

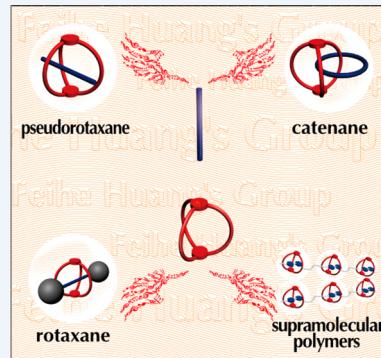
# Stimuli-Responsive Host–Guest Systems Based on the Recognition of Cryptands by Organic Guests

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**CONSPECTUS:** As the star compounds in host–guest chemistry, the syntheses of crown ethers proclaimed the birth of supramolecular chemistry. Crown ether-based host–guest systems have attracted great attention in self-assembly processes because of their good selectivity, high efficiency, and convenient responsiveness, enabling their facile application to the “bottom-up” approach for construction of functional molecular aggregates, such as artificial molecular machines, drug delivery materials, and supramolecular polymers. Cryptands, as preorganized derivatives of crown ethers, not only possess the above-mentioned properties but also have three-dimensional spatial structures and higher association constants compared with crown ethers. More importantly, the introduction of the additional arms makes cryptand-based host–guest systems responsive to more stimuli, which is crucial for the construction of adaptive or smart materials. In the past decade, we designed and synthesized crown ether-based cryptands as a new type of host for small organic guests with the purpose of greatly increasing the stabilities of the host–guest complexes and preparing mechanically interlocked structures and large supramolecular systems more efficiently while retaining or increasing their stimuli-responsiveness.



Organic molecules such as paraquat derivatives and secondary ammonium salts have been widely used in the fabrication of functional supramolecular aggregates. Many host molecules including crown ethers, cyclodextrins, calixarenes, cucurbiturils, pillararenes, and cryptands have been used in the preparation of self-assembled structures with these guest molecules, but among them cryptands exhibit the best stabilities with paraquat derivatives in organic solvents due to their preorganization and additional and optimized binding sites. They enable the construction of sophisticated molecules or supramolecules in high yields, affording a very efficient way to fabricate stimuli-responsive functional supramolecular systems.

This Account mainly focuses on the application of cryptands in the construction of mechanically interlocked molecules such as rotaxanes and catenanes, and stimuli-responsive host–guest systems such as molecular switches and supramolecular polymers due to their good host–guest properties. These cryptands are bicyclic derivatives of crown ethers, including dibenzo-24-crown-8, bis(*m*-phenylene)-26-crown-8, dibenzo-30-crown-10, and bis(*m*-phenylene)-32-crown-10. The length of the third arm has a very important influence on the binding strength of these cryptands with organic guests, because it affects not only the size fit between the host and the guest but also the distances and angles that govern the strengths of the noncovalent interactions between the host and the guest. For example, for bis(*m*-phenylene)-32-crown-10-based cryptands, a third arm of nine atoms is the best. The environmental responsiveness of these cryptand-based host–guest systems arises from either the crown ether units or the third arms. For example, a dibenzo-24-crown-8 unit introduces potassium cation responsiveness and an azobenzene group on the third arm imbues photoresponsiveness. We believe that studies on stimuli-responsive host–guest systems based on cryptands and organic guests will contribute significantly to future research on molecular devices, supramolecular polymers, and other functional supramolecular materials.

## INTRODUCTION

The development of supramolecular chemistry expanded the research objectives of chemists from molecules to molecular aggregates, consistent with the aim of the “bottom-up” approach.<sup>1</sup> Host–guest systems play a significant role in the development of advanced supramolecular materials because of their good selectivity, high efficiency, and responsiveness. As the first-generation of hosts in host–guest chemistry, crown ethers have been widely used in various areas such as artificial molecular machines,<sup>2–5</sup> drug delivery materials,<sup>6</sup> and supramolecular polymers.<sup>7–16</sup>

In order to increase association constants for the efficient preparation of host–guest complexes, three-dimensional cryptands were introduced as a new type of hosts. Park and Simmons reported a diazabicyclic “katapinand” in 1968, and this is considered to be the first cryptand.<sup>17</sup> The word “cryptand” was introduced by Lehn and co-workers to describe bicyclic ligands.<sup>18</sup> The association constants ( $K_a$ ) of crown

