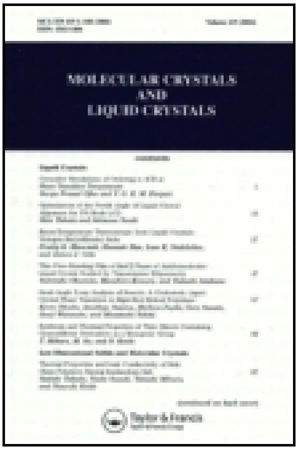

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Self-Assembly of Interlocked Structures and Open Framework Materials using Coordination Bonds

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Self-Assembly of Interlocked Structures and Open Framework Materials using Coordination Bonds

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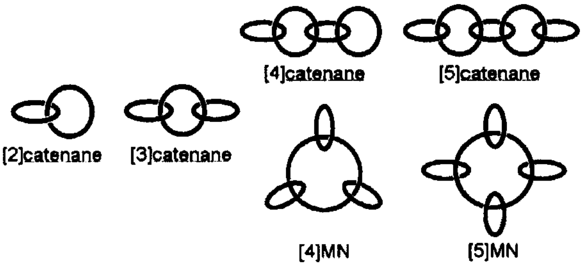
Syntheses of molecular necklaces and open framework materials using coordiantion bonds are described. In the synthesis of molecular necklaces, the barrel-shape molecule cucurbituril is used as a molecular "bead" and metal ions or metal complexes are used as "glue" or "angle connectors". Two different approaches were taken. In one approach, linear pseudorotaxanes react with Pt(en)$(NO_3)_2$ (en = ethylenediamine) to produce [4]MNs and [5]MNs. In the other approach, a '2 + 2' approach, preorganized, L-shaped pseudorotaxanes containing two molecular "beads" react with a metal ion (or a metal complex with *cis* vacant coordination sites) to form [5]MNs. Rubidium and cucurbituril form a one-dimensional coordination polymer in the solid state, in which cucurbituril molecules stack atop one another through coordination of their carbonyl groups to the rubidium ions in between. The coordination polymer chains are arranged in such a way as to produce a honeycomb structure with large linear hexagonal channels parallel to the polymer chains.

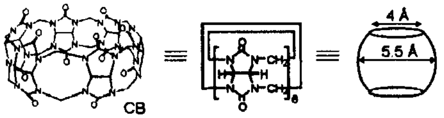
Keywords: self assembly; interlocked structures; open framework materials; metal ions; supramolecular chemistry

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.[1] We have been interested in the efficient synthesis of catenanes and rotaxanes using principles of self assembly and coordination chemistry.[2-4] Our earlier work in this area has been summarized in recent review articles.[5,6] More recently, we have been focusing our efforts on the construction of molecular necklaces (MN), in which a number of molecular "bead" are threaded on a large circular molecular "string".[3-4] They are topological isomers of classical, linear catenanes where rings are interlocked with each other one by one in a linear fashion.



One of the key building blocks in our chemistry is cucurbituril. Cucurbituril (CB)[7] is a macrocyclic cavitand with D_{6h} symmetry, having a hollow core of ~5.5 Å diameter and two identical portals surrounded by carbonyl groups. It forms very stable 1:1 host-guest complexes with diaminoalkanes such as diaminobutane and diaminopentane. Its highly symmetric structure and capability of holding guest molecules make CB a useful candidate for a molecular "bead" in synthesis of interlocked structures such as rotaxanes and molecular necklaces. The carbonyl groups at the portal also provide metal-biding sites. We have found that alkali metal ions strongly bind to or at least interact with the carbonyl groups.[8] Such strong interactions make CB soluble in neural aqueous solutions containing alkali metal ions. Furthermore, the rigid and highly symmetric structure and metal binding capability make it a useful building block for metal-organic coordination polymers.



