure S7). The *cis* coordination of the terminal pyridyl units to the metal centers results in a zigzag-shaped polymer chain similar to that in **1** (Figure 1c). In the crystal, the coordination polymer chains in **4** and **5** extend along the [111] direction with repeating units of 23.66 Å and 23.56 Å, respectively.

Other transition metal ions with preferences for different coordination geometries also work as "linkers" in organizing pseudorotaxanes into 1D polyrotaxanes. In particular, we thought that Ag^{I} with a pronounced tendency to form two-coordinate complexes and a relatively low affinity for oxygen atom donors would react with pseudorotaxanes to form linear chain 1D polyrotaxanes. Indeed, when $Ag(CH_3(C_6H_4)SO_3)$ is allowed to react with **PR44**$(CH_3(C_6H_4)SO_3)_2$ in water, another 1D polyrotaxane (**6**) is obtained.[20b] In the structure of **6**, a two-coordinate Ag^{I} ion links two **PR44**$^{2+}$ to form a 1D polyrotaxane coordination polymer similar to the ones described above. The coordination of two pyridyl units to the silver ion in a *trans* geometry results in a straight polymer chain with a repeating unit of 20.01 Å (Figure 1d). In the crystal of **6**, adjacent polyrotaxane chains are interlinked by weak interactions between the silver ion of one chain and the oxygen atoms of CB on the adjacent chains ($Ag-O_{CB}$: 2.784 Å, Figure S4 and Figure S5b). Besides the space-filling water molecules, the charge compensating tosylate ions are found in the lattice without significant interactions with the metal ions.

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 loose their integrity to fall apart into their components.

Helical 1D polyrotaxanes: Helical 1D polyrotaxanes can be obtained with the pseudorotaxane **PR53**$^{2+}$, where the "string" is longer as well as more flexible compared with that in **PR44**$^{2+}$. The reaction of $AgNO_3$ with **PR53**$(NO_3)_2$ yields the helical 1D polyrotaxane **7**[20c] (Figure 1e and 2a). The helix is extended along the *b* axis of the crystal with a pitch of 17.9 Å, which is the same as the length of the *b* axis (Figure 3a). In each helix, two **PR53**$^{2+}$ and two silver ions constitute one turn. Each silver ion is coordinated by two **PR53**$^{2+}$ in a linear fashion. However, the "string" of the pseudorotaxane is not symmetrically disposed with respect to the CB unit. One of the protonated amine nitrogen atoms of the "string" (**C5N3**) is essentially lying in the six-oxygen plane of CB, as in **PR44**$^{2+}$, while the other one is displaced considerably out of the six-oxygen plane (0.721(8) Å, Figure S8). Moreover, the methylpyridyl unit attached to the former nitrogen (N(26), see Figure S8) makes a dihedral angle of 61° with the six-oxygen plane, whereas that connected to the latter (N(27)) is nearly parallel to the portal plane (dihedral angle = 9°). The parallel conformation of the 3-pyridyl unit forces the polymer chain to change its direction sharply, which eventually leads to a helical structure.

When $Cd(NO_3)_2$ instead of $Ag(NO_3)_2$ is allowed to react with **PR53**$^{2+}$ a different type of helical 1D polyrotaxane (**8**) is formed. The X-ray crystal structure of **8** reveals that each turn of the helix contains four units of **PR53**$^{2+}$ and two types of Cd^{II} ions with each type containing two ions. This arrangement gives a pitch of 50.5 Å (Figure 2b and 3b). One type (Cd(1)) of the cadmium ions is coordinated by two pyridyl units of **PR53**$^{2+}$, a nitrate ion, and three water molecules in a distorted octahedral geometry with the pyridyl units at *trans* positions. On the other hand, the other type (Cd(2)) of the cadmium ions is coordinated by two pyridyl units of **PR53**$^{2+}$ and four water molecules in a distorted octahedral geometry with the pyridyl units at *cis* positions (Figure S9). One of the protonated amine nitrogens of the "string" (**C5N3**) is significantly displaced (1.163(7) Å) out of the six-oxygen plane of CB, as in **7**, and the corresponding pyridylmethyl unit is coordinated to Cd(2). The polymer chain changes its direction sharply at Cd(1) leading to the helical structure. It should be noted that