Special Issue: Responsive Host–Guest Systems

Received: February 1, 2014

Published: May 8, 2014

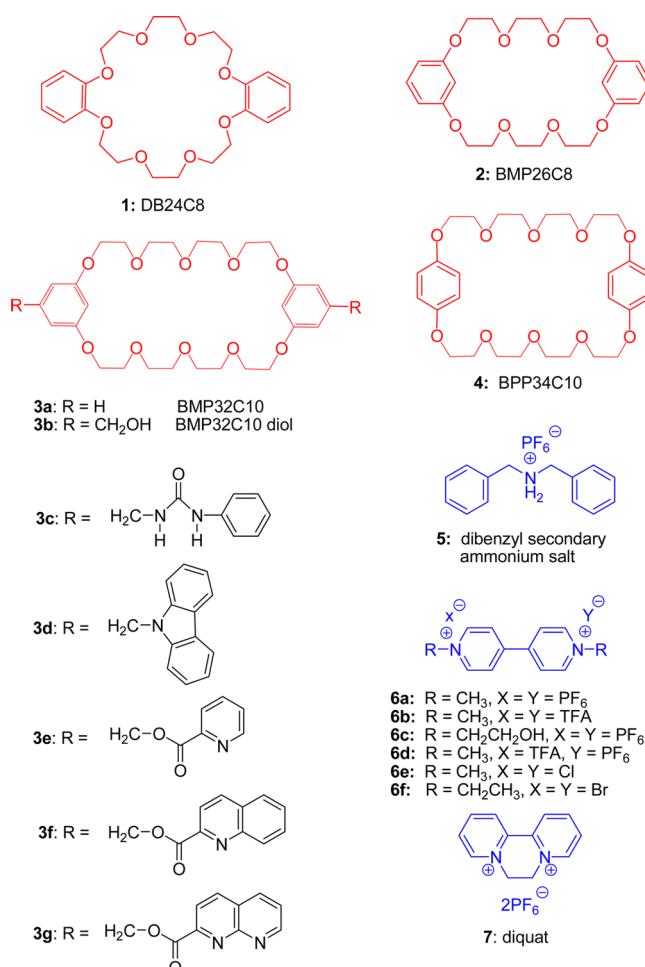
ether-based cryptands can be  $10^3$ – $10^4$  times higher than those of their analogous crown ethers due to the preorganization of their structures and additional binding sites.

Herein, we describe crown ether-based cryptands as a family of hosts that possess enormously increased host–guest association constants and enable facile formation of pseudo-rotaxanes, rotaxanes, catenanes, molecular switches, and supramolecular polymers. The common noncovalent interactions between these cryptands and their organic guests include hydrogen bonding, charge transfer,  $\pi$ – $\pi$  stacking, and C–H… $\pi$  interactions.

## PSEUDOROTAXANES

Pseudorotaxanes, self-assembled structures in which ring components are threaded onto axles, are precursors for rotaxanes and catenanes. Simple crown ethers form responsive complexes with small organic guests, and some of them exhibit pseudorotaxane-type geometries. For example, dibenzo-24-crown-8 (DB24C8, 1) forms pH-responsive pseudorotaxanes with secondary ammonium salts<sup>19</sup> (e.g., 5) and 2:1 inclusion complexes with paraquat (*N,N'*-dimethyl-4,4'-bipyridinium, 6a) and diquat (1,1'-ethylene-2,2'-bipyridinium, 7).<sup>20,21</sup> The complexation between bis(*m*-phenylene)-26-crown-8 (BMP26C8, 2) and paraquat is not K<sup>+</sup>-responsive, but a BMP26C8-based lariat ether displays K<sup>+</sup>-responsive binding affinities with paraquat derivatives.<sup>22,23</sup> Bis(*m*-phenylene)-32-crown-10 (BMP32C10) derivatives,<sup>24</sup> such as 3a and 3b, exhibit redox-responsive binding affinities with paraquat derivatives and diquat 7, but in the solid state, the complexes are found to be mostly sandwich-type structures (“taco complexes”), in which the guest molecules are enveloped within the folded host.<sup>25,26</sup> Two exceptions reported to date involve paraquat salts 6b and 6a that form pseudorotaxanes with the urea derivative 3c and the biscarbazyl derivative 3d, respectively.<sup>27,28</sup> Bis(*p*-phenylene)-34-crown-10 (BPP34C10, 4) forms pseudorotaxanes with paraquat derivatives.<sup>29</sup>

