Host–Guest Chemistry

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Precise Facial Control in Threading Guests into a Molecular Cage and the Formation of a Turtlelike Supramolecular Complex**

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The synthesis of functional interlocked molecules continues to attract attention because these machinelike molecules^[1] have potential applicability in mesoscale molecular electronic

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devices.^[2] On the other hand, some interlocked molecules are of considerable interest not for their specific function but as synthetic challenges or for their aesthetic appeal.^[3] Although many different macrocycles, including crown ethers,^[4] cyclophanes,^[5] and cyclodextrins,^[6] have been used for the construction of a range of interlocked molecules, their molecular structures are quite similar in that they present only two open faces for guest penetration. In contrast, molecular cages^[7] containing internal voids may possess more than two openings for the threading of rodlike components. Conceptually, different [2]pseudorotaxane complexes can be generated from a cubic molecular cage^[8] by threading the guest species through its different faces, but such supramolecular systems have not been constructed previously, possibly because of synthetic difficulties (e.g., the number of macrocyclization reactions required) and the less-predictable nature of guest complexation by the host.

Recently, we demonstrated that molecular cage **1** forms an extremely stable supramolecular complex with the dimethyldiazapyrenium (DMDAP) ion (Scheme 1).^[9] Herein, we

Scheme 1. Complexation of molecular cage **1** with DMDAP.

report that two different thread components are capable of selectively penetrating **1** through its two different sets of open faces (namely, the 24-^[10] and 34-membered rings, respectively) to result in two different [2]pseudorotaxane-like complexes. The mixture of these two thread components and **1** represents a new type of molecular machinery; the two thread components alternate between their corresponding [2]pseudorotaxane complexes upon threading through the different faces of the molecular cage under the control of K^+ ions. A small tetrasubstituted macrocycle forms a unique turtle-like supramolecular complex with **1**; in this complex, the four substituent groups penetrate through the four opening faces of the molecular cage.

Previously, we demonstrated that the methyl and α -pyridinium protons of the DMDAP dication form multiple $C-H\cdots O$ hydrogen bonds with the oxygen atoms in the ethylene glycol chains of **1**. Based on this finding, we synthesized the rod-shaped salt **2** $\cdot 2PF_6$ by reaction of commercially available 1,2-bis(4-pyridyl)ethane and 1-bromopentane. We expected that the **2** $^{2+}$ ions would form [2]pseudorotaxane complexes with **1** upon the threading of two pentyl groups through the two 24-membered ring faces of **1**. This complex should be stabilized not only through $C-H\cdots O$ hydrogen bonds between the α -pyridinium protons and

the oxygen atoms of the ethylene glycol chains but also through π stacking of the two pyridinium rings with the concave aromatic surfaces of the molecular cage (Scheme 2).^[11]

Scheme 2. Complexation of molecular cage **1** with **2** $\cdot 2PF_6$.

The 1H NMR spectrum of an equimolar mixture of **1** and thread **2** $\cdot 2PF_6$ in $CDCl_3/CD_3CN$ (9:1, 3 mm) at room temperature displays significant changes in the chemical shifts of the protons of the complex relative to those of its free components (Figure 1). To confirm that the disappearance of the

Figure 1. Partial 1H NMR spectra (400 MHz, $CDCl_3/CD_3CN$ (9:1), 298 K) of a) **1**, b) an equimolar mixture of **1** and **2** $\cdot 2PF_6$ (3 mm), and c) **2** $\cdot 2PF_6$.

signals of the free species in the spectrum is due to complete complexation of the two components, rather than being the result of fast rates of exchange for the complexation/decomplexation processes under these conditions, we obtained the 1H NMR spectrum of a non-stoichiometric mixture of **1** (2 mm) and **2** $\cdot 2PF_6$ (3 mm) in $CDCl_3/CD_3CN$ (9:1). We observed two sets of signals, which integrated in a 2:1 ratio, with the weaker absorption set corresponding to the signals of free **2** $\cdot 2PF_6$ (see the Supporting Information). This result suggests that the binding stoichiometry of **1** to **2** $\cdot 2PF_6$ is 1:1 and that the exchange rates for their complexation and decomplexation are slow under these conditions. We did not observe any signals of the free species in the 1H NMR spectra upon diluting equimolar mixtures of **1** and **2** $\cdot 2PF_6$ from 1 mm

to 20 μM (see the Supporting Information), thus suggesting that the binding between **1** and **2**· 2PF_6 is extremely tight.