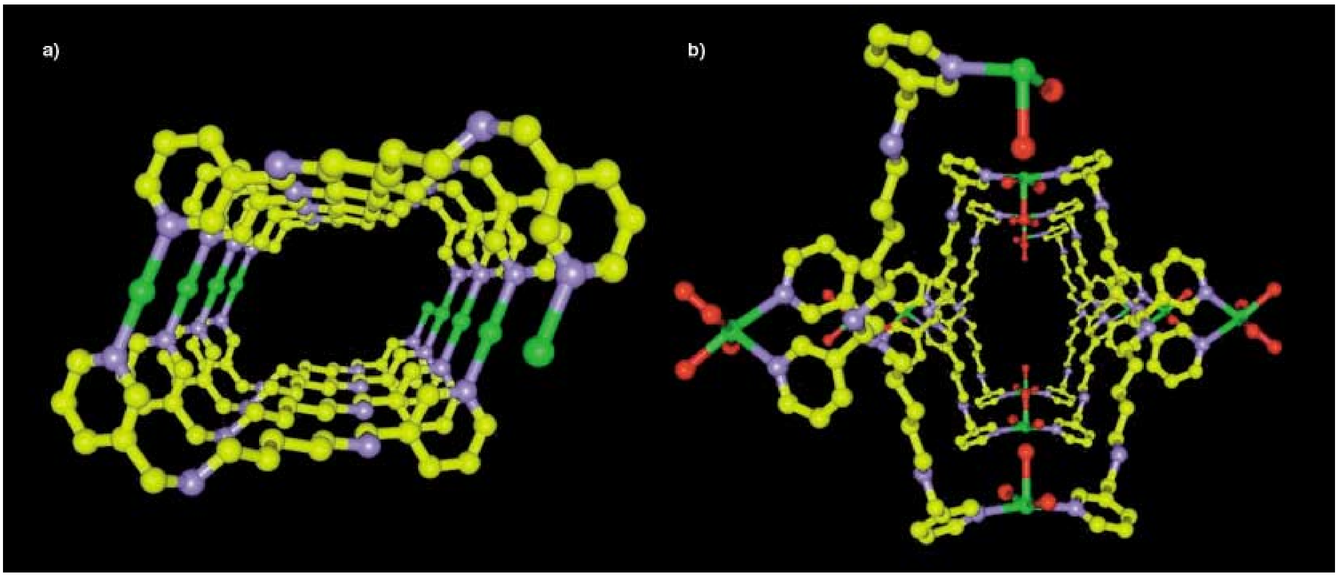


Figure 2. Ball and stick representations for the helical structures of the polymer backbones in a) **7** and b) **8**. CB beads, counterions, and solvated water molecules are omitted for clarity. Color codes: carbon, yellow; nitrogen, purple; oxygen, red; metal ion, green.

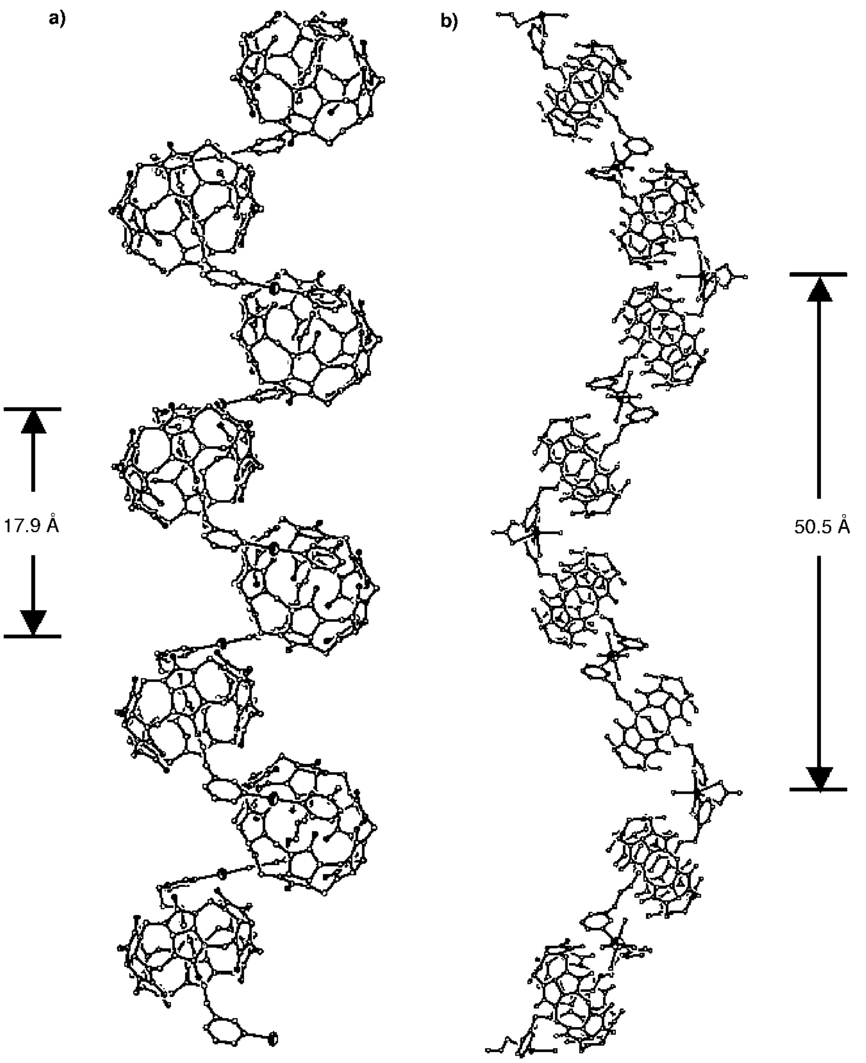


Figure 3. Comparison of the two helical polyrotaxanes **7** and **8**.

the crystals of **7** and **8** are racemic mixtures containing equal amounts of right-handed and left-handed helices in the same crystal.

2D Polyrotaxane nets: As described above, when silver tosylate is treated with **PR44**$^{2+}$, 1D polyrotaxane **6** is formed.[20b] However, when the counteranion is changed to nitrate, which has better coordinating ability, the same procedure yields a novel 2D polyrotaxane **9**. The X-ray crystal structure of **9** reveals cucurbituril "beads" threaded onto a 2D coordination polymer network (Figure 4a). The 2D network[22] 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 average length of the edge is 20.9 Å, and the separation of the opposite corners is 38.0 Å. Each silver ion is coordinated by three **PR44**$^{2+}$ and a nitrate ion in a distorted tetrahedral geometry (Figure S10). The 2D polyrotaxane network forms layers stacked on each other with a mean interplane