Mechanically interlocked structures have been widely constructed based on the above-mentioned recognition motifs.<sup>15,30,31</sup> Functionalization is required to prepare homoditopic hosts or heteroditopic analogues; the introduction of a substituent on bis(*p*-phenylene) or bis(*o*-phenylene) crown ethers renders them axially unsymmetric, and difunctional analogues are produced as mixtures of regioisomers, resulting in lower yields of purified products. The lower symmetry of such difunctional hosts can lead to stereoisomers in the fabrication of complicated systems, limiting further applications of these recognition motifs.<sup>23</sup> This is not an issue with bis(*m*-phenylene) crown ethers, since substitution conveniently takes place at the 5-position(s) of the aromatic rings, preserving the axial symmetry of the hosts. However, complexes of bis(*m*-phenylene) crown ethers often form taco complex geometries with paraquat derivatives,<sup>25,26,32</sup> limiting their application in the construction of mechanically interlocked structures. Moreover, the association constants of the crown ether-based systems are often less than  $10^3$  M<sup>-1</sup> (Table 1); these are not strong enough



for the efficient preparation of many complicated supramolecular systems. It can be concluded that hosts with not only better affinities for useful organic guests but also pseudorotaxane-type geometries of the host–guest complexes and without symmetry-related isomeric problems should be synthesized and applied to construct functional host–guest systems.

Inspired by the folded structures of the complexes based on BMP32C10 derivatives, we synthesized a BMP32C10-based cryptand (8a) in 1999.<sup>32</sup> This cryptand exhibits good binding affinities with paraquat derivatives; the association constant of complex 8a $\square$ 6a is  $6.1 \times 10^4$  M<sup>-1</sup>, 100-fold greater than that of complex 3a $\square$ 6a. This increase was demonstrated to be purely due to preorganization; the enthalpy terms for complexation by the crown ether and the cryptand were exactly the same, but the entropic penalty with the latter was significantly reduced.<sup>33</sup> More importantly, the complex 8a $\square$ 6a exhibits “pseudorotaxane-like” geometry in the solid state, which is crucial for the construction of mechanically bonded systems, especially for molecular machines. X-ray crystallographic analysis indicates that complexation is primarily driven by interactions of the hydrogens of the guest with ether oxygen atoms of the host and  $\pi$ -stacking charge transfer between the aromatic moieties.

Later, we synthesized cryptands from different crown ethers (DB24C8, BMP26C8, dibenzo-30-crown-10, and BMP32C10) and with different third arms.<sup>22,33–41</sup> Their paraquat complexes exhibit the following common characteristics: (1) they are all yellow-orange due to the charge transfer interactions between the electron-rich aromatic rings of the cryptands and the

**Table 1. Association Constants for Complexes of Crown Ethers with Organic Guests in Acetone at Room Temperature**

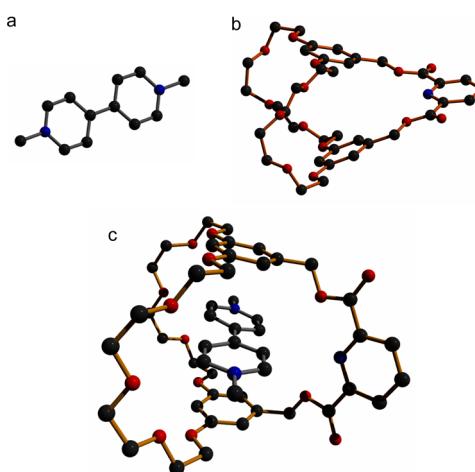
	1 $\square$ 5	2 $\square$ 6a	3a $\square$ 6a	4 $\square$ 6a
$K_a \times 10^{-2}$ (M <sup>-1</sup> )	3.6 <sup>19</sup>	3.9 <sup>22</sup>	5.5 <sup>22</sup>	7.3 <sup>29</sup>

electron-poor pyridinium rings of paraquat derivatives; (2) they display 1:1 stoichiometry in solution; (3) they are fast-exchanging systems on the  $^1\text{H}$  NMR time scale at room temperature; (4) they display higher  $K_a$ 's than the corresponding crown ethers (Tables 1 and 2). The BMP32C10-based