The spectrum of the complex displays shifts downfield of the signals of the methylene protons H_f adjacent to the pyridinium center and the α -pyridinium protons H_d of **2**· 2PF_6 (Figure 1), in conjunction with weak, but discernable, shifts in the signals of the ethylene glycol protons of **1**. These shifts suggest the existence of C–H···O hydrogen bonds in the complex.^[9,12] The considerable upfield shifts of signals for aromatic protons of both components (namely, H_a and H_e) and of the ethylene protons of **2**· 2PF_6 (H_g) imply that π stacking of the aromatic rings occurs in the complex. We grew single crystals suitable for X-ray crystallography through liquid diffusion of isopropyl ether into an equimolar solution of **1** and **2**· 2BF_4 in CH_3CN .^[13] The solid-state structure reveals a [2]pseudorotaxane-like molecular geometry for the complex $[\mathbf{1} \supset \mathbf{2}]^{2+}$ (Figure 2),^[14,15] in which the rodlike component **2**²⁺ penetrates through the two 24-membered rings of the molecular cage.

Figure 2. Ball-and-stick representations of the solid-state structure of $[\mathbf{1} \supset \mathbf{2}]^{2+}$: a) side and b) top views. C gray, O red, N blue.

The addition of four equivalents of KPF_6 to a solution of **1** and **2**· 2PF_6 in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (9:1, 3 mM) led to the appearance of characteristic absorptions of free **2**· 2PF_6 in the ^1H NMR spectrum (see the Supporting Information), which suggests that complex $[\mathbf{1} \supset \mathbf{2}]^{2+}$ dissociated through competitive binding of K^+ ions to **1**.

Previously, we demonstrated that a complex formed between **1** and two K^+ ions involved the cooperation of each triethylene glycol loop (namely, each K^+ ion binds to all of the oxygen atoms of a 24-membered-ring crown ether). In that solid-state structure, two acetonitrile solvent molecules behaved as ligands for the K^+ ions and were positioned within the molecular cage.^[9] We suspected that a suitable bidentate ligand, such as anthraquinone, would bind to the two K^+ ions, in place of the two labile acetonitrile ligands, to result in an additional supramolecular complex stabilized through ion–dipole interactions. Because each K^+ ion would be bound to

the oxygen atoms of both the anthraquinone and the 24-membered rings, the two aryl rings of the anthraquinone thread would extend out of the complex through the two 34-membered rings of the molecular cage to result in a [2]pseudorotaxane-like complex (Scheme 3).

Scheme 3. The complexation of molecular cage **1** with K^+ ions and **3**.

As indicated in Figure 3b, the signals of the protons of an equimolar mixture of **1** and anthraquinone (**3**) in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (50:1, 5 mM) at room temperature do not undergo

Figure 3. Partial ^1H NMR spectra (400 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$ (50:1), 298 K) of a) **3**, b) an equimolar (5 mM) mixture of **1** and **3**, and c) the mixture obtained after adding KPF_6 (2 equiv) to solution (b).

significant shifts relative to those of the free species. This observation suggests that the binding affinity between the two species is negligible under these conditions. After the addition of two equivalents of KPF_6 to the solution, however, the ^1H NMR spectrum displays significant shifts for the signals of both of the organic components (Figure 3c). In particular, the upfield shifts of the signals of the aromatic protons of both components imply that stacking of the aromatic rings occurs within this supramolecular complex.

We grew single crystals suitable for X-ray crystallography through liquid diffusion of isopropyl ether into a solution of **1**, KPF_6 , and **3** (1:2:1) in CH_3CN . The solid-state structure (Figure 4) reveals the expected [2]pseudorotaxane binding

Figure 4. Ball-and-stick representations of the solid-state structure $[3C1D2K2]^{2+}$: a) side and b) top views. C gray, O red, N blue, K purple.

geometry of the complex $[3C1D2K2]^{2+}$.^[16] The rodlike **3** penetrates the two 34-membered rings, whereas the two oxygen atoms coordinate to the two K^+ ions. Thus, we can form [2]pseudorotaxane complexes from **1** with precise facial control (namely, threading through either the 24- or 34-membered rings) by using the rod-shaped salt **2**·2PF₆ or a combination of K^+ ions and **3**.