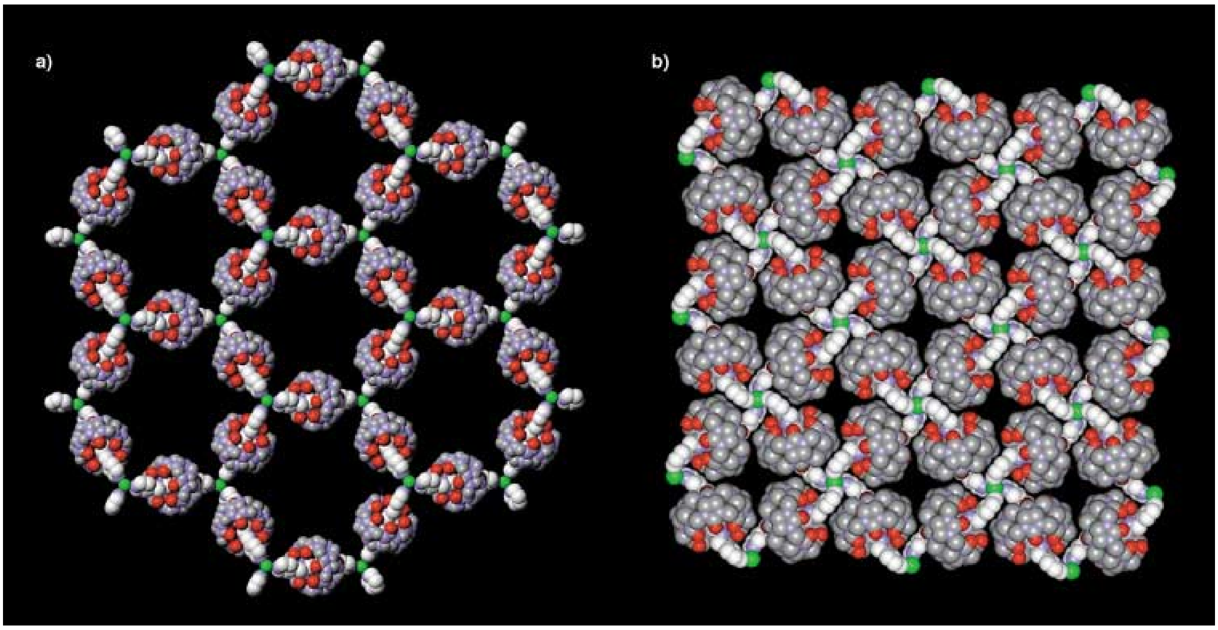


Figure 4. Space-filling representations for a) hexagonal 2D polyrotaxane net of **9**, and b) square-grid-shaped 2D polyrotaxane net of **10**. Hydrogen atoms are omitted for clarity. Color codes: carbon (organic strings), gray; carbon (CB beads), dark gray; nitrogen, purple; oxygen, red; metal ion, green.

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separation of 9.87 Å (Figure S11). There is another 2D polyrotaxane network (denoted **B**) almost perpendicular to the first one (denoted **A**). The dihedral angle between the mean planes of the two networks **A** and **B** is 69.34°. These networks interpenetrate with full interlocking of the hexagons as illustrated in Figure 5: a hexagon belonging to the network **A** (solid lines) interlocked with four hexagons belonging to **B** (open lines) and vice versa. Although interlocking of simple 2D networks has been known (polycatenated 2D nets),[23–32] this structure is the first example of polycatenated 2D polyrotaxane nets reported in the literature.[33]

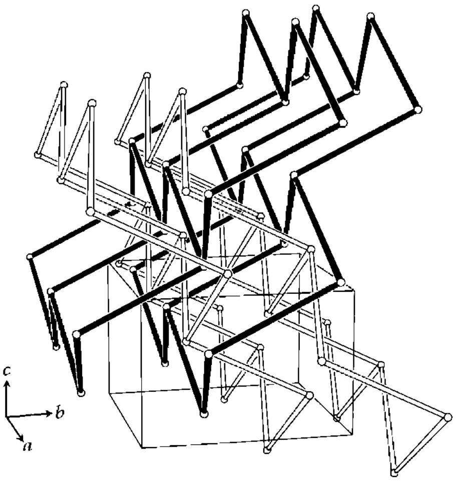

Figure 5. Schematic illustration of interlocking of the hexagons in **9**: a hexagon belonging to the network **A** (solid lines) interlocked with four hexagons belonging to **B** (open lines) and vice versa. Small circles represent silver ions, and lines represent pseudorotaxane **PR44**$^{2+}$ linking two silver ions.

When the pseudorotaxane **PR43**$^{2+}$ is used in place of **PR44**$^{2+}$ the same procedure affords another 2D polyrotaxane network with a different structure. For example, reaction of $Ag(CF_3SO_3)$ with **PR43**$(CF_3SO_3)_2$ produces a novel square-grid-shaped 2D polyrotaxane (**10**). The X-ray crystal structure of **10** reveals that CB "beads" are threaded on a square-grid-shaped 2D coordination polymer network,[22] which consists of large edge sharing squares with a Ag^I ion at each corner and a pseudorotaxane **PR43**$^{2+}$ at each edge connecting two Ag^I ions. The length of the edge is 17.29 Å (Figure 4b). Each silver ion is located on the crystallographic S_4 center and coordinated by four pyridyl groups of pseudorotaxane **PR43**$^{2+}$ in a slightly distorted tetrahedral geometry (Figure S12). The silver ions and the center of CB "beads" are lying on the same plane. The 2D layers stack along the c axis in the crystal with a mean interlayer separation of 12.69 Å (Figure 6a). In contrast to **9**, no catenation of the 2D network is observed in this structure. Because the channels passing through the center of the squares are almost filled with CB "beads", only small molecules or ions such as triflate ions can be clathrated at the middle of the square grid.

