

Iptycene-Derived Crown Ether Hosts for Molecular Recognition and Self-Assembly

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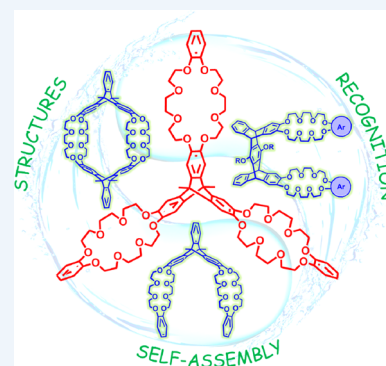
CONSPECTUS: Synthetic macrocyclic hosts have played key roles in the development of host–guest chemistry. Crown ethers are a class of macrocyclic molecules with unique flexible structures. They have served as the first generation of synthetic hosts, and researchers have extensively studied them in molecular recognition. However, the flexible structures of simple crown ethers and their relatively limited modes of complexation with guests have limited the further applications of these molecules. In recent years, researchers have moved toward fabricating interlocking molecules, supramolecular polymers, and other assemblies with specific structures and properties. Therefore, researchers have developed more complex crown ether-based macrocyclic hosts with multicavity structures and multicomplexation modes that provide more diverse and sophisticated host–guest systems.

In this Account, we summarize our research on the synthesis and characterization of iptycene-derived crown ether hosts, their use as host molecules, and their applications in self-assembled complexes.

Iptycenes including triptycenes and pentyptycenes are a class of aromatic compounds with unique rigid three-dimensional structures. As a result, they are promising building blocks for the synthesis of novel macrocyclic hosts and the construction of novel self-assembled complexes with specific structures and properties. During the last several years, we have designed and synthesized a new class of iptycene-derived crown ether hosts including macrotricyclic polyethers, molecular tweezer-like hosts, and tritopic tris(crown ether) hosts, which are all composed of rigid iptycene building blocks linked by flexible crown ether chains.

We have examined the complexation behavior of these hosts with different types of organic guest molecules. Unlike with conventional crown ethers, the combination of iptycene moieties and crown ether chains provides the iptycene-derived crown ether hosts with complexation properties that differ based on the structure of the guests. The rigid iptycene moieties within these synthetic host molecules both maintain their inherent three-dimensional cavities and generate multicavity structures. The flexible crown ether chains allow the iptycene-derived hosts to adjust their conformations as they encapsulate guest molecules. Moreover, the expanded complexation properties also allow the host–guest systems based on the iptycene-derived crown ethers to respond to multiple external stimuli, resulting in a variety of supramolecular assemblies.

Finally, we also describe the construction of mechanically interlocked self-assemblies, molecular switches/molecular machines, and supramolecular polymers using these new host molecules. We expect that the unique structural features and diverse complexation properties of these iptycene-derived crown ether hosts will lead to increasing interest in this field and in supramolecular chemistry overall.



1. INTRODUCTION

Since Pedersen¹ at Du Pont first reported the synthesis of crown ethers and their cation-complexing properties in 1967, host–guest chemistry² has attracted much attention, and developing new kinds of macrocyclic hosts has always been one of the most important and hottest topics in this research area. Consequently, various synthetic macrocyclic hosts, including crown ethers,³ cryptands,⁴ calixarenes,⁵ cucurbiturils,⁶ pillararenes,⁷ and others^{8–10} have been successively designed and synthesized during the past decades. And these synthetic hosts with the capability of binding substrate species strongly and selectively have undoubtedly played a key role in host–guest chemistry.

Crown ethers as the first generation of macrocyclic hosts have been extensively studied in the complexation with metal ions, ammonium, and primary alkylammonium salts in the earlier years. Since Stoddart et al. first reported the complexation of

crown ethers with paraquat and diquat in 1987,¹¹ various host–guest systems and functionalized supramolecular assemblies based on crown ether hosts and different organic guests have been developed.¹² In this regards, Gibson and co-workers,¹³ Huang and co-workers,¹⁴ Chiu and co-workers,¹⁵ Balzani and co-workers,¹⁶ and Loeb¹⁷ besides Stoddart's group¹⁸ have made great achievements. However, flexible structures and relatively monotonous complexation modes of simple crown ethers could limit their further applications to a certain extent. Thus, developing novel crown ether-based hosts with multicavity structures and multicomplexation modes is still a very attractive

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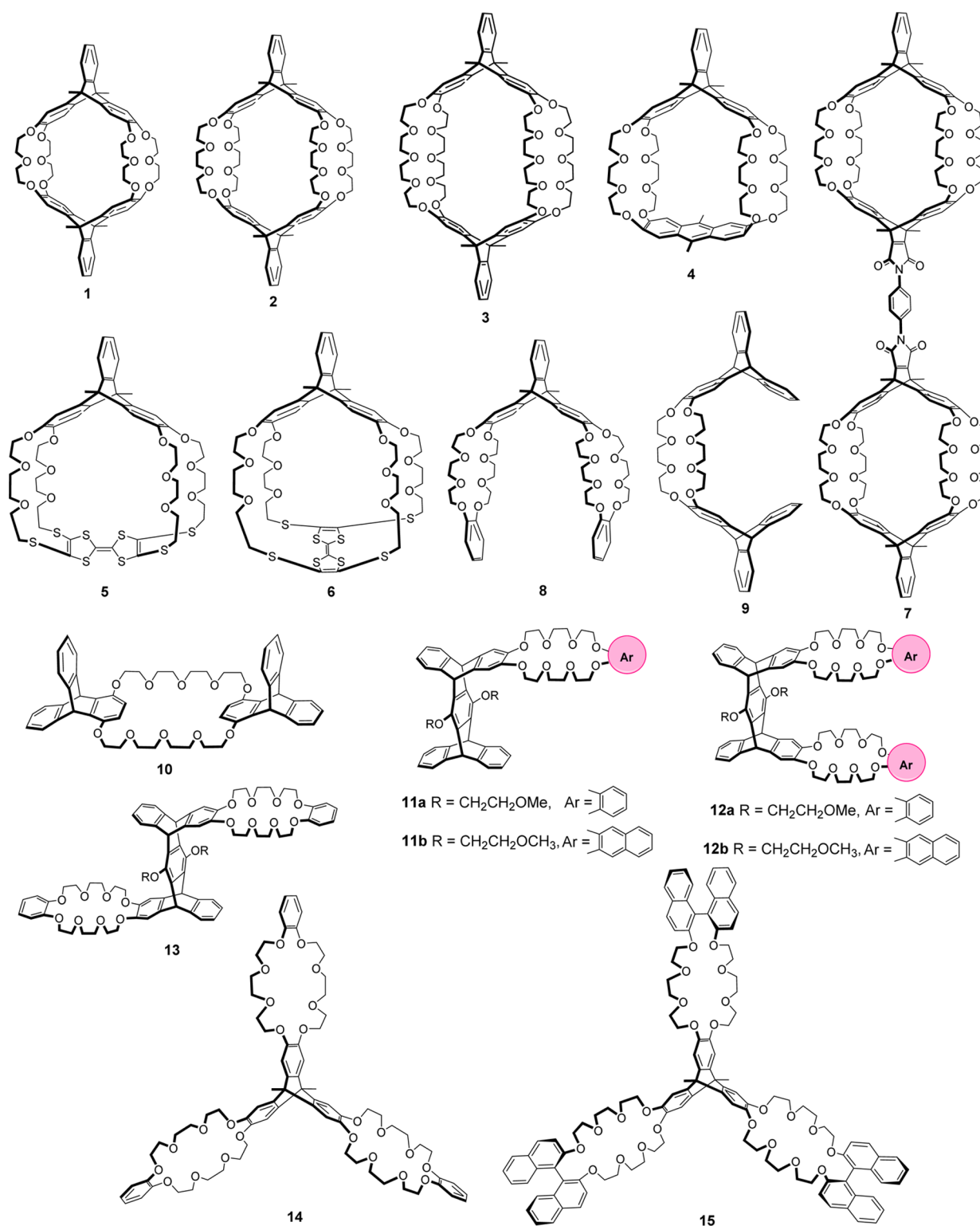


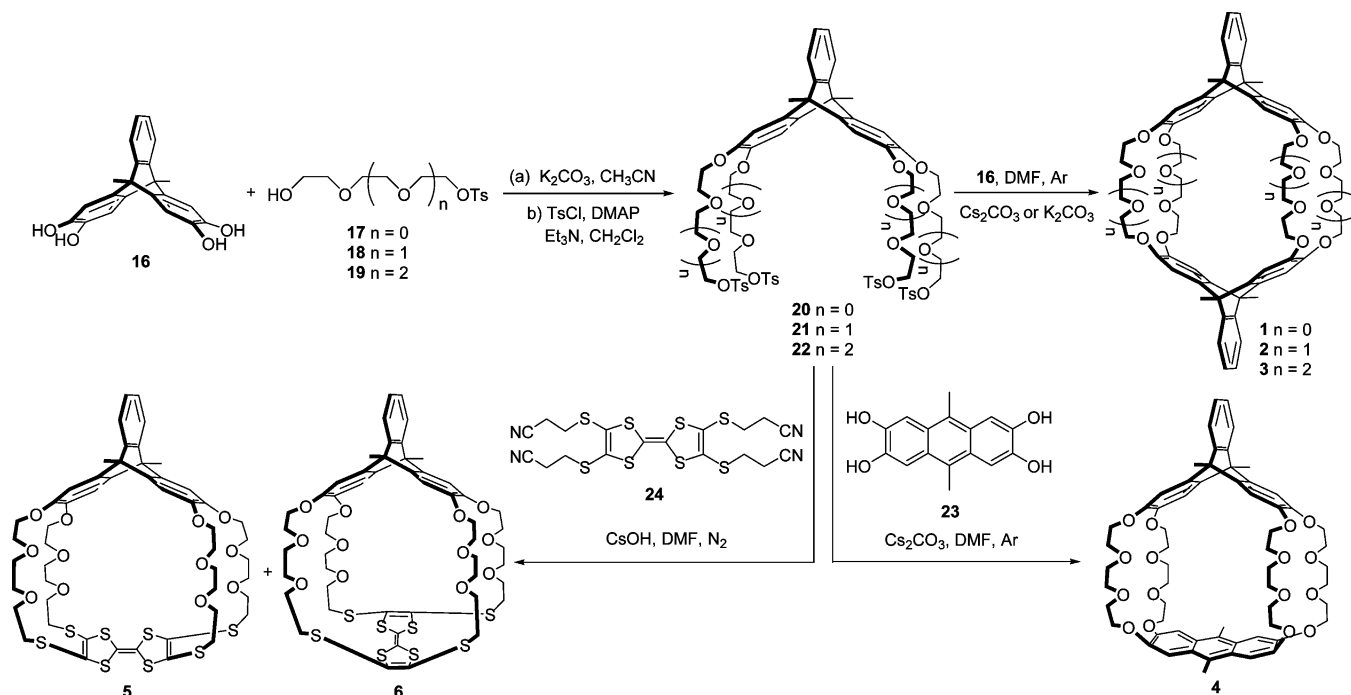
Figure 1. Structures of iptycene-derived crown ether hosts 1–15.

and hot topic for their potential in developing diverse and sophisticated host–guest systems.

