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Self-Assembly of Interlocked Structures: Rotaxanes, Polyrotaxanes and Molecular Necklaces

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Our recent work on construction of interlocked structures such as rotaxanes, polyrotaxanes and molecular necklaces using the principles of self assembly and coordination chemistry is described. In the synthesis of these structures, the barrel-shape molecule cucurbituril is used as a molecular "bead" and metal ions or metal complexes are used as "glue" or "angle connectors". Judicious choice of metal ions, counter ions and "strings" is important in order to construct the desired supramolecular structures.

Keywords: self assembly; interlocked structures; metal ions; supramolecular chemistry

INTRODUCTION

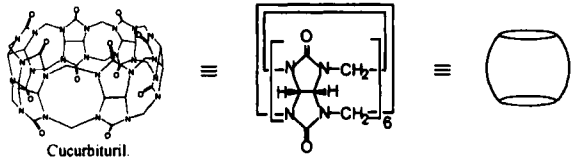
Interlocked structures such as catenanes, rotaxanes and knots have intrigued synthetic chemists not only because of their beauty but also because of their potential applications in materials for molecular electronics.[1] The simplest catenane, [2]catenane consists of two mechanically interlocked rings (Figure 1). In a [2]rotaxane, a circular component is threaded on a linear component having two bulky stoppers at the ends, which prevent dethreading. A molecular necklace (MN) is a catenane in which a number of small rings are threaded onto a large ring. It is a topological isomer of a linear catenane where rings are interlocked with each other one by one in a linear fashion.

FIGURE 1 Catenanes, rotaxanes, and molcular necklaces.

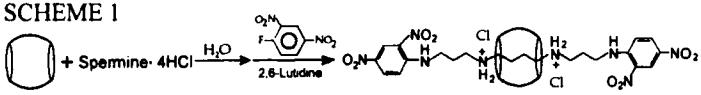
In this account, we describe our recent work on construction of interlocked structures using the barrel-shape molecule cucurbituril as a molecular "bead", and metal ions or complexes as "glue" or "angle connectors".

SIMPLE ROTAXANES

Cucurbituril is a macrocyclic cavitand with an internal cavity of ~5.5 Å diameter which is accessible from the exterior by two carbonyl laced portal of ~4 Å diameter.[2,3] It forms very stable 1:1 host-guest complexes with diaminoalkanes. Its highly symmetric structure and capability of holding guest molecules make cucurbituril a useful candidate for a molecular "bead" in synthesis of interlocked structures, particularly rotaxanes.



SCHEME 1



1

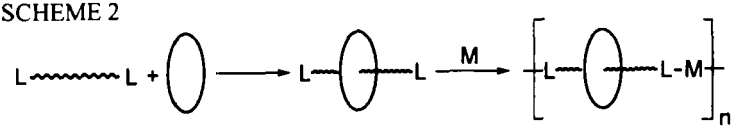
The first simple rotaxane containing cucurbituril as a molecular bead was synthesized by threading cucurbituril with spermine to form a pseudorotaxane and then attaching dinitrophenyl groups to both ends of the spermine unit to prevent dethreading (Scheme 1).[4]

POLYROTAXANES

One-Dimensional Polyrotaxanes

Our synthetic strategy to polyrotaxanes is (1) to thread a molecular "bead" with a short "string" to make a pseudorotaxane, and then (2) to link the pseudorotaxanes by using transition metal ions as "glue" to construct a polyrotaxane on which molecular "beads" are threaded, as shown in Scheme 2.[5]

SCHEME 2



The 1D polyrotaxane **2** was obtained when a solution of $Cu(NO_3)_2$ was allowed to diffuse slowly into a solution of pseudorotaxane $\mathbf{PR44}^{2+}$ (Scheme 3).[5]

SCHEME 3

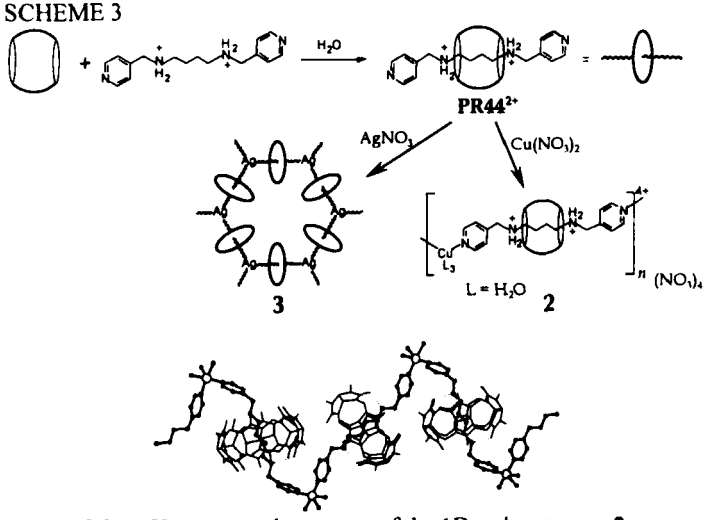


FIGURE 2 X-ray crystal structure of the 1D-polyrotaxane **2**.