The 2D polyrotaxane **11** is formed upon reacting **PR43**$(NO_3)_2$ with $Cu(NO_3)_2$. The 2D network in **11**, similar to that in **10**, consists of large edge sharing distorted tetragons

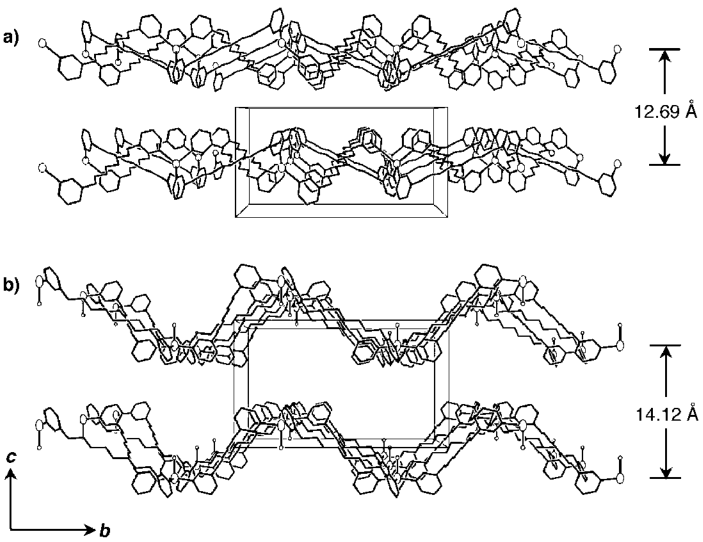

Figure 6. The stacking of 2D polyrotaxane layers in a) **10** and b) **11**. The mean separations between the layers are 12.69 Å and 14.12 Å, for **10** and **11**, respectively. Small circles represent metal ions. CB beads, counterions, and solvated water molecules are omitted for clarity.

with a Cu^{II} ion at each corner and a molecule of **PR43**$^{2+}$ at each edge connecting two Cu^{II} ions. Each copper ion is located on the crystallographic fourfold axis and coordinated by four pyridyl groups of pseudorotaxane **PR43**$^{2+}$ and a water molecule in a distorted square pyrimidal geometry (Figure S13). The 2D layers are highly undulating, which makes the mean interlayer separation (14.12 Å) larger than that in **11** (Figure 6b).

Discussion

As described above, the overall topologies and structures of polyrotaxanes in the solid state are determined by various factors such as the coordination tendency of the metal ions, the structure of pseudorotaxanes, and the nature of the counterions (Figure 7). Since these factors work together to affect the structures, it is difficult, if not impossible, to separate them. Nevertheless, we have observed some general trends which are discussed below.

Effects of metal ions: The topology and structure of polyrotaxanes can be determined by the number of pseudorotaxane units coordinated to a metal linker and its coordination geometry. As described earlier, the first row transition metal ions such as Co^{II}, Ni^{II}, and Cu^{II} tend to form 1D polyrotaxanes without exception, whereas the larger and softer Ag^+ ion affords both 1D and 2D polyrotaxanes with pseudorotaxane **PR44**$^{2+}$. Among the first row transition metal ions, Cu^{II} seems to prefer a square pyramidal coordination geometry with two pyridyl groups coordinated to the metal center in a *cis* mode, whereas Co^{II} and Ni^{II} prefer an octahedral geometry with two pyridyl groups attached to the metal center in a *trans* geometry. With **PR44**$^{2+}$, as a result, Cu^{II} produces a zigzag-shaped 1D polyrotaxane, whereas Co^{II} and Ni^{II} yield 1D polyrotaxanes in the shape of a square wave under the same reaction conditions. A similar trend has been observed in the formation of “molecular necklaces”.[34] However, we must point out that with **PR43**$^{2+}$, Co^{II} and Ni^{II} also can have an octahedral geometry with two pyridyl groups attached to the metal center in a *cis* geometry that results in zigzag-shaped 1D polyrotaxanes as seen in **4** and **5**. In all of these 1D polyrotaxanes, the remaining coordination sites are occupied by water molecules which form hydrogen bonds with oxygen atoms of the CB beads in the adjacent polyrotaxane chains, and they thereby stabilize the solid-state structures. However, Ag^{I} having a relatively low affinity for oxygen donors and a tendency to form two-coordinate complexes produces 1D polyrotaxanes with linear or helical structures, in which two pyridyl units are coordinated to the metal in a *trans* geometry, or 2D polyrotaxane nets, in which three pyridyl units are coordinated to the metal center.

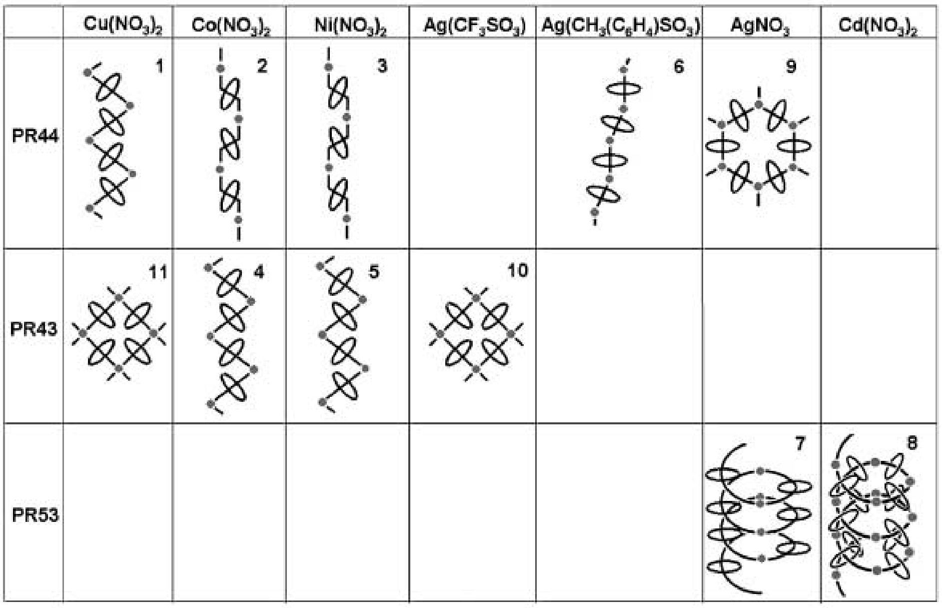

Figure 7. Schematic diagram illustrating topologies and structures of polyrotaxanes resulting from various pseudorotaxanes and metal salts.