Iptycenes including triptycenes and pentiptycenes are a class of aromatic compounds with unique three-dimensional rigid structures, and they have found wide applications in materials science, molecular machines, and other research fields.^{19,20} Several years ago, we have proved that iptycene derivatives could also be utilized as useful building blocks for developing novel

macrocyclic hosts. Consequently, new kinds of iptycene-derived crown ether hosts, including cylindrical macrotricyclic polyethers, molecular tweezer-like hosts, and tris(crown ether) hosts (Figure 1), have been designed and synthesized. These novel synthetic hosts are all composed of rigid iptycene building blocks linked by flexible crown ether chains. On one hand, the rigid iptycene moieties with electron-rich arene rings induce the iptycene-derived hosts to not only maintain inherent 3D cavities

Scheme 1. Synthesis of Triptycene-Derived Hosts 1–6



and generate multicavity structures but also provide additional sites to form intermolecular π - π and C-H \cdots π interactions with organic guests, which are important for formation of the stable complexes. On the other hand, the flexible crown ether moieties can also facilitate the conformation adjustment of the hosts by the encapsulated guests. These specific structural features by the combination of the iptycene moieties and the crown ether chains make the iptycene-derived hosts show diverse complexations with different kinds of guests, which are obviously different from those of the conventional crown ethers with relatively monotonous complexation modes. Moreover, the diverse complexation properties also make the host-guest systems based on these hosts easily responsive to multiple external stimuli, which can be helpful to construct various functionalized supramolecular assemblies.

In the feature article published in 2011,²¹ synthesis of some triptycene-derived hosts and their applications in supramolecular chemistry have been summarized. In this Account, we will highlight our recent endeavors toward the synthesis and structural characterization of iptycene-derived crown ether hosts and their applications in molecular recognition and self-assembly. Stimuli responsive host-guest properties will be emphasized.

2. SYNTHESIS AND STRUCTURAL CHARACTERIZATION

Synthesis of iptycene-derived crown ether hosts 1–6 is depicted in Scheme 1. Treatment of 2,3,6,7-tetrahydroxytriptycene **16** with ditosylates **17–19** in the presence of K₂CO₃, followed by reaction with *p*-toluenesulfonyl chloride gave compounds **20–22**, which were then reacted with **16** under a high dilution condition in the presence of Cs₂CO₃ or K₂CO₃ to give hosts **1–3**,^{22–24} respectively. Reaction of compound **21** with 9,10-dimethyl-2,3,6,7-tetrahydroxyanthracene **23** gave host **4**.²⁵ When **21** was reacted with **24** in the presence of CsOH, macrocycles **5** and **6**²⁶ were obtained. Starting from **4**, triptycene-derived

bis-macrotricyclic host **7** was synthesized in 32% total yield in three steps as shown in Scheme 2.²⁷ Similarly, iptycene-derived crown ether hosts **8–15**^{28–36} could also be conveniently synthesized by the treatment of the corresponding polyhydroxy-substituted iptycene derivatives with ditosylates. Additionally, these synthetic hosts all showed good solubilities in CHCl₃ and CH₂Cl₂.

Crystal structure of macrotricyclic host **2**²² showed that it is composed of two triptycene units linked by four tri(ethylene glycol) bridges to form two lateral dibenzo-24-crown-8 (DB24C8) cavities and one belt-like central cavity with a size of ca. 10.2 × 13.9 Å². Compared with **2**, host **1**²⁴ has one smaller central cavity and two lateral dibenzo-18-crown-6 cavities, while host **3**²³ contains one larger and more flexible central cavity besides two lateral dibenzo-30-crown-10 cavities. The flexible tetra(ethylene glycol) chains of host **3** also separate the two triptycene subunits far from each other to form a rectangle-like cavity in the solid state. Besides one central cavity and two lateral crown ether cavities, host **4**²⁵ contains an anthracene unit as well. Similarly, one triptycene unit in **2** is replaced by a tetrathiafulvalene (TTF) unit to form macrocycles **5** and **6**²⁶ as a pair of structural isomers. The electron-rich anthracene ring in **4** and TTF moiety in **5** and **6** provided strong π - π interactions between the hosts and guest molecules, which could make the macrocycles able to host electron acceptors, such as quinones.

Iptycene-derived crown ether hosts **8–12**^{28–34} are composed of one or two rigid iptycene moieties and one or two flexible crown ether moieties to form an open 3D cavity with tweezer-like structures. Host **13** is the structural isomer of **12**, and it contains one pentiptycene skeleton and two DB24C8 moieties in a *trans* arrangement, which forms two open tweezer-like cavities. The triptycene-derived tris(crown ether) **14**³⁵ with three DB24C8 cavities positioned in three orientations is a homotritopic host, which shows a D_{3h} symmetrical structure. Host **15**³⁶ has similar structural features to those of **14** except containing three chiral crown ether cavities.

Scheme 2. Synthesis of Triptycene-Derived Bis-macrotricyclic Host 7

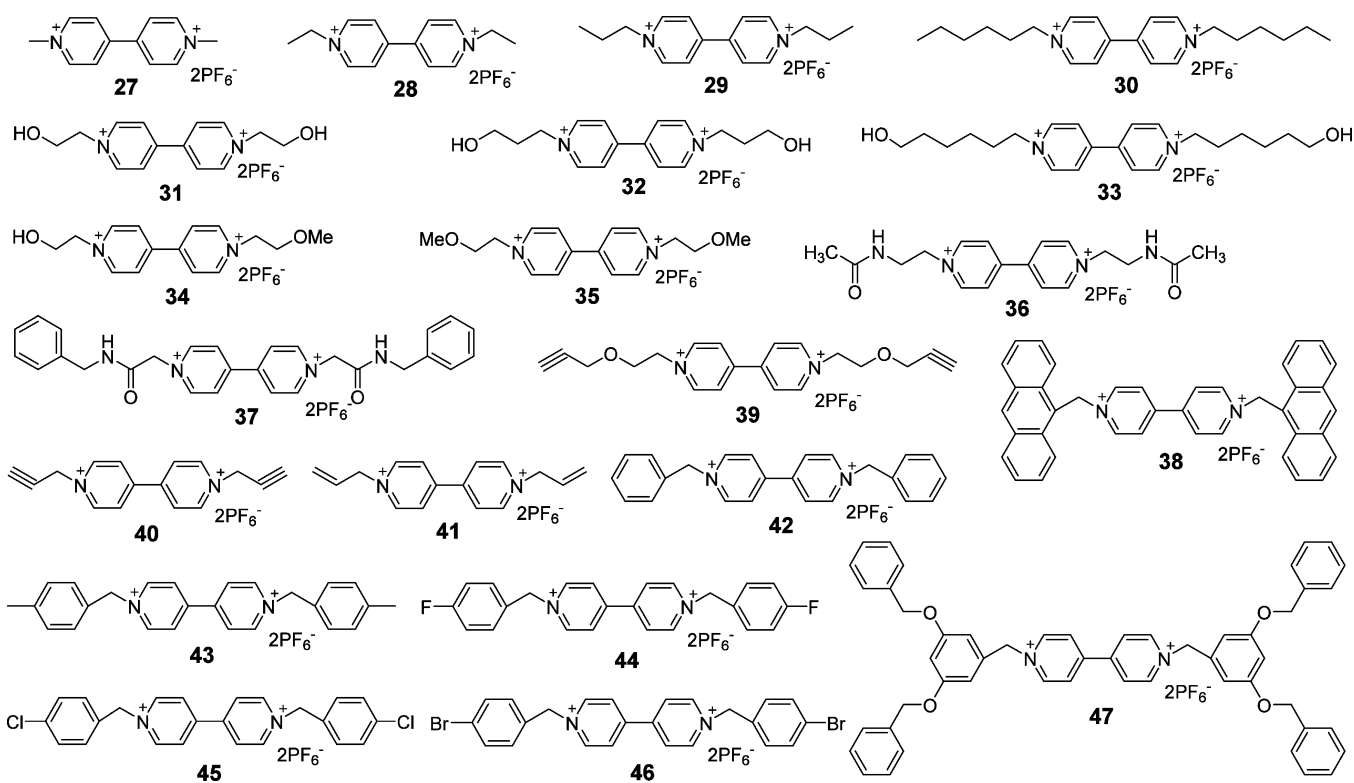
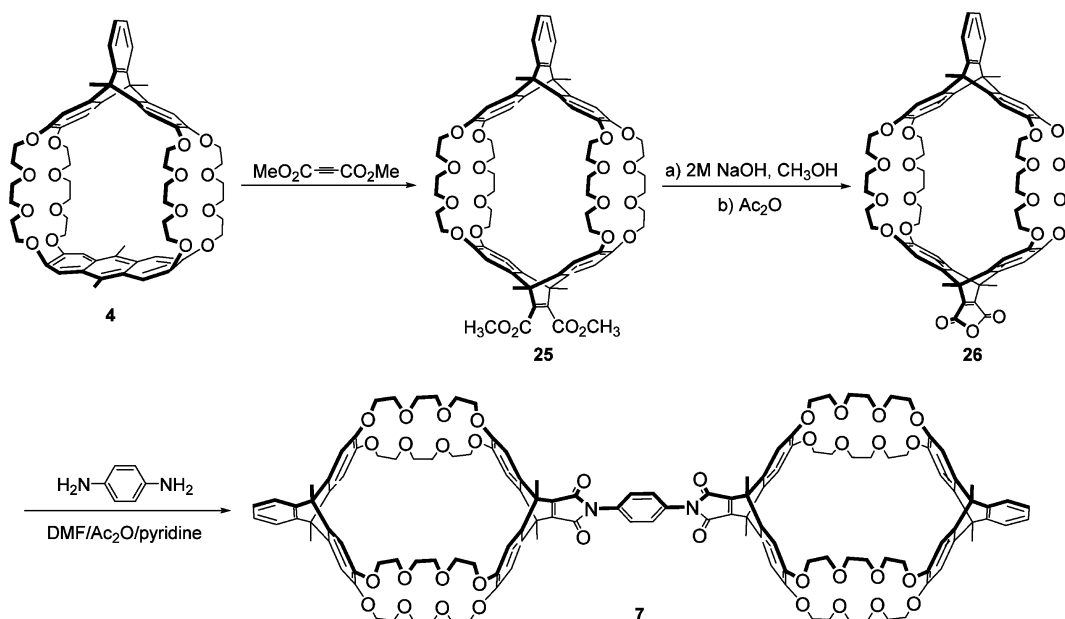