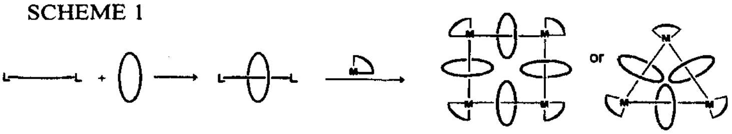
In the first part of this account, we describe our recent work on construction of molecular necklaces using CB as a molecular "bead", and metal ions or complexes as "glue" or "angle connectors". In the second part, we present an open-framework structure self-assembled form CB and Rb^+ ion.

MOLECULEAR NECKLACES

[4]MN and [5]MN

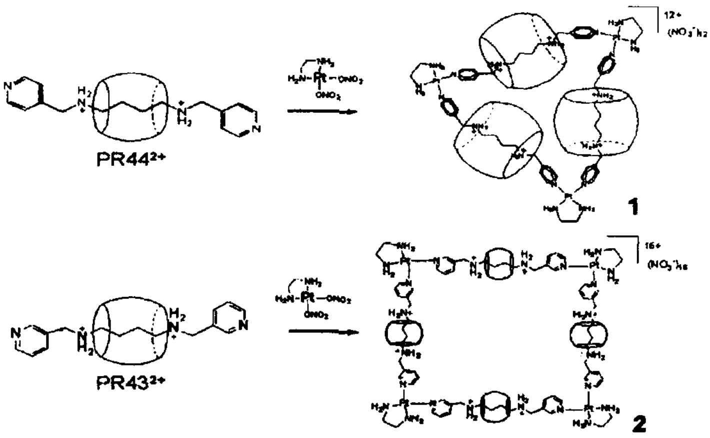
Our strategy to the construction of molecular necklaces is (1) to thread a molecular "bead" with a short "string" to make a pseudorotaxane, and then (2) to link the pseudorotaxanes by using a metal complex with *cis* vacant coordination sites, instead of simple metal salt, as "glue" or an "angle connector", as shown in Scheme 1.[3]

SCHEME 1



Reaction of **PR44**$(NO_3)_2$ with $Pt(en)(NO_3)_2$ (en = ethylenediamine) in refluxing water for 24 h produces **1** (Scheme 2) in near quantitative yield (by NMR).[3]

SCHEME 2



The X-ray crystal structure of **1** (Figure 1) 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 **PR44**$^{2+}$, which links the two Pt moieties by coordination at its terminal pyridyl groups. The Pt···Pt separation is 19.476(1) Å.

You can also make square shaped molecular necklace using the same approach. If we change the position of nitrogen atom on the pyridyl group from 4 to 3 (**PR43**$^{2+}$), the (major) product is a [5]MN (**2**) with a square shape (Scheme 2). The structure of **2** has been confirmed by X-ray crystallography. In **2**, four molecular beads are threaded on a square framework whose corners are occupied by the Pt(en) units (Figure 1). The average Pt···Pt distance is ~17.7 Å. Although it looks like a planar structure in this view but actually it has a butterfly structure. The distance between the two wingtips is ~22 Å.

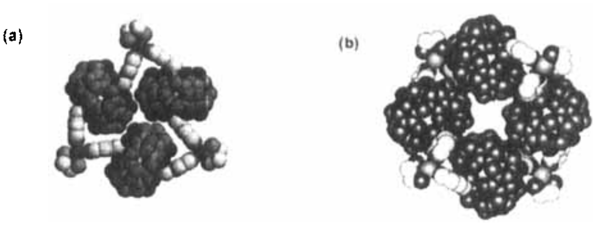
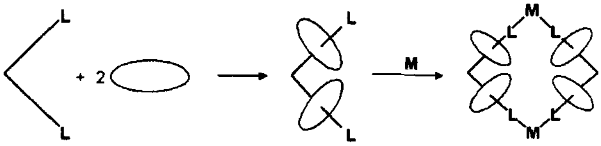


FIGURE 1 X-ray Crystal Structure of (a) [4]MN (**1**) and (b) [5]MN (**2**).