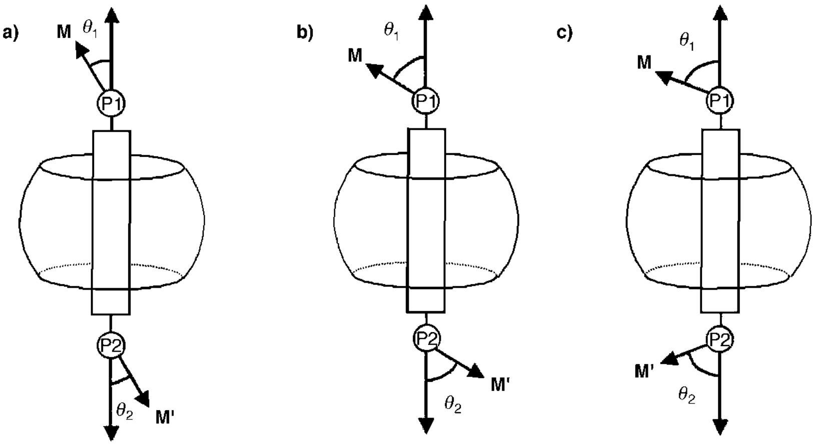

Figure 8. Schematic diagram of pseudorotaxanes: a) **PR44**$^{2+}$; b) **PR43**$^{2+}$, and c) **PR53**$^{2+}$. The “bending” angles θ_1 and θ_2 are the angles between the P1–P2 axis and M–P1 and M′–P2, respectively, and ϕ is the dihedral angle **M–P1–P2–M′**, in which **P1** and **P2** are the centroids of the terminal pyridyl groups of a pseudorotaxane, and **M** and **M′** are the two metal ions to which the pseudorotaxane unit is coordinated.

Effects of pseudorotaxanes: The structural features of pseudorotaxanes, **PR44**$^{2+}$, **PR43**$^{2+}$, and **PR53**$^{2+}$ are quite different from each other and strongly affect the ultimate structures of the resulting polyrotaxanes. In all of the pseudorotaxanes, the CB “molecular beads” are held tightly onto the organic “string” by strong hydrogen bonds between the protonated amino nitrogen atoms of the “string” and the oxygen atoms at the CB portals. The structural variation of the pseudorotaxanes originates from i) rotation of the pyridyl moiety about the methylene group attached to the protonated amine nitrogen and ii) matching/mismatching of the length of the linear chain with the distance between the two carbonyl portals of CB. To compare the structural features of the pseudorotaxanes, we define “bending” angles θ_1 and θ_2 (angles between the P1–P2 axis and M–P1 and M′–P2, respectively) and the dihedral angles ϕ (M–P1–P2–M′) of the pseudorotaxanes as illustrated in Figure 8. We also list these values in Table 1.

In the structure of **PR44**$^{2+}$, the separation between two portals of CB is well-matched with the distance between two ammonium nitrogen atoms of the organic string **C4N4**$^{2+}$ in its fully extended conformation. Hence, the otherwise flexible organic “string” **C4N4**$^{2+}$ in **PR44**$^{2+}$ assumes a rigid, fully extended structure with all methylene units in an *anti* conformation; the structure makes the resulting pseudorotaxane behave as a linear, rigid, and bulky organic building block (Figure 8a). Consequently, the dihedral angles of the two coordination bonds made by **PR44**$^{2+}$ are almost fixed at 180°, and the separation between two centroids of the terminal pyridyl groups lies in a narrow range (13.3 – 13.9 Å).

The organic string **C4N3**$^{2+}$ of the pseudorotaxane **PR43**$^{2+}$ also assumes a fully extended structure (Figure 8b). However, the “bending” angles of **PR43**$^{2+}$ (78.1 – 64.5°) are much larger than those of **PR44**$^{2+}$ (42.4 – 18.9°) since the former has the *meta*-substituted pyridine groups, whereas the latter has *para*-substituted ones. This leads to a shorter distance between the two metal centers bridged by **PR43**$^{2+}$ (16.7 – 17.8 Å) compared with that bridged by **PR44**$^{2+}$ (18.82 – 21.11 Å).

Table 1. Structure parameters for pseudorotaxanes in polyrotaxanes **1**–**11**.[a]

	compound	θ_1, θ_2 [°]	ϕ [°]	P1$\cdots$P2 [Å]	M$\cdots$M′ [Å]
PR44^{2+}	**1**[b]	42.4, 42.4	180	13.28	18.82
		22.4, 22.4	180	13.65	20.09
	2	29.9, 27.8	176.6	13.58	20.09
	3	29.7, 27.2	177.3	13.61	19.99
	6[b]	28.6, 28.6	180	13.67	20.77
		18.4, 18.4	180	13.84	20.18
	9[b]	23.9, 23.9	180	13.75	20.64
		21.2, 21.2	180	13.95	21.11
PR43^{2+}	**4**[b]	76.6, 76.6	180	13.83	16.91
		72.9, 72.9	180	13.64	17.12
	5[b]	78.1, 78.1	180	13.82	16.68
		72.1, 72.1	180	13.68	17.15
	10	75.1, 75.1	180	13.77	17.29
	11	64.5, 64.5	180	13.79	17.82
PR53^{2+}	**7**	94.8, 69.3	17.9	12.98	13.97
	8	81.7, 64.1	167.5	14.93	18.55

[a] The "bending" angles θ_1 and θ_2 are the angles between the P1–P2 axis and M–P1, and M′–P2, respectively, and ϕ is the dihedral angle **M–P1–P2–M′**, in which **P1** and **P2** are the centroids of the terminal pyridyl groups of a pseudorotaxane, and **M** and **M′** are the two metal ions to which the pseudorotaxane unit is coordinated. [b] Two independent pseudorotaxanes exist in the structures.