Figure 2. Structures of paraquat derivatives.

3. HOST-GUEST PROPERTIES

The specific structural features of the triptycene-derived crown ether hosts provided them with broad complexation abilities toward different kinds of organic guests, especially electron-deficient guests, which resulted in a series of new host-guest systems.

3.1. Complexation with Paraquat Derivatives

Paraquat derivatives are a class of electron deficient guests, and they have been widely utilized in host-guest chemistry. We found that triptycene-derived macrotricyclic hosts could form

stable complexes with paraquat derivatives (Figure 2). Especially, depending on the guests, the hosts can form 1:1 or 1:2 complexes in both solution and the solid state in different complexation modes. For alkyl substituted paraquat derivatives 27–30, host 2 could form 1:1 complexes in the complexation mode as shown in Figure 3a,²² in which two *N*-substituted groups were positioned in or threaded the two DB24C8 cavities. Fast exchange processes between the hosts and the guests were found except for complex 2-27 in which the rates of complexation and decomplexation are both slow at room temperature. The X-ray crystal structure of

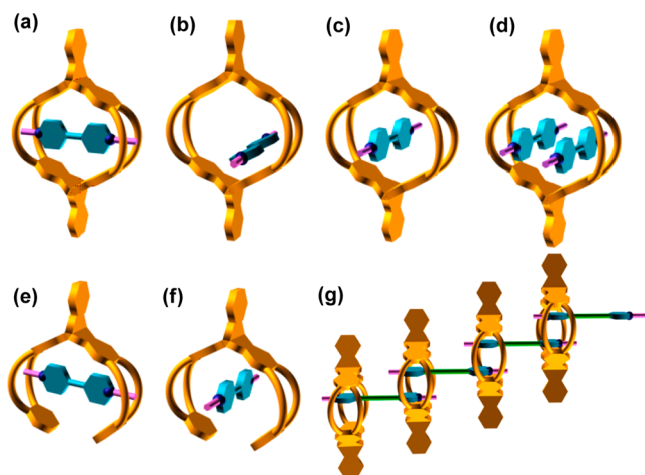


Figure 3. Cartoon representations for complexation modes of the complexes based on iptycene-derived crown ether hosts.

complex **2**·**27** (Figure 4a) showed that multiple C–H···O hydrogen bonding between the protons of methyl groups in paraquat and ether oxygen atoms of the host might play a key role in formation of the stable complex. Host **2** could also form 1:1 complexes with guests **33**–**38**, but the guests were included in the central cavity of host **2** (Figure 3b,c).³⁷ For **31** and **32** containing two β -hydroxyethyl and β -hydroxypropyl groups, two of the guests simultaneously threaded the central cavity of host **2** to form 1:2 complexes (Figure 3d), in which the terminal groups were all located outside the cavity (Figure 4b).³⁷

Host **1**²⁴ with a smaller cavity than host **2** only formed 1:1 complexes with paraquat derivatives **27**, **29**, **31**, **34**, **35**, and **38**–**41** in solution. However, depending on the guests with different terminal groups, the host can form 1:1 or 1:2 complexes in different complexation modes in the solid state, which is significantly different from those of host **2**. For host **3** containing two DB30C10 moieties,^{38,39} it could form 1:1 complexes with

paraquat derivatives **27**, **38**, **45**, and **46** and 1:2 complexes with guests **29**, **31**, **35**, and **42**–**44**. For complexes **3**·**29**, **3**·**31**, and **3**·**35**, anion– π interactions between one PF_6^- and the bipyridinium rings (Figure 4c) might be important to the formation of the complexes. Especially, we also found that the conformation of host **3** could be efficiently adjusted by the encapsulated guests because of its more flexible structure than those of hosts **1** and **2**.

For the tweezer-like hosts **8**,²⁸ **9**,²⁹ and **11**³² with one open cavity, they could also form 1:1 complexes with paraquat derivatives **27**–**31**, **35**, **38**, **41**, and **47**, while host **13**⁴⁰ with two open cavities could form 1:2 complexes with paraquat derivatives. Except complex **8**·**27** with the complexation mode as described in Figure 3e,²⁸ other complexes all showed the complexation modes in Figure 3f.^{29,32,40} In the case of host **10**, the crystal structure of complex **10**·**27** (Figure 4d) showed that the paraquat ring was located in a crystallographic symcenter to form a pseudo-sandwiched structure with the two triptycene moieties.³⁰

3.2. Complexation with Diquaternary Salts and π -Extended Viologens

It was found that both diquaternary salts **48** and **49** (Figure 5) could form stable 1:1 complexes with host **2**.⁴¹ Crystal structures

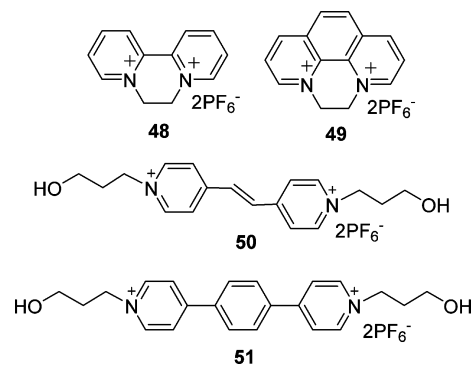


Figure 5. Structures of guests **48**–**51**.

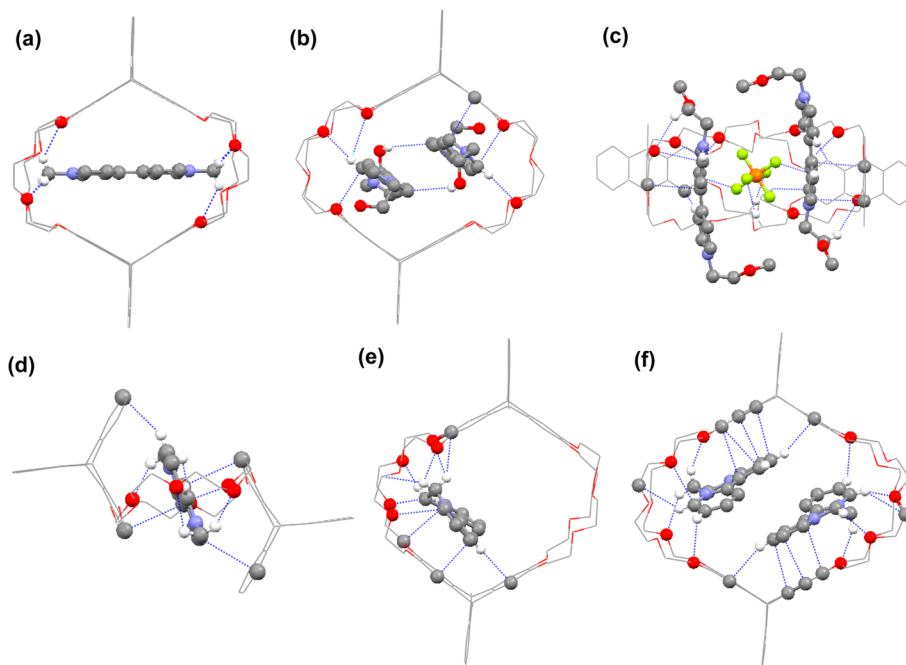


Figure 4. Crystal structures of complexes **2**·**27** (a), **2**·**31** (b), **3**·**35** (c), **10**·**27** (d), **2**·**48** (e), and **3**·**48** (f). Blue lines denote the noncovalent interactions between the hosts and the guests.