**Table 2. Association Constants for Complexes of Cryptands with Paraquat Derivatives in Acetone at Room Temperature**

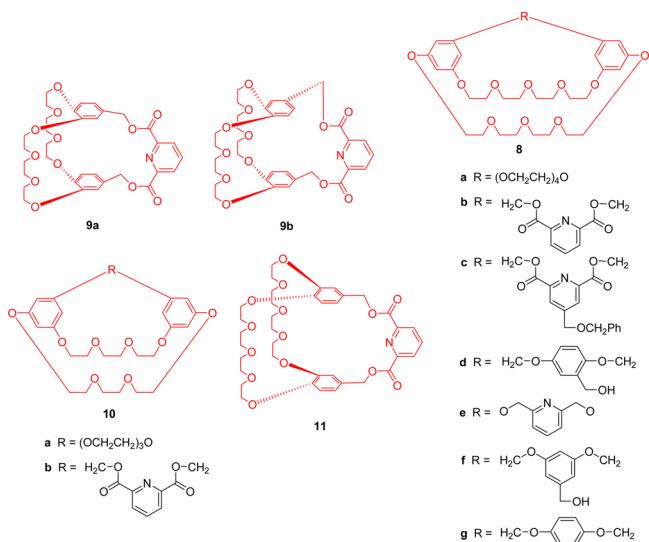
	8a $\supset$ 6a	8b $\supset$ 6a	9a $\supset$ 6c	10a $\supset$ 6a	10b $\supset$ 6a	11 $\supset$ 6a
$K_a \times 10^{-5} (\text{M}^{-1})$	0.61 <sup>32</sup>	50 <sup>33</sup>	0.10 <sup>37</sup>	0.14 <sup>22</sup>	6.5 <sup>40</sup>	2.0 <sup>39</sup>

cryptand **8b** exhibits the highest association constant with paraquat,  $5.0 \times 10^6 \text{ M}^{-1}$ , 9000 times greater than that of BMP32C10.<sup>33</sup> By comparison of the crystal structures (Figure 1) and the thermodynamic parameters of these cryptand-based



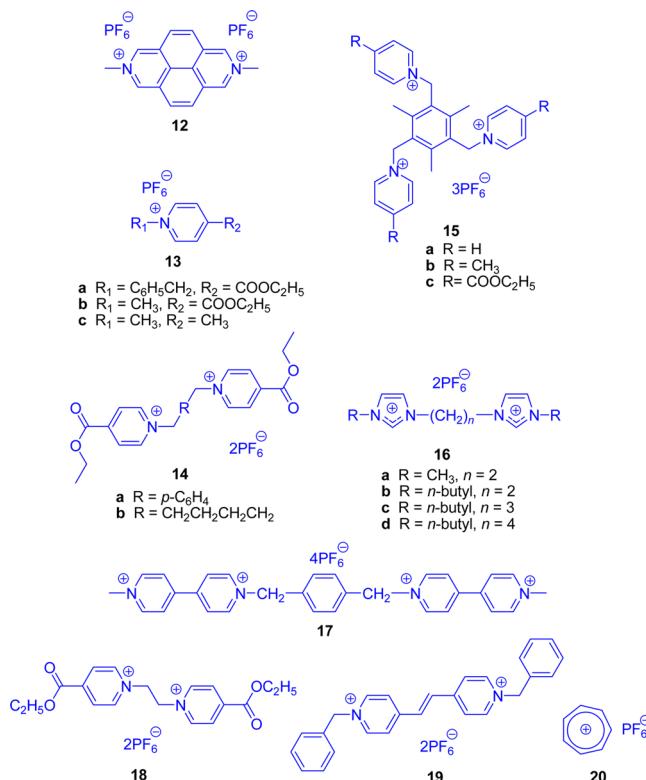
**Figure 1.** Crystal structures of (a) **6a**, (b) **8b**, and (c) **8b** $\supset$ **6a**.<sup>33</sup>

complexes with crown ether-based complexes, we concluded that the improvement in complexation was the result of the combination of the preorganization of the cryptand and the introduction of additional or optimized binding sites, including interactions of the pyridyl nitrogen on the third arm with hydrogens of the guest.<sup>30</sup>



In cryptand complexes, we mainly focused on paraquat-based systems not only because they are widely used precursors for