These structural differences in the bridging pseudorotaxanes probably lead to two different 2D polyrotaxane nets generated with Ag$^{\mathrm{I}}$: the interpenetrating hexagonal 2D net formed with **PR44**$^{2+}$ versus the square-grid-shaped 2D net with **PR43**$^{2+}$. This may also explain the fact that the reaction of Cu$^{\mathrm{II}}$ with **PR43**$^{2+}$ produces a square-grid-shaped 2D polyrotaxane net, whereas that with **PR44**$^{2+}$ yields a 1D polyrotaxane.

In contrast to **PR44**$^{2+}$ and **PR43**$^{2+}$, **PR53**$^{2+}$ has an odd number of atoms having a sp^3 configuration between two terminal pyridyl groups, which leads to a *syn*-type bridging mode ($\phi \approx 0°$) of **PR53**$^{2+}$ (Figure 8c). The *meta*-substituted pyridine groups at the terminals also make the "bending angle" of **PR53**$^{2+}$ relatively large (64.1–94.8°). In the structure of helical 1D polyrotaxane **7**, the *syn*-type bridging mode ($\phi = 17.9°$) of **PR53**$^{2+}$ makes the polymer chain turn around, which leads to the helical structure even though the Ag$^{\mathrm{I}}$ ions have a linear coordination geometry. This structural feature of **PR53**$^{2+}$ has also been observed in the structure of a "six-membered molecular necklace" formed from **PR53**$^{2+}$ and a Cu$^{\mathrm{II}}$ ion.[36]

However, the conformation of **PR53**$^{2+}$ is dissymmetric and more flexible than other pseudorotaxanes because the separation between two portals of CB does not match the distance between two amine nitrogen atoms of **C5N3**$^{2+}$ in its fully extended conformation. The longer organic "string" **C5N3**$^{2+}$ allows the resulting pseudorotaxane **PR53**$^{2+}$ to enjoy more freedom in terms of the orientations of the terminal pyridyl groups. It is therefore not too surprising to see that **PR53**$^{2+}$ also displays an *anti*-type bridging mode as observed ($\phi = 167.5°$) in the helical 1D polyrotaxane **8**. The formation of helical polyrotaxanes from **PR53**$^{2+}$ is congruent with the fact that rigid rodlike organic building blocks have a tendency to form highly symmetric coordination polymers, whereas dissymmetric and flexible building blocks have the ability to produce asymmetric and/or more complicated structures, such as helical and polycatenated structures.[35]

Effects of counterions and other effects: Although the overall structure seems to be predominantly controlled by the coordination preferences of the transition metal and the structure of the organic building blocks, subtle contributions from the counterions, steric interactions as well as packing efficiency are also observed to have a significant effect upon the structures of the resulting polyrotaxanes. With the same pseudorotaxane **PR44**$^{2+}$, for example, silver tosylate and silver nitrate produce a 1D polyrotaxane (**6**) and a 2D polyrotaxane (**9**), respectively. The larger, noncoordinating tosylate ion allows the silver ion to adopt a linear, two-coordinate geometry that leads to the 1D polyrotaxane, whereas the smaller, coordinating nitrate ion encourages the silver ion to assume a four-coordinate, tetrahedral geometry that forms a 2D polyrotaxane.

An interesting feature of the square-grid-shaped 2D polyrotaxanes **10** and **11** is the fact that the overall structures of the two are similar despite the different coordination geometries of the metal centers (distorted tetrahedral (**10**) vs. square pyramidal (**11**)). For example, both crystal structures of **10** and **11** belong to the same space group and display an almost identical packing mode of bulky CB "beads", although the 2D layers in **11** are "wavier" than those in **10**. The result suggests that the solid-state structures of the 2D polyrotaxanes may be more influenced by the packing efficiency of the CB "beads" rather than by the coordination geometry of metal-ion "linkers".

Conclusion

In this paper, we present a general strategy to organize pseudorotaxanes into 1D and 2D polyrotaxanes with high structural regularity in the solid state by utilizing the principles of self-assembly and coordination chemistry. The results reported here demonstrate the efficiency as well as the control of this approach. A key to the success of this approach is the highly symmetric structure of CB and its tendency to form exceptionally stable pseudorotaxanes, which ensures complete threading of all the recognition sites of polyrotaxanes. The ultimate overall structure of a polyrotaxane by this route is the result of interplay among various factors which include the coordination preferences of the metal ion, spatial disposition of the donor atoms with respect to the CB beads in the pseudorotaxane, and the size and coordination ability of the counteranion. 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. The interlocked structures described may have interesting physical and chemical properties, which are currently under investigation.

The present approach can be followed to construct other extended or discrete interlocked structures. For example, we have recently succeeded in the synthesis of 3D polyrotaxanes[34] and "molecular necklaces"[36] by using essentially the same approach with minor modifications. More recently, we have also demonstrated that this approach is useful for synthesizing open-framework materials with large cavities and channels.[37] Furthermore, the present work may provide insights into the construction of well-defined 2D or 3D organization of molecular machines and switches. For example, using the same approach, we may be able to construct highly organized 1D or 2D arrays of rotaxane-based molecular machines,[38] which may behave coherently to perform specific functions.

Experimental Section

General methods: All reagents and solvents employed were commercially available high-grade purity materials (Aldrich Chemicals), used as supplied without further purification. ^{1}H NMR spectra were recorded on a Bruker DRX500 spectrometer at 500.23 MHz, 25 °C. Polyrotaxane samples for elemental analysis were dried under vacuum for several hours or overnight.

Pseudorotaxane PR43(NO$_3$)$_2$: CB (2.78 g, 2.79 mmol) was added to *N*,*N*′-bis(3-pyridylmethyl)-1,4-diaminobutane dihydronitrate (**C4N3**(NO$_3$)$_2$) (1.00 g, 2.54 mmol) dissolved in water (10 mL). After stirring for 3 h at room temperature, undissolved CB was filtered off, and the volume of the solution was reduced to ≈2 mL by evaporation under reduced pressure. Addition of ethanol to the solution produced a precipitate, which was filtered, washed, and dried in vacuo (3.22 g, 91 %). m.p. > 330 °C (decomposed).