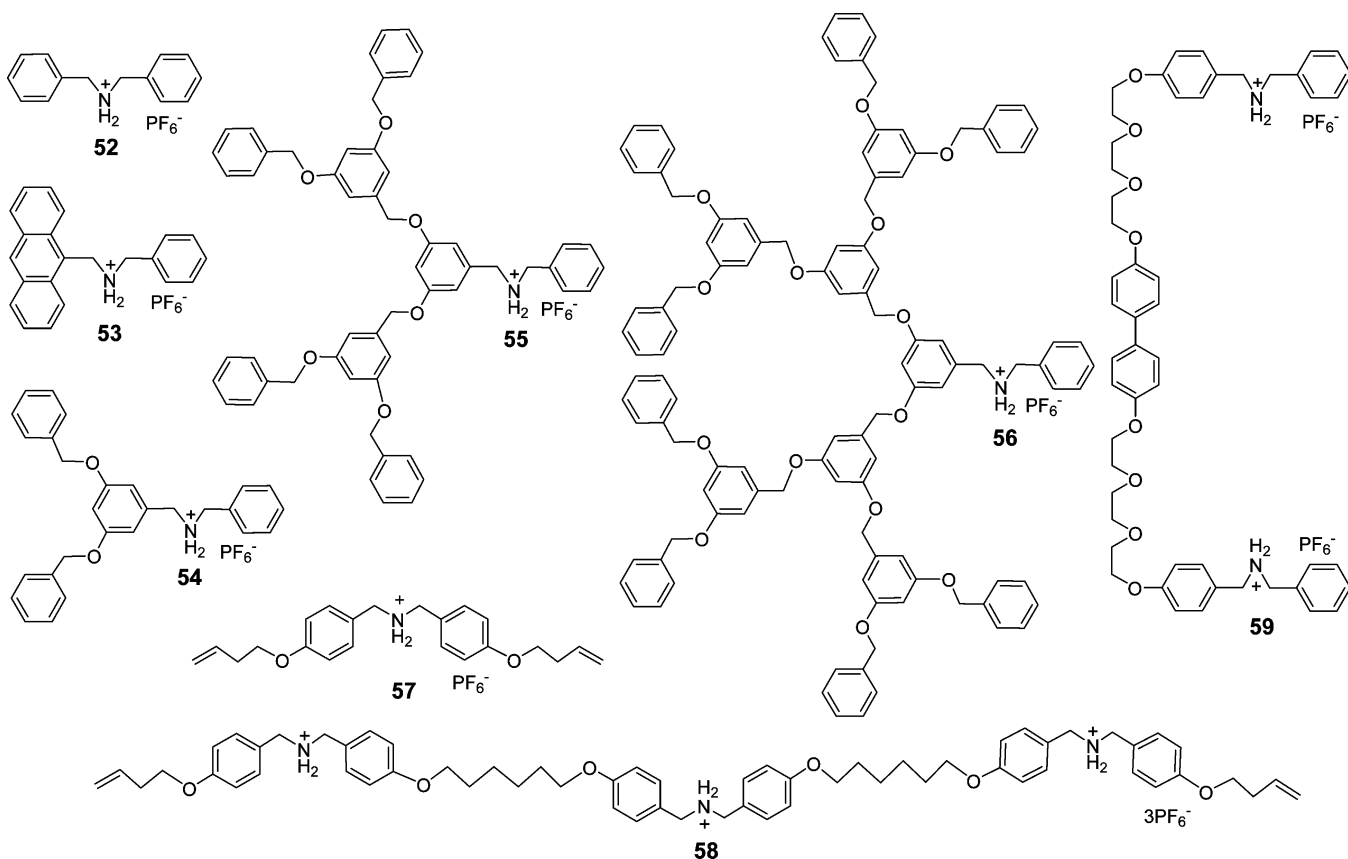


Figure 6. Structures of guests 52–59.

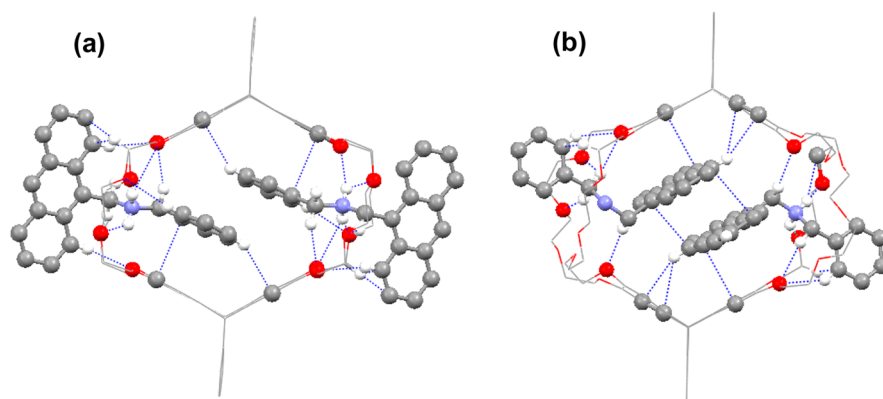


Figure 7. Crystal structures of complexes $2 \cdot 53_2$ and $3 \cdot 53_2$. Blue lines denote the noncovalent interactions between the hosts and guest 53.

of the complexes showed that guest 49 positioned in the center of the cavity of the host, but 48 was located in only one side of the central cavity (Figure 4e), which implied that the free volume of host 2 was available for another guest to result in ternary complexes. Thus, we found that host 2 could simultaneously encapsulate 48 and electron-rich aromatics including benzidine, biphenyl-4,4'-diol, or 4,4'-dibutoxybiphenyl to form 1:1:1 stable ternary complexes in both solution and the solid state, which were stabilized not only by the charge-transfer interactions between the electron-deficient and electron-rich guests but also by the face to face π - π stacking interactions between host 2 and the guests.⁴²

Additionally, host 3 could form a 1:2 complex with two guests of 48 in both solution and the solid state (Figure 4f),³⁸ which is different from that of host 2. Recently, we also found that host 3

could form 1:1 complexes with the π -extended paraquat derivatives 50 and 51 in diluted solution but ladder-like supramolecular polymers (Figure 3g) in both high concentration solution and the solid state.⁴³

3.3. Complexation with Secondary Ammonium Salts

Since host 2 contains two DB24C8 cavities, it could expectedly form a 1:2 complex $2 \cdot 52_2$ with dibenzylammonium salts 52 (Figure 6), and the association constants K_1 and K_2 for the first and second binding events were calculated to be 1.2×10^4 and $2.4 \times 10^3 \text{ M}^{-1}$, respectively, in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (10:1, v/v).⁴⁴ Formation of $2 \cdot 52_2$ encouraged us to further construct a series of dendritic complexes $2 \cdot 54_2$ – $2 \cdot 56_2$.⁴⁴ For guest 53, host 2 could selectively form a 1:2 complex $2 \cdot 53_2$ in both solution and the solid state (Figure 7a), in which the 9-anthracyl groups were

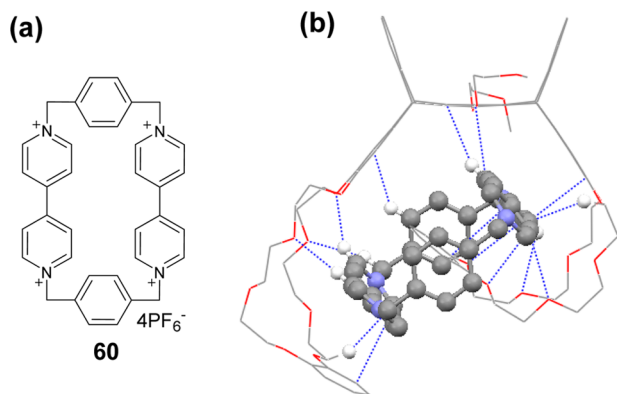


Figure 8. (a) Chemical structure of **60**. (b) Crystal structure of **12a-60**. Blue lines denote the noncovalent interactions between the host and the guest.

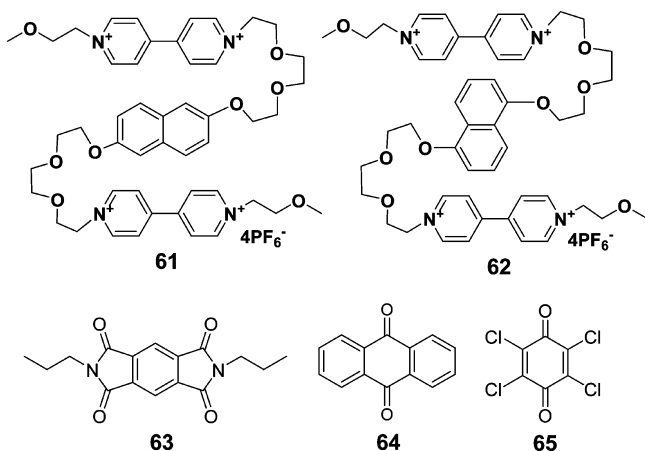


Figure 9. Structures of guests **61–65**.

positioned outside the lateral crown ether cavities of **2**. Similarly, host **3** could also form a 1:2 complex **3-53₂** with two guests of **53**,²³ but the two anthracyl groups were selectively positioned inside the crown ether cavities of **3**, which was completely different from that of **2-53₂**. Crystal structure of complex **3-53₂** (Figure 7b) showed that besides the multiple noncovalent interactions between host **3** and guest **53**, there also exist a pair of $\pi \cdots \pi$ interactions between the anthracyl rings of two guests, which may play an important role in formation of the stable complex. For host **8**²⁸ containing two DB24C8 cavities and host **14**³⁵ containing three DB24C8 cavities, they could expectedly form 1:2 and 1:3 complexes with secondary ammonium salts (**52** or **57**) in solution, respectively. It was also found that host **14**

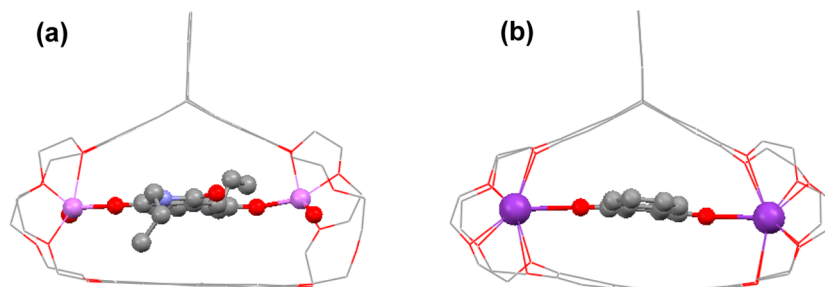


Figure 10. Crystal structures of complexes **4-63-2Li⁺** and **4-64-2K⁺**.