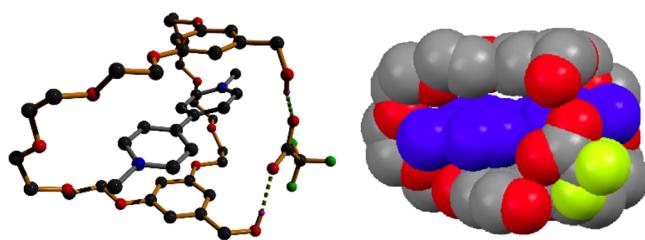
the construction of rotaxanes, catenanes, and even metal–organic frameworks but also because their interesting redox properties make them good building blocks for molecular machines, nanocontainers, and molecular devices. Cryptands are also wonderful hosts for other organic guests such as diquat (**7**)<sup>39,42,43</sup> diazapyridinium (**12**)<sup>44</sup> monopyridinium (**13**)<sup>45</sup> bispyridinium (**14**)<sup>46</sup> trispyridinium (**15**)<sup>47</sup> bisimidazolium (**16**)<sup>48</sup> bisparaquat (**17**)<sup>49</sup> 1,2-bis(pyridinium)ethane (**18**)<sup>50</sup> vinylogenous viologen (**19**)<sup>51</sup> and tropylium salts (**20**).<sup>52</sup> Due to the preorganization and additional or optimized binding sites, the cryptand complexes all display better stabilities than the corresponding simple crown ether-based analogues.



## PSEUDOCRYPTANDS

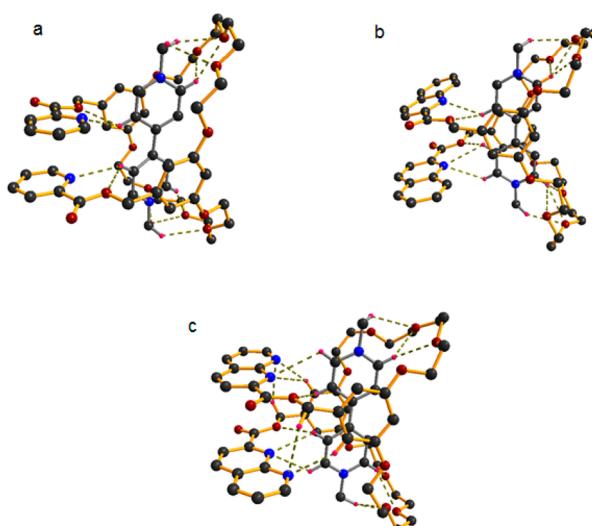
Nabeshima designed pseudocryptands whose third ring closure took place via metal coordination.<sup>53</sup> Considering that the complexation of paraquat by BMP32C10 derivatives involved folding to allow donor–acceptor interactions of the aromatic moieties, we sought ways to reinforce the folding by introducing noncovalent interactions between the “ends” of the crown ether host. The first demonstration of this concept was the 14-fold increase in  $K_a$  upon addition of 2.35 equiv of tetrabutylammonium trifluoroacetate to a 2.00 mM equimolar acetone solution of BMP32C10 diol **3b** and paraquat **6a**. Indeed, the X-ray crystal structure proved that the additional stability of the complex resulted from binding the two hydroxyl groups of the host by the bidentate trifluoroacetate anion, thus closing the third “pseudo-ring” of the host and forming a pseudocryptand (Figure 2).<sup>54</sup> The tosylate anion provided a similar but less dramatic increase in binding ability. Subsequently we found that adventitious water also served to tie the two hydroxyl groups of diol **3b** together, forming a pseudocryptand, in its complex with a bisammonium salt.<sup>55</sup>

Continuing along these lines, we explored a different noncovalent interaction to bring about formation of pseudo-



**Figure 2.** Crystal structure of  $3b\supset D6d$ . (left) Ball and stick representation; the two O···H bonds are 1.81 and 1.98 Å long. (right) Space filling representation; the guest is blue.

cryptands, namely  $\pi$ -stacking. These studies focused on simple ester derivatives **3e**, **3f**, and **3g** as hosts for paraquat **6a**.<sup>28,56</sup> These esters are available in nearly quantitative yields from diol **3b**. In the X-ray crystal structure of  $3e\supset D6a$  (Figure 3a), the