Because K^+ ions not only template the formation of the [2]pseudorotaxane complex $[3C1D2K2]^{2+}$ but also cause dissociation of complex $[1D2]^{2+}$ in solution, the addition and removal of K^+ ions from a solution of **1**, **2**·2PF₆, and **3** could be used to mediate an unprecedented type of machinelike molecular motion,^[17] in which the rodlike components penetrate the molecular cage alternately through its different faces (Figure 5).

The ¹H NMR spectrum of an equimolar mixture of **1**, **2**·2PF₆, and **3** in CDCl₃/CD₃CN (9:1) indicates the formation of the [2]pseudorotaxane complex $[1D2]^{2+}$ exclusively (Figure 6a). The addition of four equivalents of K^+ ions to this solution not only leads to the dissociation of most of the $[1D2]^{2+}$ but also to the generation of the other [2]pseudorotaxane complex $[3C1D2K2]^{2+}$ (Figure 6b). The subsequent

Figure 5. K^+ ion and [2,2,2]cryptand-controlled threading and dethreading processes associated with the alternate formation of [2]pseudorotaxane complexes $[1D2]^{2+}$ and $[3C1D2K2]^{2+}$.

Figure 6. Partial ¹H NMR spectra (400 MHz, CDCl₃/CD₃CN (9:1), 298 K) of a) an equimolar (3 mM) mixture of **1**, **2**·2PF₆, and **3**; b) the mixture obtained after adding KPF₆ (4 equiv) to solution (a); and c) the mixture obtained after adding [2,2,2]cryptand (4 equiv) to solution (b).

addition of [2,2,2]cryptand (4 equiv), which is a very strong binder of K^+ ions, to the solution leads to the disappearance of the signals that are diagnostic of $[3C1D2K2]^{2+}$ and the reappearance of the signals of $[1D2]^{2+}$. Thus, sequential addition of K^+ ions and [2,2,2]cryptand to a mixture of **1**, **2**·2PF₆, and **3** in solution controls the mechanical threading of the different rodlike components within the molecular cage through selective formation of $[1D2]^{2+}$ and $[3C1D2K2]^{2+}$ (Figure 5).

Having proven that precise facial control is achievable in the formation of [2]pseudorotaxane complexes from **1** and that machinelike molecular motion can occur with these supramolecular systems, we turned our attention to the construction of a supramolecular complex in which each of the four macrocyclic openings in **1** encircles a rodlike unit. We synthesized the four-armed salt **5**·2PF₆ through the reaction of the bipyridine **4**^[18] with 1-bromopropane. We expected that the complexation of **5**·2PF₆ with **1** would lead to the formation of a symmetrical complex $[1D5](PF_6)_2$, in which each of the four substituting groups of **5**·2PF₆ would thread through a different opening of the **1** (Scheme 4).

The ¹H NMR spectrum (see the Supporting Information) of an equimolar mixture (2.6 mM) of **1** and **5**·2PF₆ in CDCl₃/CD₃CN (3:17) displays three sets of resonances—one set for free **1**, one for free **5**·2PF₆, and one for the 1:1 complex formed between **1** and **5**·2PF₆—which suggests that the rates of complexation and decomplexation are both slow on the ¹H NMR timescale at 400 MHz and 298 K. Using a single-

Scheme 4. Complexation of molecular cage **1** with **5**·2PF₆. DMF = dimethylformamide, Ts = toluenesulfonyl.

point method,^[19] we determined the association constant (K_a) of this system at 298 K to be 300 M^{-1} in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (3:17).

We grew single crystals suitable for X-ray crystallography through liquid diffusion of isopropyl ether into an equimolar solution of **1** and **5**·2PF₆ in CH₃CN.^[13] The solid-state structure reveals a binding geometry for the complex [1⊃5]²⁺^[20] in which the *n*-propyl groups penetrate through the 24-membered rings and the two tosyl groups emerge from the 34-membered rings of **1** (Figure 7). The structure of [1⊃5]²⁺ is unique, which may be correlated to a turtle's four legs protruding from its hard shell.

Figure 7. Ball-and-stick representation of the solid-state structure of [1⊃5]²⁺: a) side and b) top views. C gray, O red, N blue, S yellow.

