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Selectivity Algorithm for the Formation of Two Cryptand/Paraquat Catenanes

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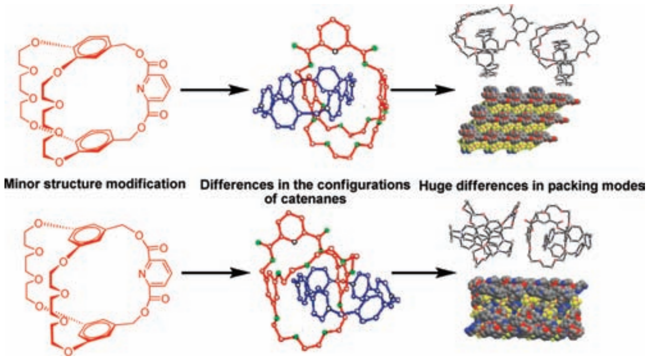
ABSTRACT



Two [2]catenanes based on two different cryptand hosts, a dibenzo-24-crown-8-based cryptand and a bis(*m*-phenylene)-26-crown-8-based cryptand, have been synthesized and characterized. These two cryptand hosts only have a minor difference in chemical structure. However, this minor structural difference leads to big differences in the configurations and packing modes of the resulting catenanes. In addition, from the crystal structures of the two catenanes, we found that the cyclophane guest seems to have a selectivity algorithm and chooses the larger-size rings to go through and interlock with.

Chemists have been intrigued with the extent to which chemical self-assembly can be explored.[1] Self-assembly is a process in which components spontaneously form ordered aggregates.[2] The studies of self-assembly are booming nowadays in both biological and chemical systems.[2] Actually, the formation of single crystals from solution is a typical and vivid example of chemical self-assembly. Single molecules in solution choose their own optimal way to assemble and precipitate into solid materials driven by hydrogen bonding, hydrophobic/hydrophilic, $\pi-\pi$ stacking, and/or other weak interactions.[3] Therefore, by the study of the information stored in the chemical compounds' single crystals, not only their structural features can be known but also their self-assembly behavior can be understood. Great progress has been achieved in exploiting different packing modes influenced by the minor changes in chemical structures. On this basis, by appropriate design, some organic crystals have exhibited applications in many fields.[4]

On the other hand, the formation of many self-assembly systems relies on molecular recognition between hosts and guests. A lot of supramolecular units such as pseudorotaxanes, rotaxanes, and catenanes have been successfully constructed by template-directed protocols.[5] In recent years,

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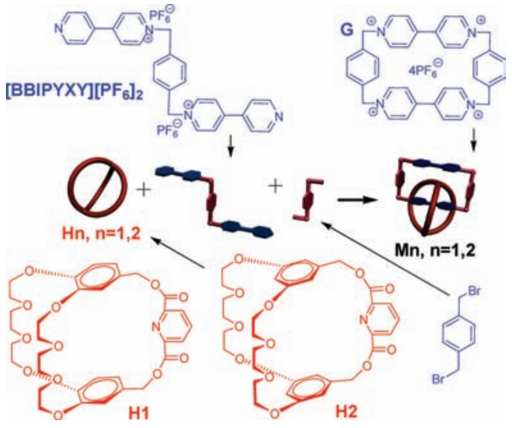
using these supramolecular units, especially the ones based on cyclodextrins[6] and calixarenes[7] and interlocked structures,[8] as building blocks in crystal engineering has attracted increasing interest not only because of their unique potential applications but also due to their exemplary role of self-assembly. Here we report two new [2]catenanes based on two cryptand hosts, which have only a subtle structural difference. It was found that this minor structural difference influences the self-assembly process at two levels: (1) the process of forming [2]catenanes and (2) the process of assembly into 3D structure (i.e., forming single crystals).

Cryptands **H1** and **H2**[9] are derivatives of dibenzo-24-crown-8 (**DB24C8**) and bis(*m*-phenylene)-26-crown-8 (**BMP26C8**), respectively. They are different only by the positions of the ether chains on the phenyl rings. Both of them have been proven to be able to bind paraquat derivatives (*N*,*N*′-dialkyl-4,4′-bipyridinium salts) strongly and used in the efficient preparation of pseudorotaxanes and rotaxanes.[10,11]

[2]Catenanes **M1** and **M2** were synthesized in 30.6% and 24.7% yields, respectively, based on the π-donor/π-acceptor interaction of the cryptand **H1** or **H2** with paraquat derivatives (Scheme 1).[12]