^{1}H NMR (300 MHz, D$_2$O): $\delta = 0.65$ (br s, 4H), 2.55 (br s, 4H), 4.42 (d, $J = 15.65$ Hz, 12H), 4.51 (s, 4H), 5.67 (s, 12H), 5.76 (d, $J = 15.62$ Hz, 12H), 7.62 (dd, $J = 7.83$ Hz, 2H), 8.34 (d, $J = 8.29$ Hz, 2H), 8.67 (d, $J = 5.02$ Hz, 2H), 8.97 (s, 2H). Neither free CB nor **C4N3**$^{2+}$ in the filtrate was detected by ^{1}H NMR spectroscopy; elemental analysis calcd (%) for $C_{52}H_{60}N_{30}O_{18} \cdot 10H_2O$: C 42.11, H 4.76, N 28.33; found: C 42.12, H 4.89, N 28.56.

Pseudorotaxane PR44(NO$_3$)$_2$: This compound was prepared by the same procedure as that for (**PR43**(NO$_3$)$_2$) described above except that *N*,*N*′-bis(3-pyridylmethyl)-1,4-diaminobutane dihydronitrate (**C4N4**(NO$_3$)$_2$) instead of **C4N3**(NO$_3$)$_2$ was used (0.90 g, 95 %). m.p. > 270 °C (decomposed).

^{1}H NMR (300 MHz, D$_2$O): $\delta = 0.68$ (br s, 4H), 2.55 (br s, 4H), 4.42 (d, $J = 15.64$ Hz, 12H), 4.51 (s, 4H), 5.69 (s, 12H), 5.76 (d, $J = 15.62$ Hz, 12H), 7.88 (d, $J = 6.00$ Hz, 4H), 8.69 (d, $J = 6.04$ Hz, 4H); elemental analysis calcd (%) for $C_{52}H_{60}N_{30}O_{18} \cdot 8.5H_2O$: C 40.39, H 5.01, N 27.17; found: C 40.60, H 5.23, N 26.81.

Pseudorotaxane PR53(NO$_3$)$_2$: This compound was prepared by the same procedure as that for **PR43**(NO$_3$)$_2$ described above except that *N*,*N*′-bis(3-pyridylmethyl)-1,5-diaminopentane dihydronitrate (**C5N3**(NO$_3$)$_2$) instead of **C4N3**(NO$_3$)$_2$ was used (3.99 g, 98 %). m.p. > 300 °C (decomposed).

^{1}H NMR (300 MHz, D$_2$O): $\delta = 0.45$ (br s, 2H), 0.76 (br s, 4H), 2.86 (br s, 4H), 4.33 (d, $J = 15.61$ Hz, 12H), 4.50 (s, 4H), 5.61 (s, 12H), 5.71 (d, $J = 15.58$ Hz, 12H), 7.57 (dd, $J = 7.96$ Hz, 2H), 8.25 (d, $J = 6.17$ Hz, 2H), 8.61 (d, $J = 4.95$ Hz, 2H), 8.89 (s, 2H); elemental analysis calcd (%) for $C_{53}H_{62}N_{30}O_{18} \cdot 10H_2O$: C 42.51, H 4.85, N 28.06; found: C 42.48, H 5.15, N 27.86.

Cu zigzag-shaped 1D polyrotaxane (1): A solution of Cu(NO$_3$)$_2$ (0.2 M) in methanol was layered over an aqueous solution of **PR44**(NO$_3$)$_2$ (0.002 M) in a diffusion tube to produce pale blue, X-ray quality crystals of **1** after a week (21 mg, 26 %). m.p. > 175 °C (decomposed); elemental analysis calcd (%) for $CuC_{52}H_{60}N_{32}O_{24} \cdot 8H_2O$: C 36.21, H 4.44, N 25.98; found: C 36.08, H 4.05, N 25.94.

Co square-wave-shaped 1D polyrotaxane (2): A solution of **PR44**(NO$_3$)$_2$ (0.002 M) in water was layered over an aqueous solution of Co(NO$_3$)$_2$ (0.2 M) in a diffusion tube to produce red, X-ray quality crystals of **2** after a week (18 mg, 25 %). m.p. > 310 °C (decomposed); elemental analysis calcd (%) for $CoC_{52}H_{60}N_{32}O_{24} \cdot 13H_2O$: C 35.20, H 4.66, N 25.26; found: C 35.45, H 4.98, N 25.22.

Ni square-wave-shaped 1D polyrotaxane (3): Green, X-ray quality crystals of **3** were prepared by the same procedure as that for **2** except that Ni(NO$_3$)$_2$ instead of Co(NO$_3$)$_2$ was used (23 mg, 30 %). m.p. > 240 °C (decomposed); elemental analysis calcd (%) for $NiC_{52}H_{60}N_{32}O_{24} \cdot 22H_2O$: C 31.67, H 5.31, N 22.73; found: C 31.61, H 5.20, N 22.91.

Co zigzag-shaped 1D polyrotaxane (4): A solution of **PR43** (0.002 M) in water was layered over the aqueous solution of Co(NO$_3$)$_2$ (0.2 M) in a diffusion tube to produce red, X-ray quality crystals of **4** after a week (32 mg, 40 %). m.p. > 255 °C (decomposed); elemental analysis calcd (%) for $CoC_{52}H_{60}N_{32}O_{24} \cdot 16H_2O$: C 33.50, H 4.97, N 24.04; found: C 33.63, H 5.19, N 23.95.