The X-ray crystal structure of **2** (Figure 2) reveals cucurbituril "beads"

threaded on the coordination polymer, the chain of which is composed of alternating copper ions and **PR44**$^{2+}$. The 1D polyrotaxane adopts a zigzag structure (Figure 2).

Two-Dimentional Polyrotaxanes

When silver nitrate is reacted with **PR44**$^{2+}$ the same procedure yields a novel 2D polyrotaxane **3**. The X-ray crystal structure of **3** reveals cucurbituril "beads" threaded onto a 2D coordination polymer network (Figure 3).[6]

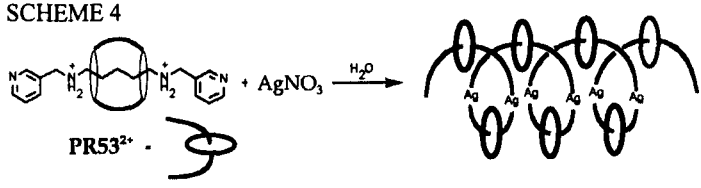
The 2D network consists of large edge-sharing chair-shaped hexagons with a Ag(I) ion at each corner and a molecule of **PR44**$^{2+}$ at each edge connecting two Ag(I) ions. The edge of the hexagon is 20.9 Å and the separation of the opposite corners is 38.0 Å.

FIGURE 3 X-ray structure of 2D-polyrotaxane **3**. Each corner of the hexangons is occupied by Ag^+.

Helical One-Dimensional Polyrotaxane

The reaction of **PR53**$(NO_3)_2$ with $AgNO_3$ yielded the first helical polyrotaxane **4** (Scheme 4).[7] In the structure of **4**, cucurbituril "beads" are threaded on a helical 1D coordination polymer. The helix is extended along

SCHEME 4

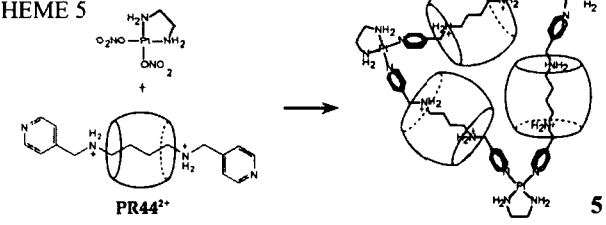


the *b* axis of the crystal with a pitch of 17.9 Å. In each helix, two $\mathbf{PR53}^{2+}$ and two silver ions constitute one turn.

MOLECULAR NECKLACES

Our strategy to the construction of molecular necklaces is similar to that for polyrotaxanes. In the synthesis of molecular necklaces, however, we use a metal complex with *cis* vacant coordination sites, instead of simple metal salt, as "glue" or an "angle connector".

SCHEME 5



5

Reaction of $\mathbf{PR44}(NO_3)_2$ with $Pt(en)(NO_3)_2$ (en = ethylenediamine) in refluxing water for 24 h prod **5** (Scheme 5) in near quantitative yield (by NMR).[8]

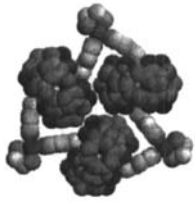


FIGURE 4 The minimal molecular necklace [4]MN (**5**).

The X-ray crystal structure of **5** (Figure 4) reveals that three cucurbituril molecular "beads" are threaded on a molecular triangle. Each corner of the triangle is occupied by a Pt(en) moiety and each side by a sigmoidal shaped pseudorotaxane unit $\mathbf{PR44}^{2+}$, which links the two Pt moieties by coordination

at its terminal pyridyl groups. The Pt···Pt separation is 19.476(1) Å.

CONCLUSION

In this account, we describe our efforts to construct interlocked structures such as rotaxanes, polyrotaxanes and molecular necklaces incorporating cucurbituril as a molecular bead by utilizing the principles of self-assembly and coordination chemistry. The examples given here demonstrate the efficiency and control in the self-assembly of highly organized supramolecular species. Such a highly efficient synthesis of a topologically intriguing supermolecule may provide insights into construction of nanoscale particles with well-defined structures and functions.

Acknowledgment

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