Molecular necklace: a 2 + 2 approach

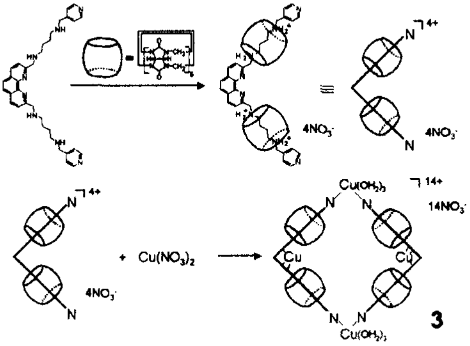
As described above, this approach generates both triangular necklaces and square necklaces. We therefore decided to take another approach to square necklaces with 4 moleuclar beads which we now call a 2 + 2 approach.[4] In this appraoch, we use an L-shaped preorganized pseudorotaxane in which two molecular beads are already in place, and using metal ion as glue we can construct the molecular necklace [5]MN containing 4 molecular beads (Scheme 3).

SCHEME 3



The L-shaped string we designed has a phenanthroline core with two arms. Each arm contains a diaminobutane unit and a pyridyl unit. We first threaded 2 equiv of CB with the L-shaped 'string' to form a pseudorotane. When we allowed the resulting pseudorotaxane to react with $Cu(NO_3)_2$ it formed a molecular necklace [5]MN (**3**), as we expected (Scheme 4).

SCHEME 4



The X-ray crystal structure of **3** (Figure 2) reveals that two copper ions (Cu(1) and Cu(3)) link the two L-shaped pseudorotaxanes to form a molecular necklace. One interesting thing to note is that 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 cucurbituril. 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 ~19.3 x 17.0 Å.

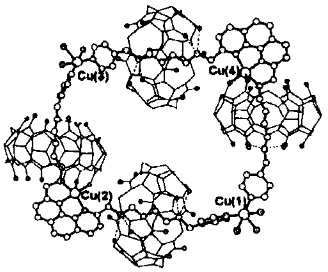
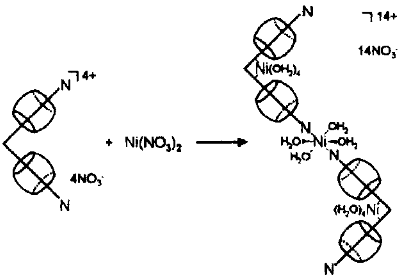


FIGURE 2 Molecular necklace [5]MN (**3**) from the '2+2' approach.

What if we use other transition metal ions? All other transition metal salts we tried so far (such as Ni^{2+}, Zn^{2+}, Cd^{2+} and Ag^{+}) did not yield molecular necklaces when they reacted with the L-shaped pseudorotaxane. For instance, reaction between $Ni(NO_3)_2$ and the L-shaped pseudorotaxane results in a [5]rotaxane (or [5]pseudorotaxane) (Scheme 5). In this structure, a $[Ni(OH_2)_4]^{2+}$ unit links two molecules of the L-shaped pseudorotaxane through the coordination of their pyridyl groups at the axial positions of the Ni ion with an octahedral geometry. The *trans* coordination of the two pyridyl groups to the metal center results in the [5](pseudo)rotaxane with a sigmoidal shape rather than a [5]MN.

SCHEME 5



OPEN-FRMAEWORK STRUCTURE

Metal-organic solids containing large pores or channels with controlled sizes, shapes and chemical environments have drawn much attention in recent years because they may have applications in separation, catalysis and optoelectronics. We recently reported a crystal structure that demonstrates a novel way to construct metal-organic open-framework materials with large hexagonal channels using a modular approach.[9]

Diffusion of methanol into an aqueous solution containing CB and Rb_2SO_4 produces needle-shaped crystals of **4**. The X-ray structure of **4** shows a 1D coordination polymer in which CB molecules stack atop one another with Rb ions in between (Figure 3). Two Rb ions, being bridged by two hydroxide ions, hold two CB molecules. A weakly coordinating water molecule is bound to each of the Rb ions. A three-fold axis parallel to the *c* axis passes through the center of the coordination polymer. The $Rb_2(\mu\text{-}OH)_2(\mu\text{-}CH_3OH)_2(OH_2)_2$ unit is disordered over three sites due to the crystallographically required three-fold symmetry.