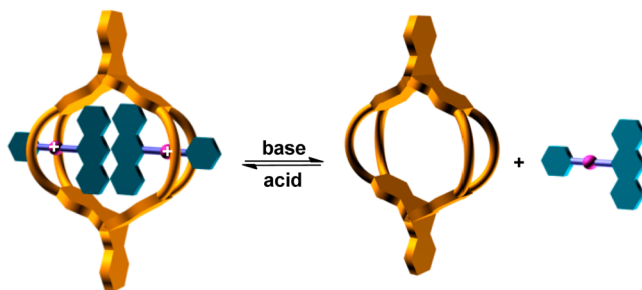


Figure 11. Cartoon description of acid–base controlled binding and release process of guest **53**.

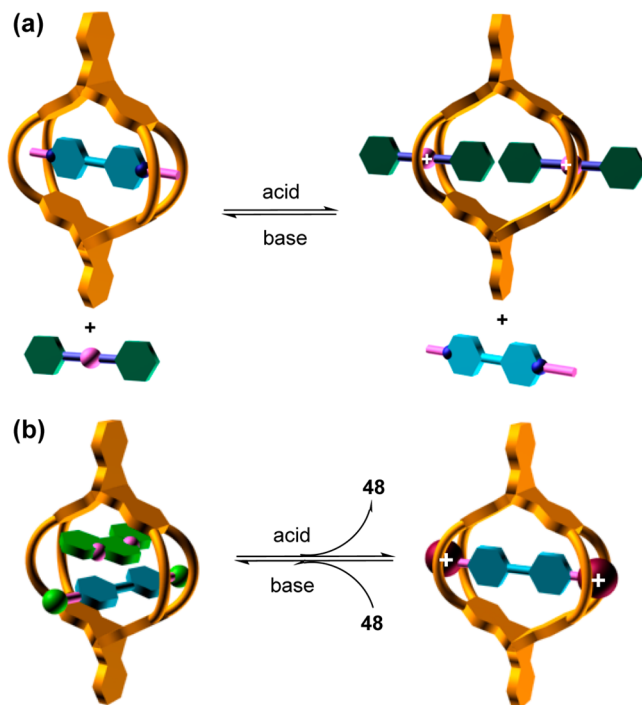


Figure 12. Cartoon descriptions of (a) acid–base controlled competitive complexation process and (b) acid–base controlled selective complexation process between the ternary complex and the binary complex.

could form a 1:1 complex with tritopic guest **58**,⁴⁵ while bis-macrocyclic host **7** could form a 1:2 complex with guest **59**.²⁷

3.4. Complexation with Cyclobis(paraquat-*p*-phenylene)

Cyclobis(paraquat-*p*-phenylene) **60**⁴⁶ is usually used as a host for construction of various interlocked assemblies. But we found that host **12a** with a large open cavity could encapsulate **60** to

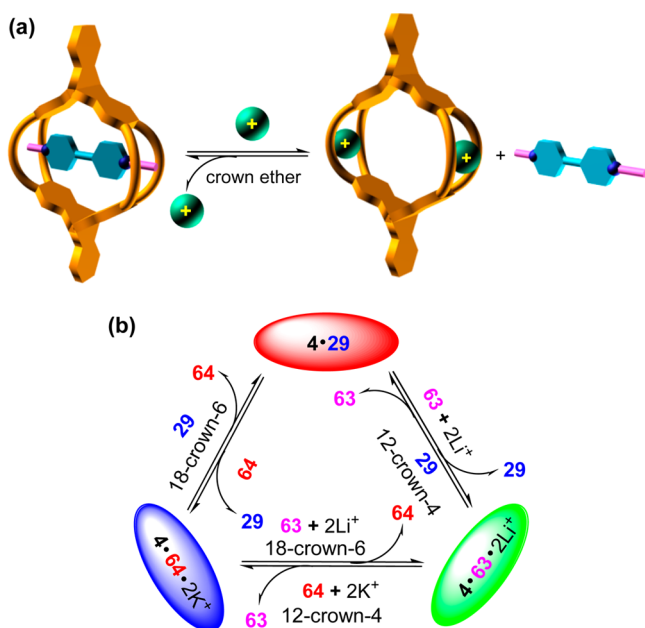


Figure 13. (a) Cartoon description of the ion-controlled binding and release process. (b) Schematic representation of ion-controlled switchable processes between 4·29, 4·63·2Li⁺, and 4·64·2K⁺.

form a 1:1 complex in both solution and the solid state.³³ The crystal structure of complex 12a·60 (Figure 8) showed that 60 was included in the cavity of 12a, but one benzene ring in 12a was positioned inside the cavity of 60, which suggested that 12a and 60 in the complex acted as both host and guest. Similar phenomena were also found in the complexation between 10–13^{30,34,47} and 60, which represented a kind of new host–guest systems.

3.5. Complexation with Other Guests

Recently, we found that host 12 with a large and open cavity could include self-folding A–D–A guests 61 and 62 (Figure 9) to form stable 1:1 complexes.⁴⁸ Moreover, we also tested the complexation between the iptycene-derived hosts and neutral guests. Consequently, we found that host 4 could not encapsulate pyromellitic diimide 63 but could form a stable

cascade complex 4·63·2Li⁺ with 63 in both solution and the solid state in the presence of lithium ions (Figure 10a). Similarly, we also found that 4 could selectively form cascade complex 4·64·2K⁺ with anthraquinone 64 in both solution and the solid state in the presence of potassium ions (Figure 10b).²⁵

Host 5 incorporating a TTF unit could form stable complexes with 65 in the presence of Sc³⁺, Pb²⁺, and Zn²⁺ ions. Both absorption and electron spin resonance spectroscopic studies clearly indicated that intermolecular electron transfer occurred from TTF in 5 to guest 65 in the presence of metal ions.²⁶

3.6. Stimuli Response Properties

Stimuli response properties are a very important and attractive motif in host–guest chemistry for their potential in developing functionalized supramolecular systems. Since host 3 contains two crown ether cavities, it is reasonable that the binding and release of the secondary ammonium guests in complex 3·53₂ or the association and disassociation of the complex could be chemically controlled by the addition of trifluoroacetic acid and tributylamine (Figure 11).²³

Host 2 could form stable complexes with both paraquat derivatives and secondary ammonium salts, which inspired us to further examine the competitive binding abilities of the host toward two different kinds of guests. Consequently, it was found that a competitive complexation process between host 2 and two different guests (propyl-substituted paraquat derivative 29 and dibenzylammonium salt 52) could be chemically controlled by acid and base (Figure 12a).³⁷ A similar process was also observed in the complexation between host 8 and guests 29 and 52.²⁸ For the ternary complex formed by host 2 and guests of diquat 48 and benzidine 66, it was found that since host 2 could form a stable 1:1 complex 2·66·2H⁺ with protonated benzidine, a selective complexation process between the ternary complex and binary complex 2·66·2H⁺ could be effectively controlled by the use of acid and base (Figure 12b).⁴²

Iptycene-derived crown ether hosts can form complexes with metal ions, and the complexation of the cations would introduce extra electrostatic repellent force to the complex containing organic cationic guest, which can subsequently dissociate the previously formed host–guest complex. Consequently, it was found that for the complexes formed by hosts 1–3^{23,24,38,39} and

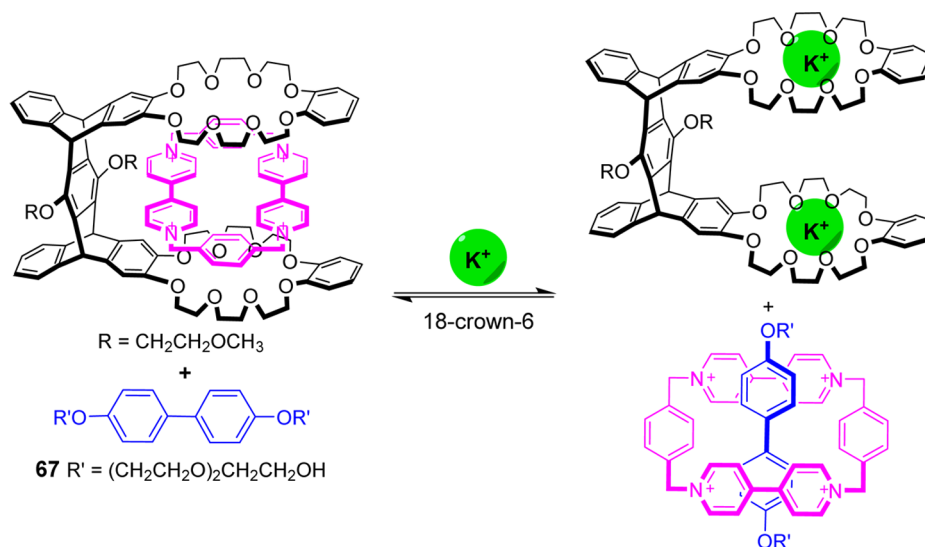


Figure 14. Schematic representation of the changeable role of 60.