Scheme 1. Syntheses of Two Cryptand/Paraquat [2]Catenanes



Both of the [2]catenanes provided single crystals suitable for X-ray analysis when grown by vapor diffusion of *i*-Pr_2O into their MeCN solutions. As shown in Figure 1, the host and guest components of **M1** have strong and compact π-donor/π-acceptor interactions. The two aromatic rings of the cryptand **H1** are nearly parallel (torsion angle 11.5°) with a centroid−centroid distance of 6.793 Å. The two electron-deficient bipyridinium units in the cyclophane also show good coplanarity: the torsion angle of the two pyridinium rings inside the cryptand cavity is 12.3°, and the corresponding value is 12.8° for the two outside pyridinium rings. The interplanar separations between the phenyl rings on the cryptand and their accompanying bipyridinium units are all around 3.4−3.5 Å. These indicate good π-donor/π-acceptor interactions between the cryptand **H1** and the cyclophane **G**. Six hydrogen bonds (**A**−**F** in Figure 1a) further stabilize the interlocked structure. Specially, a β-pyridinium hydrogen of the cyclophane **G** is hydrogen-bonded to the pyridine nitrogen atom of **H1**. Actually, the design intention of introducing a pyridine nitogen atom onto the third chains of cryptands is to introduce a hydrogen bonding acceptor for β-pyridinium hydrogens, which should increase host−guest binding between cryptand hosts and paraquat derivatives.[10,11] Furthermore, the inside phenyl ring of **H1** is also in an optimal position, which brings two [C−H···π] interactions with the *p*-xylyl spacers of the tetracationic cyclophane **G**. In the interlocked structure of **M1**, good integration of three kinds of weak noncovalent interactions was achieved.

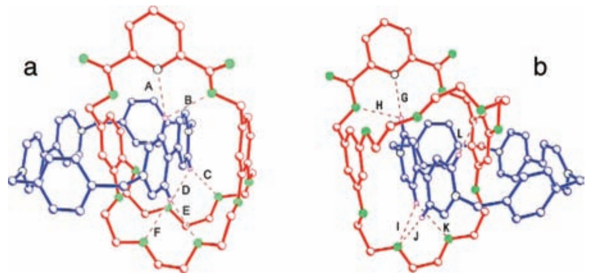


Figure 1. Ball−stick views of the X-ray crystal structures of [2]catenanes **M1** (a) and **M2** (b). **H1** and **H2** are red, **G** is blue, hydrogens are magenta, oxygens are green, and nitrogens are black. PF_6^- counterions, other solvent molecules, and hydrogens except the ones involved in hydrogen bonding were omitted for clarity. Hydrogen bond parameters: H···O distance (Å), C−H···O(N) angle (deg), C···O(N) distance (Å) **A**, 2.43, 145, 3.231; **B**, 2.54, 125, 3.167; **C**, 2.27, 140, 3.040; **D**, 2.59, 135, 3.316; **E**, 2.55, 139, 3.310; **F**, 2.55, 122, 3.135; **G**, 2.34, 166, 3.250; **H**, 2.47, 110, 2.929; **I**, 2.62, 146, 3.265; **J**, 2.47, 148, 3.543; **K**, 2.52, 135, 3.345; **L**, 2.38, 156, 3.255.

In the crystal packing structure of **M1**, **M1** molecules form chains, linear supramolecular polycatenanes (Figure 2a), driven by hydrogen bonding (a pyridyl 4-hydrogen interacts

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(9) The synthetic route to **H2** is shown in Scheme S1 (Supporting Information). **H1** can also be synthesized by a similar route, employing methyl 3,4-dihydroxybenzoate as starting material.

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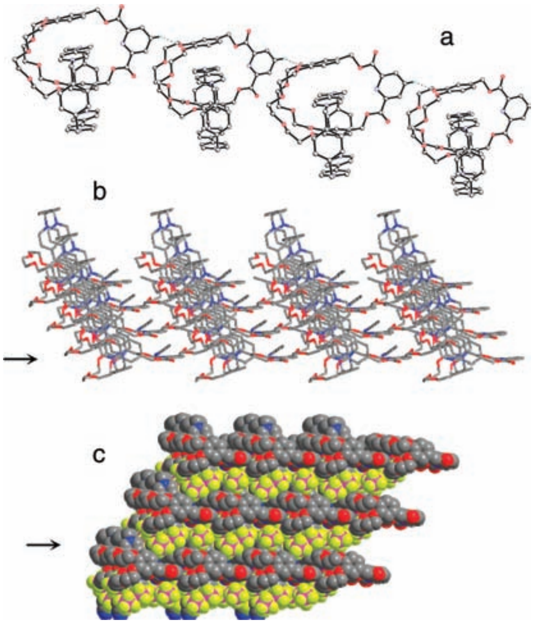