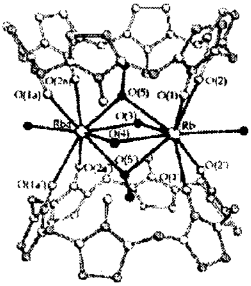


FIGURE 3 Coordination geometry around the Rb ions in **4**.

The 1D polymer has a self-complementary curvature with alternating bumps and hollows. The packing of the 1D coordination polymer reveals that the chain at the center is offset by one half of the repeating unit along the *c* axis with respect to the neighboringchains so that the 'bumps' of the chain fit into 'hollows' of the neighboring chains (Figure 4).

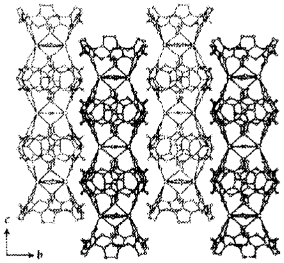


FIGURE 4 Packing of the 1-D coordination polymer in **4**.

The most interesting feature of the crystal structure is that the coordination polymer chains are arranged in such a way as to produce a honeycomb structure with linear, hexagonal channels extended along the *c* axis (Figure 5). The mean diameter of the channels is ~10Å and the void volume of the channels is estimated to be ~23% of the total volume. The channels are filled with water molecules. However, taken out of the mother liquor, the crystals quickly lose solvent and crystallinity.

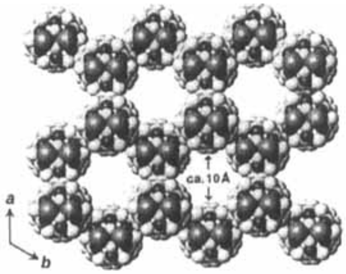
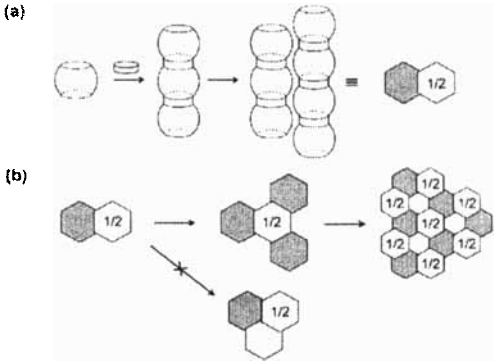


FIGURE 5 Honeycomb structure of **4**.

This is not the first structure to show such large hexagonal channel structures. However, the way that the present structure is built is unique. Here, cucurbituril, a barrel-shaped molecule with D_{6h} symmetry is used as a bulky, linear, bifunctional building block. The 'barrels' are stacked up with metal ion 'cement' to form a rigid column with alternating bumps and hollows. In the crystal, the next column is offset by one-half repeating unit along the column direction to maximize the interactions between the two columns (with a self-complementary curvature by fitting the bumps of one column into hollows of the other). To achieve a close packing you may want to place the third column at the indentation between the two touching columns. However, it is not possible because the third column can not have the one-half unit offset relationship with *both* the first and the second columns. Instead, the one half unit offset relationship between the neighboring columns and the three-fold cross-sectional symmetry of the column encourage them to take a Y-shaped arrangement of columns, which eventually turns into the hexagonal open-framework structure (Scheme 6). This structure demonstrates the shape and symmetry of a building block can induce a specific crystal structure.

SCHEME 6



CONCLUSION

In this account, we describe our efforts to construct molecular necklaces incorporating CB as a molecular bead by utilizing the principles of self-assembly and coordination chemistry. We have demonstrated that such topologically intriguing supramolecular species can be readily assembled from carefully designed organic building blocks and properly chosen metal ions or metal complexes. We also present a crystal structure showing that CB can be used as a building block to construct metal-organic open-framework material. This novel structure and building principle may provide further insight into designing new porous materials as well as other supramolecular architectures.

Acknowledgment

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