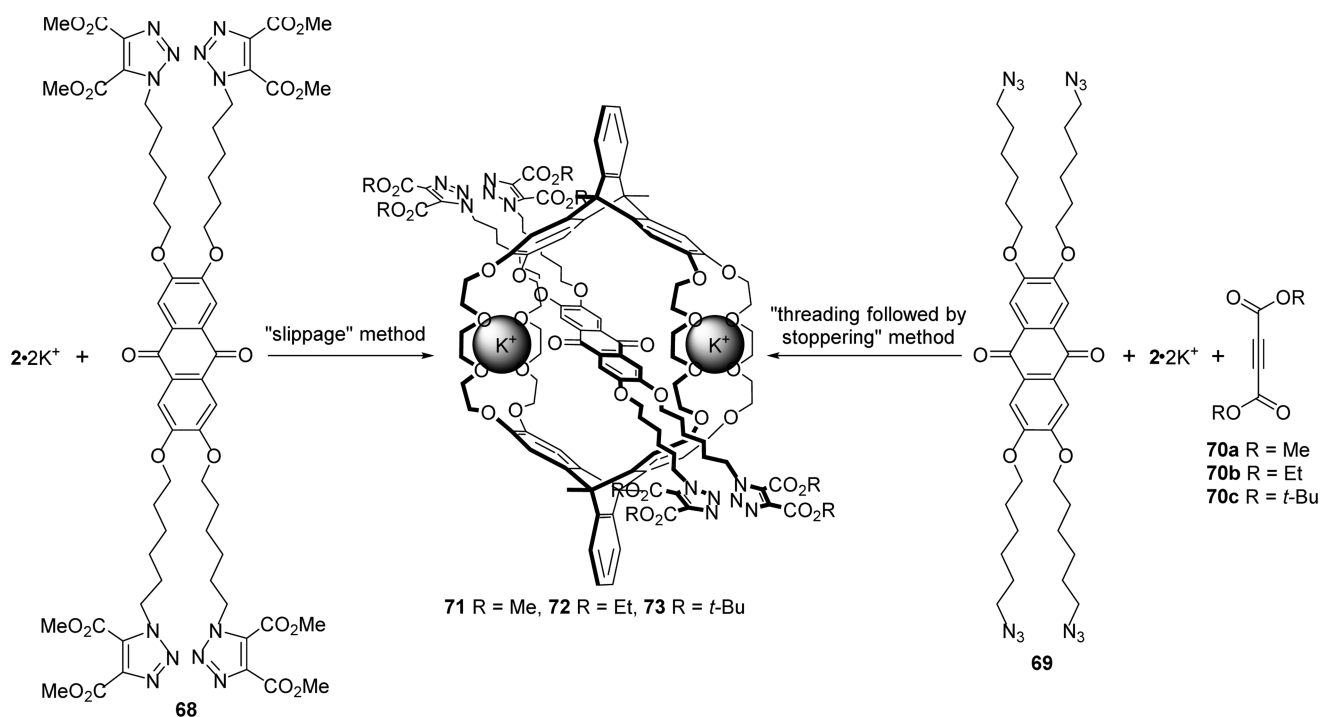


Figure 15. Synthesis of rotaxanes 71–73.

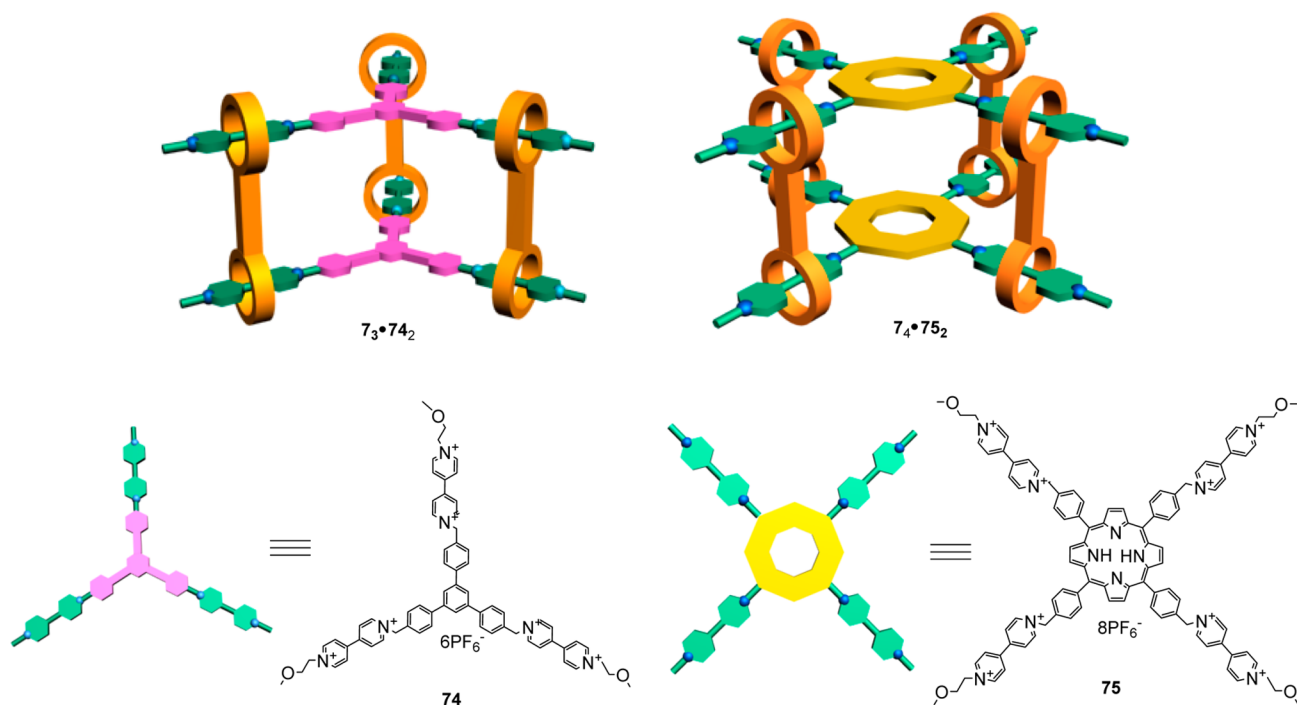


Figure 16. Schematic representations of novel organic supramolecular cages.

11–13^{32,34,40} and paraquat derivatives, the binding and release of the guests could be controlled by adding and removing lithium or potassium ions (Figure 13a). On the basis of the selective complexation of host 4 with paraquat derivative, pyromellitic diimide, and anthraquinone in the presence of lithium or potassium ions, we also found that three ion-controlled switchable processes could be efficiently performed (Figure 13b).²⁵

Inspired by formation of complex 12a·60 and the fact that cyclobis(paraquat-*p*-phenylene) 60 as a host could form

complexes with electron-rich aromatic guests, we further examined the switchable process between two different complexes 12a·60 and 60·67. The results showed that the switchable process could be efficiently controlled by adding and removing potassium ions. Interestingly, the role of macrocycle 60 acting as a host or a guest could thus be changeable (Figure 14), which represents a new host–guest system.³⁴ These varied complexation behaviors, especially the stimuli response properties between the iptycene-derived crown ether hosts and different

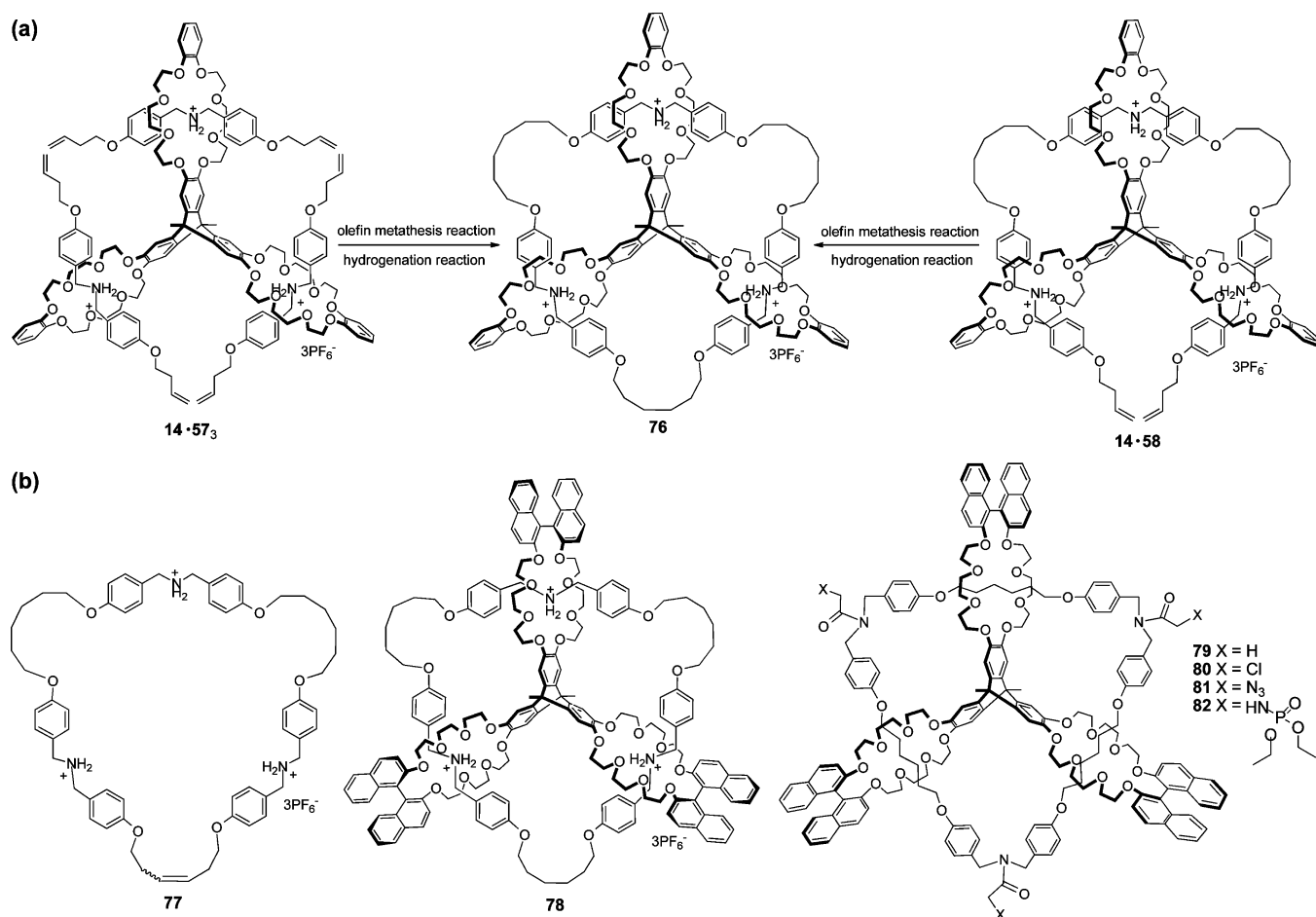


Figure 17. (a) Synthesis of [4]pseudocatenane 76 and (b) structures of macrocycle 77 and chiral [4]pseudocatenanes 78–82.

kinds of guests can provide many opportunities to develop diverse host–guest systems and construct functionalized supramolecular assemblies.