Ni zigzag-shaped 1D polyrotaxane (5): A solution of **PR43** (0.002 M) in water was layered over the aqueous solution of Ni(NO$_3$)$_2$ (0.2 M) in a diffusion tube to produce green, X-ray quality crystals of **5** after a week (25 mg, 32 %). m.p. > 270 °C (decomposed); elemental analysis calcd (%) for $NiC_{52}H_{60}N_{32}O_{24} \cdot 17H_2O$: C 33.18, H 5.03, N 23.81; found: C 33.02, H 5.03, N 23.54.

Ag linear-shaped polyrotaxane (6): A solution of Ag(CH$_3$(C$_6$H$_4$)SO$_3$) (0.2 M) in methanol was layered over an aqueous solution of **PR44**(CH$_3$(C$_6$H$_4$)SO$_3$)$_2$ (0.002 M) in a diffusion tube to produce X-ray quality crystals of **6** after a week (41 mg, 29 %); elemental analysis calcd (%) for $AgC_{73}H_{81}N_{28}O_{21}S_3 \cdot 9H_2O$: C 42.73, H 4.86, N 19.11, S 4.69; found: C 43.10, H 5.32, N 18.73, S 5.10.

Ag helical 1D polyrotaxane (7): A solution of AgNO$_3$ (0.2 M) in methanol was layered over an aqueous solution of **PR53**(NO$_3$)$_2$ (0.002 M) in a diffusion tube to produce colorless, X-ray quality crystals of **7** after a week (36 mg, 21 %). m.p. > 215 °C (decomposed); elemental analysis calcd (%) for $AgC_{53}H_{62}N_{31}O_{21} \cdot 12H_2O$: C 35.50, H 4.83, N 24.21; found: C 35.62, H 4.51, N 24.12.

Cd helical 1D polyrotaxane (8): A solution of **PR53**(NO$_3$)$_2$ (0.01 M) in water was layered over an aqueous solution of Cd(NO$_3$)$_2$ (0.2 M) in a diffusion tube to produce colorless, X-ray quality crystals of **8** after a week (23 mg, 15 %). m.p. > 240 °C (decomposed); elemental analysis calcd (%) for $CdC_{53}H_{62}N_{31}O_{21} \cdot 9H_2O$: C 34.86, H 4.39, N 25.01; found: C 35.07, H 4.55, N 25.40.

Ag polycatenated 2D polyrotaxane net (9): A solution of AgNO$_3$ (0.2 M) in methanol was layered over an aqueous solution of **PR44**(NO$_3$)$_2$ (0.002 M) in a diffusion tube to produce colorless, plate-like, X-ray quality crystals of **9** after a week (56 mg, 37 %). m.p. > 160 °C (decomposed); elemental analysis calcd (%) for $AgC_{78}H_{90}N_{46}O_{30} \cdot 10H_2O$: C 38.39, H 4.54, N 26.40; found: C 38.62, H 4.51, N 26.21.

Ag square-grid 2D polyrotaxane (10): A solution of Ag(CF$_3$SO$_3$) (0.2 M) in methanol was layered over an aqueous solution of **PR43**(CF$_3$SO$_3$)$_2$ (0.002 M) in a diffusion tube to produce colorless, block, X-ray quality crystals of **10** after a week (27 mg, 29 %). m.p. > 260 °C (decomposed); elemental analysis calcd (%) for $AgC_{109}H_{120}N_{56}O_{39}S_5F_{15} \cdot 20H_2O$: C 34.89, H 4.40, N 20.91; found: C 34.78, H 4.31, N 21.33.

Cu square-grid 2D polyrotaxane (11): A solution of **PR43**(NO$_3$)$_2$ (0.002 M) in water was layered over an aqueous solution of Cu(NO$_3$)$_2$ (0.2 M) in a diffusion tube to produce blue, X-ray quality crystals of **11** after a week (15 mg, 20 %). m.p. > 210 °C (decomposed); elemental analysis calcd (%) for $CuC_{104}H_{120}N_{62}O_{42} \cdot 23.5H_2O$: C 36.77, H 4.95, N 25.58; found: C 36.44, H 4.59, N 25.89.

X-ray crystal structure determination: The crystal data for all the polyrotaxanes are listed in Table S1 (Supporting information). The data collection was performed on an Enraf-Nonius CAD diffractometer at 293(2) K equipped with a graphite-monochromated Mo$_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation source for **1**, **3**, **6**, **7**, and **9**. Cell parameters and an orientation matrix for data collection were obtained from a least-squares refinement by using the setting angles of 25 reflections. The intensities of three standard reflections, monitored every 3 h of X-ray exposure during the data collection, showed no systematic changes. For other compounds, data collection was performed with a Bruker SMART 1000 CCD-based diffractometer at 170(2) K with Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The crystallographic data and additional details of data collection and refinement are summarized in Table S1. Data reduction was performed by using the SAINT software, which corrected for Lp (Lorentz and polarization effects) and decay. Absorption corrections were applied by using SADABS supplied by G. Sheldrick. The structure was solved by direct methods by using SHELXS in Bruker SHELXTL (version 5.1). All non-hydrogen atoms were refined anisotropically, and all hydrogens were calculated by geometrical methods and refined by using a riding model. The positions of hydrogen atoms, bonded to carbon atoms, were idealized

(d(C–H) = 0.96 Å) with their thermal parameters of 1.2 times those of attached atoms. These hydrogen atoms were refined by riding them on the attached carbon atoms. Final cycles of refinement on F^2 converged to the residuals listed in Table S1.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. TUBVUH (**1**), CCDC-167483 (**2**), CCDC-167484 (**3**), CCDC-167638 (**4**), CCDC-167639 (**5**), REKHOE (**6**), PAPQUS (**7**), CCDC-167485 (**8**), REKHIY (**9**), CCDC-167486 (**10**), and CCDC-167487 (**11**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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