Figure 2. Packing representation of **M1**'s self-assembly to form the crystalline solid. (a) **M1** molecules form a supramolecular main-chain polycatenane-like structure driven by hydrogen bonding. (b) The polycatenane chains grow to a "planar" structure driven by π-donor/π-acceptor interactions. (c) The "planar" structures assemble to a 3D structure driven by the hydrogen bonding interactions with the help of numerous PF_6^- anions.

with an ether oxygen atom on the neighboring cryptand). Then, these steplike chains stacked to form "planes" driven by continuous π-donor/π-acceptor interactions between the outside pyridinium and phenyl rings (Figure 2b). This is a common characteristic of reported donor/acceptor [2]catenanes.[12] At last, numerous PF_6 anions occupy voids in the planes through hydrogen bonds (C−H•••F) to form an orderly 3D structure (Figure 2c). Therefore, there are at least two kinds of weak interactions involved in the self-assembly process of single-crystal formation from **M1**.

To our surprise, in the crystal structure of **M2**, the cyclophane **G** threads through the two ethylene glycol chains on cryptand **H2** instead of through the other opening. Cyclophane **G** is interlocked with the bis(*m*-phenylene)-26-crown-8, and the 2,6-pyridyl linkage reinforces the interlocking. In fact, this kind of cryptand/paraquat [2]catenane, in which the guest ring is interlocked with the cryptand molecular cage, can be looked at as the guest ring interlocked by two of the three rings of the cryptand cage at the same time. If the three rings of the cryptand cage have different sizes, there will be some isomers when the interlocked pattern is different. Therefore, there are three potential isomers for [2]catenane **M1** because of the different sizes of the three rings in **H1** but only two potential isomers for **M2** because of its higher symmetry. However, it seems that the guest ring has a selectivity algorithm and chooses the two larger-size rings to interlock with. In **M1**, the cyclophane ring chose the larger rings, the 27-membered and 25-membered rings. In **M2**, the cyclophane ring also chose the larger rings, the 26-membered and 25-membered rings. The size effect and steric hindrance effect were believed to be the main reasons that introduced this interesting phenomenon. For example, in **M1**, the kinetic effect may cause the bipyridinium salt a slow threading of the smallest ring (24-membered ring). However, this smallest ring can not accommodate the bipyridinium unit, imposing strain on the molecule. Ultimately, they find the most "comfortable" place with the help of all kinds of weak interactions.

In the crystal structure of [2]catenane **M2**, the two aromatic rings of cryptand **H2** are nearly parallel (torsion angle 7.9°); the centroid−centroid distance is 6.793 Å. As the π-electron-accepting group, the bipyridinium units inside the cryptand have good coplanarity with a torsion angle of 12.9°. The interplanar separations between this π-acceptor unit and the accompanying π-donor units (phenyl rings on cryptand **H2**) are 3.217 Å (with the phenyl ring inside the cyclophane cavity) and 3.378 Å (with the outside one). These parameters indicate strong donor/acceptor interactions. Six hydrogen bonds further stabilize the interlocked structure (**G**−**L** in Figure 1b). Just like the case of **M1** (Figure 1a), a β-pyridinium hydrogen of the inside bipyridinium units forms two hydrogen bonds with the pyridine nitrogen atom and an ester oxygen atom on the third chain of the cryptand host in the crystal structure of **M2** (Figure 1b). Furthermore, two strong [C−H•••π] interactions can also be found between the two hydrogens on the inside phenyl ring of the cryptand host and the two *p*-xylyl spacers of the tetracationic cyclophane **G** in **M2** (Figure 1b).

The torsion angle of the bipyridinium rings outside the cryptand (**H2**) cavity is 35.0°; they show poor coplanarity. Therefore, in the packing mode, **M2** molecules cannot grow by continuous π-donor/π-acceptor stacking. Alternately, they pack by the $\pi-\pi$ stacking between the aromatic rings at four directions in one plane (a phenyl ring of the cyclophane stacks with a phenyl ring on the cryptand of the neighboring [2]catenane, and then one pyridinium ring of the uncovered bipyridinium unit stacks with a phenyl ring on the cyclophane of the third [2]catenane molecule). In this way, they grow to the plane-like structure. It is worth noting that some PF_6 anions and solvent molecules help to form the "plane" by H-bonding interactions. Finally, the planes assemble to the 3D structure by H-bonding interactions with the help of numerous PF_6^- and solvent molecules (Figure 3).