4. SELF-ASSEMBLY

Iptycene-derived crown ether hosts, with their unique rigid–flexible 3D structures, multiple binding cavities, and good affinities to various guests, have been proven to be a kind of versatile building block for constructing different types of assemblies with specific structures and properties, including mechanically interlocked molecules, molecular switches or machines, and supramolecular polymers.

4.1. Mechanically Interlocked Assemblies

Based on formation of the cascade complexes between macrotricyclic host 2 and anthraquinone derivatives in the presence of potassium ions, three potassium-ion-templated [2]rotaxanes 71–73 could be synthesized by the “slippage” or “threading followed by stoppering” approaches (Figure 15).⁴⁹ Since potassium ions acted not only as templates during the stoppering reactions but also as nonslipping chocks to shrink the wheel cavity, the structures of 71 and 72 would be destroyed by peeling off the potassium ions with 18-crown-6, while 73 still remained an interlocked structure under the same conditions.

On the basis of formation of a 1:2 complex between bis-macrotricyclic host 7 and paraquat derivative 35, two multi-component interwoven organic supramolecular cages were successfully constructed by the [3 + 2] and [4 + 2] self-assembly of host 7 and trifurcated or cross-shaped paraquat-derived

subunits 74 and 75, respectively (Figure 16).⁵⁰ Host 7 can provide an ideal scaffold for the further construction of well-defined cages or self-assembled organic containers.

It is different from the macrotricyclic hosts that homotritopic host 14³⁵ allows three guests of 57 to thread its three DB24C8 cavities to form tris-[2]pseudorotaxane 14·57₃. By 3-fold metathesis reactions of 14·57₃ with the second-generation Grubbs’ catalyst, followed by the hydrogenation with Adam’s catalyst, [4]pseudocatenane 76 with *D*_{3h} symmetry could be efficiently synthesized. Recently, we found that trisdialkylammonium 58 could also thread the three DB24C8 cavities of 14 to form a multivalency-directed complex, which subsequently led to 76 by the olefin metathesis reaction (Figure 17a).⁴⁵ Interestingly, treatment of host 14 and trisdialkylammonium macrocycle 77 could also form 76 in a magic-like process through reversible olefin metathesis, which suggested that the combination of multivalency and olefin metathesis provided a powerful tool for the synthesis of complex interlocked molecules. Following the same synthetic strategy as described as above, we obtained a chiral [4]pseudocatenane 78 (Figure 17b) as well. Deprotonation and N-acylation of the ammonium groups in 78 could result in a new class of neutral highly ordered interlocked molecules. Especially, the incorporation of stopper units led to the isolation of an interlocked molecule 82 with an interesting ship’s wheel-like structure.³⁶

4.2. Molecular Switches and Molecular Machines

The stimuli response properties of iptycene-derived host based recognition motifs could be applied in building molecular

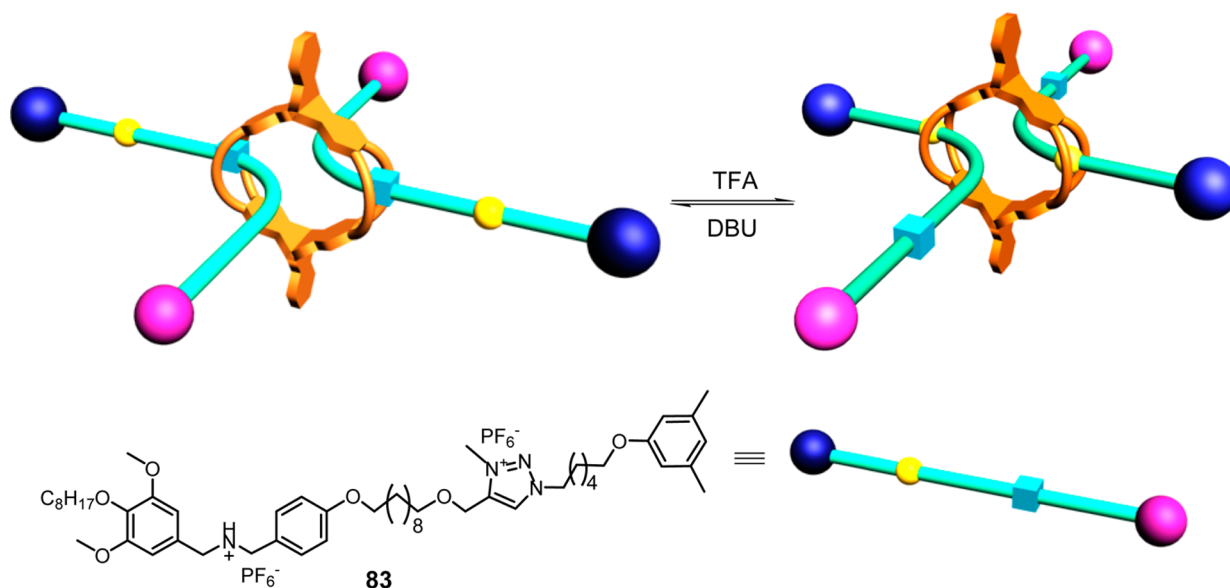


Figure 18. Acid–base controlled [3]rotaxane molecular shuttle.

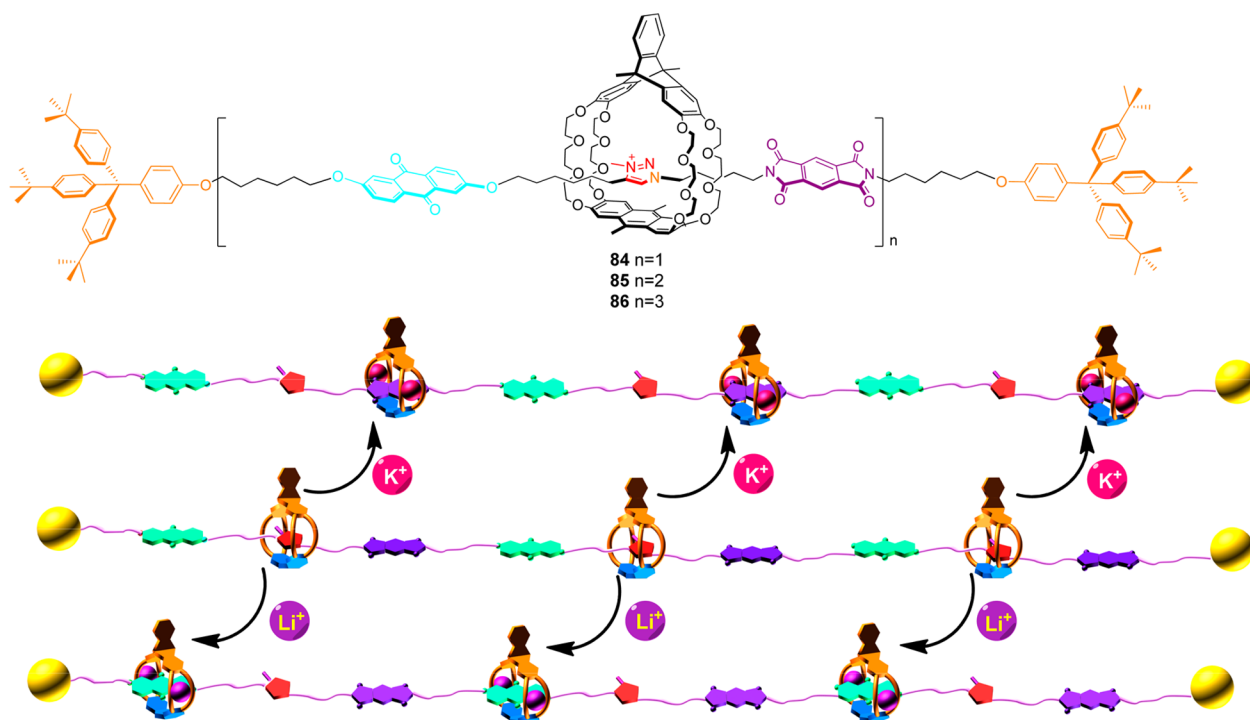


Figure 19. Structures of the tristable rotaxanes and schematic drawing of [4]rotaxane molecular cable car.

switches or machines. Based on the formation of a 1:4 complex between host 7 and dibenzylammonium salt 52, a handcuff-like complex 7·52₂ could be formed, which could be switched by the addition of diazabicycloundecene (DBU) and trifluoroacetic acid (TFA).²⁷ Recently, we also constructed a novel two-station [3]rotaxane molecular machine based on host 2 by the click reaction and subsequent methylation of the 1,2,3-triazole group and further demonstrated that the shuttle process between host 2 and the two different stations of dibenzylammonium and triazolium salts in the thread 83 could be efficiently achieved by acid–base control (Figure 18).⁵¹

To develop more sophisticated molecular machines, new kinds of tristable [2]-, [3]-, or [4]rotaxanes 84–86 (Figure 19) were

obtained, which featured host 4 containing an anthracene unit as the moveable part and pyromellitic diimide, anthraquinone, and *N*-methyltriazolium as the three stations.⁵² It was found that host 4 could be reversibly and controllably moved among the three stations in the [2]rotaxane molecular shuttle. The motion mode can be extended to the oligorotaxanes, providing an original and visual prototype molecular cable car for a molecular machine.