We have demonstrated that two different types of thread component (based on a bispyridinium ion and quinone) can be applied to molecular cage **1** to generate different [2]pseudorotaxane-like complexes with precise facial control. A mixture of the two threading components and **1** in solution undergoes a new type of molecular motion, powered through the addition and removal of K⁺ ions and [2,2,2]cryptand units, in which the rodlike components penetrate the molecular cage alternately through its different faces. In addition, the four-armed macrocyclic guest **5**·2PF₆ forms a complex with **1**, in which each of the limbs of the guest protrudes from a unique macrocyclic face of the host to result in a turtlelike supramolecular complex. We believe that the molecular recognition properties of this molecular cage will be useful

in various fields, such as the construction of molecular machinery, supramolecular polymers, and supramolecular catalytic systems, which we are presently investigating.

Experimental Section

2·2PF₆: 1-Bromopentane (403 μL , 3.2 mmol) was added to a solution of 1,2-di(4-pyridyl)ethane (100 mg, 0.54 mmol) in DMF (2 mL) at ambient temperature. The solution was stirred for 12 h before being poured into CH₂Cl₂ (5 mL) to provide a precipitate, which was collected and dissolved in MeCN (10 mL). Saturated aqueous NH₄PF₆ (10 mL) was added, and then the organic solvent was evaporated under reduced pressure. The precipitate was collected, washed with H₂O (20 mL), and dried to give **2**·2PF₆ as a pale-yellow solid (246 mg, 74%). ¹H NMR (400 MHz, CD₃CN): δ = 0.91 (t, J = 7 Hz, 6H), 1.23–1.42 (m, 8H), 2.08–2.21 (m, 4H), 3.28 (s, 4H), 4.45 (t, J = 7 Hz, 4H), 7.85 (d, J = 6 Hz, 4H), 8.54 ppm (d, J = 6 Hz, 4H); ¹³C NMR (100 MHz, CD₃CN): δ = 14.0, 22.6, 28.5, 31.3, 35.0, 61.8, 128.3, 143.9, 160.3 ppm; HR-MS (FAB): C₂₂H₃₄F₆N₂P⁺ ([2·PF₆]⁺) calcd m/z 471.2363; found m/z 471.2403.

5·2PF₆: 1-Bromopropane (50 μL , 0.53 mmol) was added to a solution of the dipyridine **4** (25 mg, 0.05 mmol) in DMF (1 mL) at ambient temperature. The solution was stirred at 90 °C for 12 h before being poured into diethyl ether (10 mL) to give a precipitate, which was dissolved in MeCN (10 mL). Saturated aqueous NH₄PF₆ (10 mL) was added, and then the organic solvent was evaporated under reduced pressure. The precipitate was collected, washed with H₂O (20 mL), and dried to give **5**·2PF₆ as a pale-yellow solid (41 mg, 98%). ¹H NMR (400 MHz, CD₃CN): δ = 0.84 (t, J = 7 Hz, 6H), 1.77–1.85 (m, 4H), 2.51 (s, 6H), 4.29 (t, J = 7 Hz, 4H), 4.66 (s, 8H), 7.54 (d, J = 8 Hz, 4H), 7.88 (d, J = 8 Hz, 4H), 8.27 (s, 4H), 8.75 ppm (s, 2H); ¹³C NMR (100 MHz, CD₃CN): δ = 10.6, 21.7, 25.1, 51.1, 64.1, 127.4, 130.7, 135.6, 137.5, 143.2, 145.4, 147.7 ppm; HR-MS (FAB): C₃₄H₄₂F₆N₄O₄PS₂⁺ ([5·PF₆]⁺) calcd m/z 779.2289; found m/z 779.2305.

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- [16] Crystal data for $[\mathbf{3} \cdot \mathbf{1} \cdot \mathbf{K}_2] \cdot 2 \text{MeCN} \cdot 0.5 \text{CHCl}_3 \cdot \text{H}_2\text{O} \cdot 2 \text{PF}_6$: $[\text{C}_{78.5}\text{H}_{90.5}\text{O}_{19}\text{N}_2\text{Cl}_{1.5}][\text{PF}_6]_2$, $M_r = 1787.34$, monoclinic, space group $C2/c$, $a = 31.5201(4)$, $b = 16.3152(3)$, $c = 19.0614(3)$ Å, $V = 9784.3(3)$ Å³, $\rho_{\text{calcd}} = 1.213 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 0.252 \text{ mm}^{-1}$, $T = 295(2)$ K, deep-yellow plates; 11101 independent measured reflections, F^2 refinement, $R_1 = 0.1235$, $wR_2 = 0.3002$.
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