M1 and **M2** were further characterized by ^1H NMR and ^{13}C NMR spectroscopy, low- and high-resolution electrospray ionization mass spectrometry, and UV−vis spectroscopy (see Supporting Information). After the formation of the [2]catenanes, the signals of protons on both the cryptands and cyclophanes split severely, which is a signature of the reduced symmetry of the interlocked structures. However, unlike the broad peaks of previously reported catenanes prepared from bis(*m*-phenylene)-32-crown-10-based cryptands,[12b,c] the signals of protons of **M1** and **M2** were quite sharp. It implies that in the solution of **M1** or **M2** the dynamic processes of the interlocked components are slower. From their crystal structures, this phenomenon could be understandable as various noncovalent interactions between

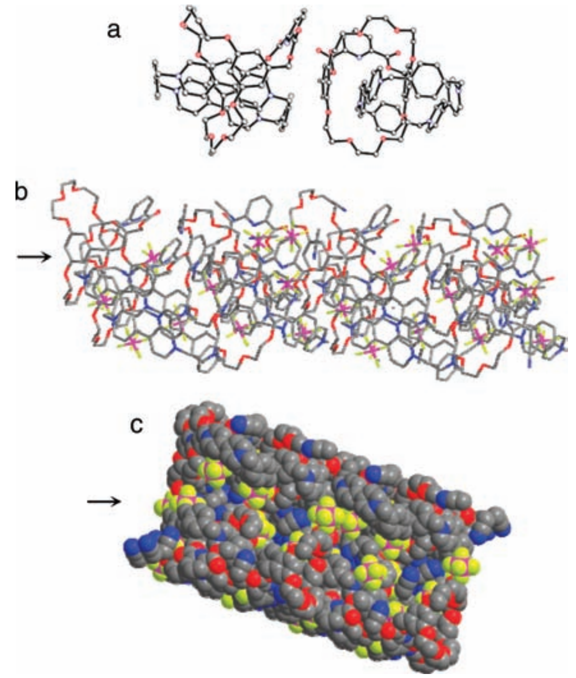

Figure 3. Packing representation of **M2**'s self-assembly to form the crystalline solid. (a) **M2** molecules grow by alternating $\pi-\pi$ stacking interactions to form a "line" structure. (b) The "lines" then grow to the "planar" structure by $\pi-\pi$ stacking interactions and H-bonding interactions. (c) The "planar" structures assemble to the 3D structure by H-bonding interactions with the help of numerous PF$_6^-$ and solvent molecules.

the host and guest components exist in **M1** and **M2**. These weak interactions hinder the relative movements of interlocked components, so the protons cannot exchange quickly and coalesce to broad signals. Variable-temperature NMR spectra studies[13] of **M2** showed that the activation barrier, for the pirouetting process of the ethylene glycol chains of the cryptand around the cyclophane **G**, was 19.3 kcal·mol^{-1}; this is higher than those of reported π-donor/π-acceptor catenanes.[14]

The UV−vis spectra of catenanes **M1** and **M2** showed charge-transfer absorption bands centered at 410 and 352 nm, respectively, corresponding to their red and orange colors. This difference may arise from their different modes of interlocking. In **M2**, the cyclophane threads through the crown ether part of the cryptand host, while in **M1** it taco complexes the crown ether part of the cryptand host. What's more, there are stronger π-donor/π-acceptor interactions both between the two components and in the packing mode of **M1**.

In summary, we have reported the syntheses and characterizations of two new cryptand/paraquat [2]catenanes, which only have a subtle difference in the cryptand structures. However, this minor difference led to big differences in the configurations and the packing modes of their corresponding catenanes, **M1** and **M2**. The X-ray crystal structures of the catenanes showed the guest and host components interlocked in very different ways. Furthermore, **M1** and **M2** adopted totally different ways in assembling to the 3D solid state structures. The subtle structural change in the hosts exert a "butterfly effect",[15] bringing about major changes in crystal engineering of the corresponding supramolecular systems. In addition, from the crystal structures of **M1** and **M2**, we found that the guest molecule acts very intelligently; it seems to have a selectivity algorithm and chooses the larger-size rings to interlock with. These studies provide us with more information about complicated self-assembly processes, especially the important role of noncovalent interactions. On the other hand, the donor/acceptor catenanes have exhibited huge potential as building blocks in supramolecular architectures, which are enhanced by this investigation of their packing process.

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Supporting Information Available: Synthetic procedures and characterizations of compounds, crystal data for catenanes **M1** and **M2**, and other materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) The method is called the "coalescence method". See: Sutherland, I. O. *Annu. Rep. NMR Spectrosc.* **1971**, *4*, 71–235.

(14) In typical crown ether-based donor/acceptor [2]catenanes, the activation barrier is about 12−16 kcal·mol^{-1}. See: ref 12 and: Halterman, R. L.; Martyn, D. E.; Pan, X.; Ha, D. B.; Frow, M.; Haessig, K. *Org. Lett.* **2006**, *8*, 2119–2121.

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