4.3. Supramolecular Polymers

Iptycene-derived crown ether hosts have been applied to construct linear and cross-linked supramolecular polymers because of their good affinities for the guests, multiple binding sites, and sensitive stimuli-responsive recognition motifs.

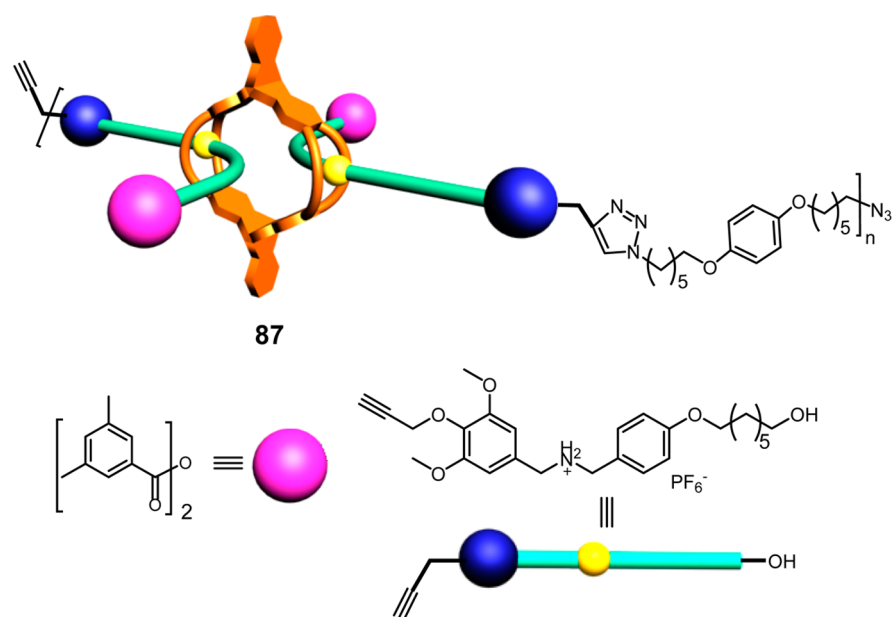


Figure 20. Schematic drawing of poly[3]rotaxane 87.

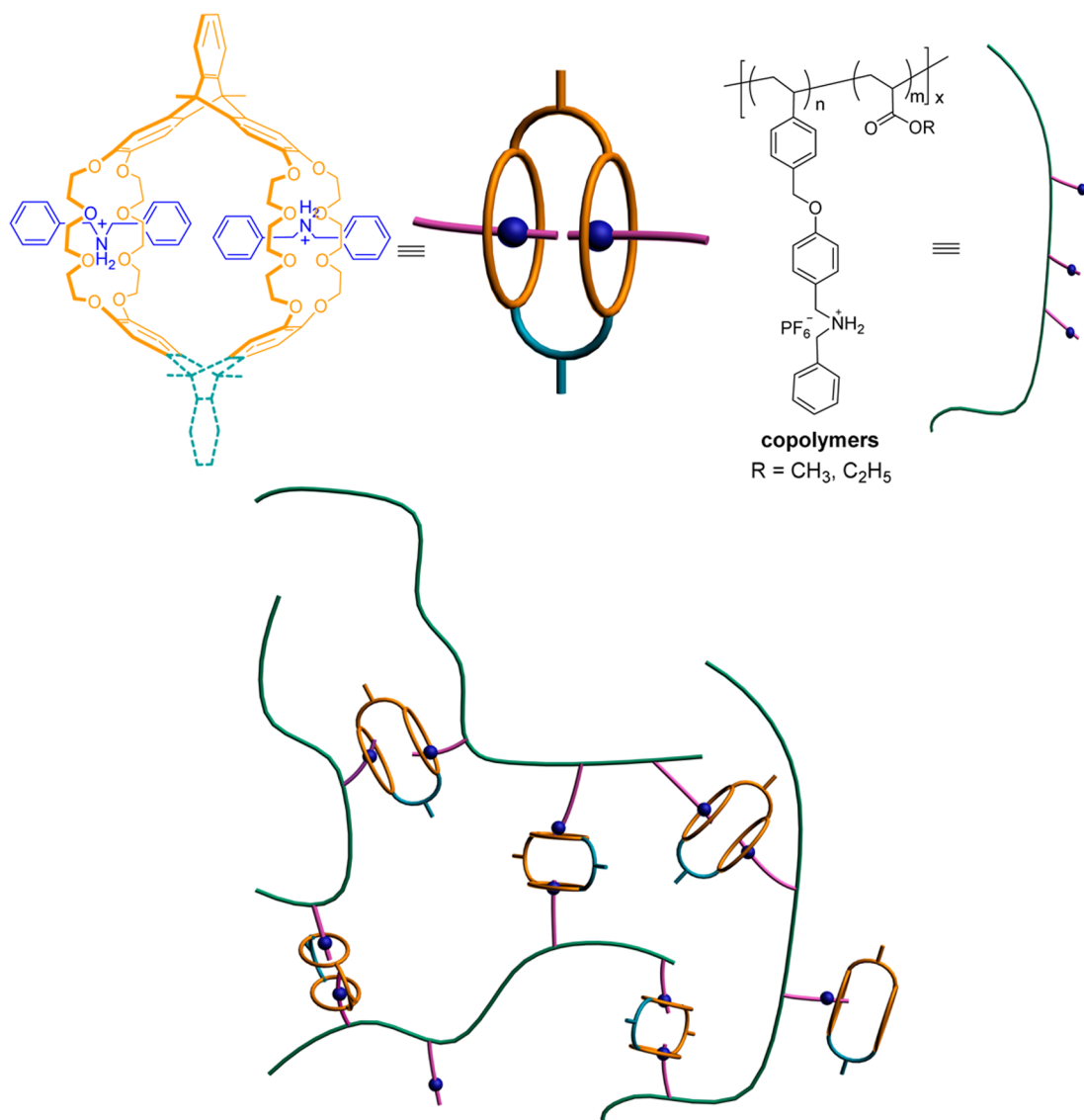


Figure 21. Schematic representation for formation of the supramolecular polymer networks.

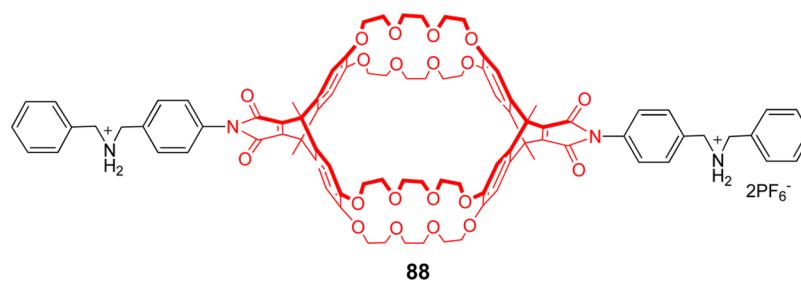


Figure 22. Structure of self-complementary monomer **88**.

As mentioned in host–guest properties, ladder-like supramolecular polymers could be formed between host **3** and π -extended viologens in high concentration solution and solid state as confirmed by X-ray powder diffraction and MALDI-TOF mass spectrometry.⁴⁷ Based on host **2**, a linear main-chain poly[3]-rotaxane **87** was synthesized by the highly efficient Huisgen 1,3-dipolar cycloaddition from the corresponding bifunctionalized [3]rotaxane monomer (Figure 20).⁵³ The calculated average molecular weight (M_m) of **87** was ca. 43 kDa with a polydispersity index (PDI) of 1.42, suggesting ca. 14 repeating units in each polymer chain.

Recently, we also prepared a kind of supramolecular polymer network with gel properties by using the triptycene-derived crown ether hosts as “molecular glue” to cross-link the copolymers containing dibenzylammonium salts (Figure 21).^{54,55} The gels based on host **2** showed acid/base- and thermo-induced reversible gel–sol transition. Moreover, a well-defined porous structure could be observed at the fully cross-linked density, which could be employed for encapsulation and controlled release of squaraine dyes. It is noteworthy that the gel obtained from host **9** showed fast self-healing properties without input of external energy or healing agents. The durable breaking–healing cycles indicated that this gel was feasible to be used as erasable material.

By combination of a macrotricyclic polyether and two dibenzylammonium moieties together, a self-complementary monomer **88** (Figure 22) was synthesized, which could self-assemble into supramolecular polymer networks by intermolecular host–guest recognition.⁵⁶ Interestingly, this supramolecular polymer showed gel properties in acetonitrile or acetonitrile/chloroform solutions, and the supramolecular gels also exhibited reversible thermo- and pH-induced gel–sol transitions. This provides a new strategy for the construction of supramolecular polymers with specific structures and properties.

5. CONCLUSION AND PERSPECTIVES

New kinds of iptycene-derived crown ether hosts including macrotricyclic polyethers, molecular tweezer-like hosts, and homotritopic tris(crown ether) hosts have been conveniently synthesized. By combination of the rigid iptycene building blocks and the flexible crown ether chains, the iptycene-derived crown ether hosts exhibited varied complexation behaviors with different kinds of organic guests. Especially, stimuli responsive complexation properties based on these hosts were displayed. Moreover, these hosts also showed potential applications in mechanically interlocked assemblies, molecular switches or molecular machines, and supramolecular polymers.

Because of the specific multicavity structures and diverse complexation properties, the iptycene-derived crown ether hosts can be promising candidates for constructing sophisticated self-assemblies and smart materials, which provide them wide applications in biological and material sciences. However, studies

on the iptycene-derived crown ether hosts are still in their infancy, and there are some fundamental challenges facing these synthetic hosts, such as efficient synthesis and functionalization of the hosts with multicavity structures, synergistic and controllable complexation of the hosts with two or more guests, and their practical applications in wide research areas. We believe that these novel synthetic hosts can attract more and more attention, and their synthesis and applications will become a new and attractive research topic in both host–guest chemistry and iptycene chemistry⁵⁷ in the near future.

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Notes

The authors declare no competing financial interest.

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