**Figure 3.** X-ray crystal structures of (a)  $3e\supset D6a$ , (b)  $3f\supset D6a$ , and (c)  $3g\supset D6a$ .

pyridyl rings were observed to be stacked, and moreover the nitrogen atoms interacted with the  $\beta$ -pyridinium hydrogens of the guest, leading to an 8-fold increase in  $K_a$  relative to unsubstituted host **3a**. Reasoning that a larger  $\pi$ -system would result in further stabilization of the complex, we prepared the quinaldate diester **3f**, and it displayed a 31-fold increase in  $K_a$  relative to unsubstituted host **3a**. The crystal structure of  $3f\supset D6a$  (Figure 3b) confirmed interactions of the nitrogen atoms with the guest and the stacking of the quinoline rings, but demonstrated a short distance between the hydrogen atom connected to the 8-carbon of the quinoline ring and  $\beta$ -hydrogens of **6a**. Clearly, the replacement of the 8-carbon of the quinoline ring with a hydrogen bond acceptor would not only remove the repulsive interaction but also lead to the formation of extra hydrogen bonds to stabilize the resulting complex further. Thus, naphthyridine rings were introduced, and the resulting **3g** provided a  $K_a$  value of  $2.5 \times 10^5 \text{ M}^{-1}$ , 625-fold higher than that of **3a**. The crystal structure of  $3g\supset D6a$  (Figure 3c) reveals the additional interactions of the second nitrogen of the naphthyridine moiety and the near parallel (off by  $5.4^\circ$ ) orientation of the two heterocyclic nuclei. The resulting high  $K_a$  value rivals those of some covalent cryptands (Table 2).

## ■ ROTAXANES AND CATENANES

The strong binding of cryptands with paraquat derivatives makes it possible to prepare rotaxanes and catenanes with high efficiency. Using a threading-followed-by-stoppering method, we prepared cryptand/paraquat rotaxanes in high yields.<sup>57–59</sup> The yield of [2]rotaxane **22** from cryptand **8a** was 92% (Scheme 1),<sup>57</sup> significantly higher than the 6% yield observed with its corresponding crown ether **3a**.<sup>60</sup> More importantly, [3]rotaxane **24** was also synthesized with high efficiency (86%) even in dilute solutions<sup>58</sup> with no [2]rotaxane as byproduct due to the cooperative complexation of cryptands with bisparaquat derivatives (Scheme 1),<sup>49</sup> affording a convenient approach to [n]rotaxanes and mechanically interlocked supramolecular polymers.

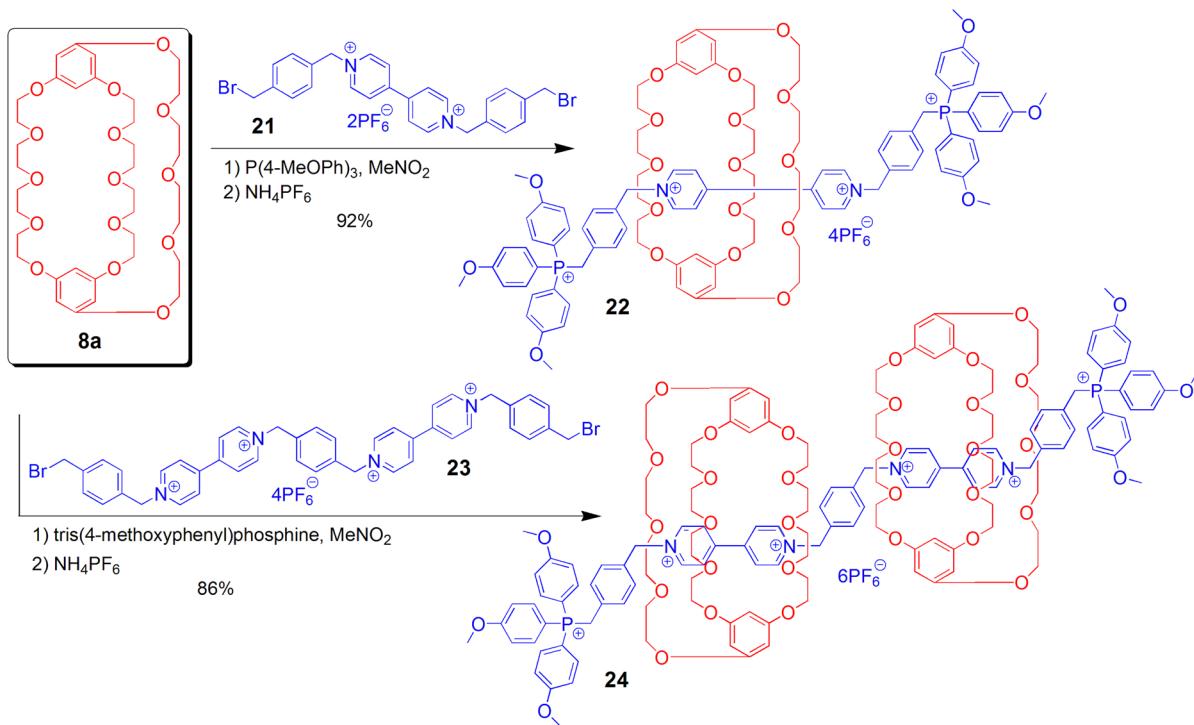
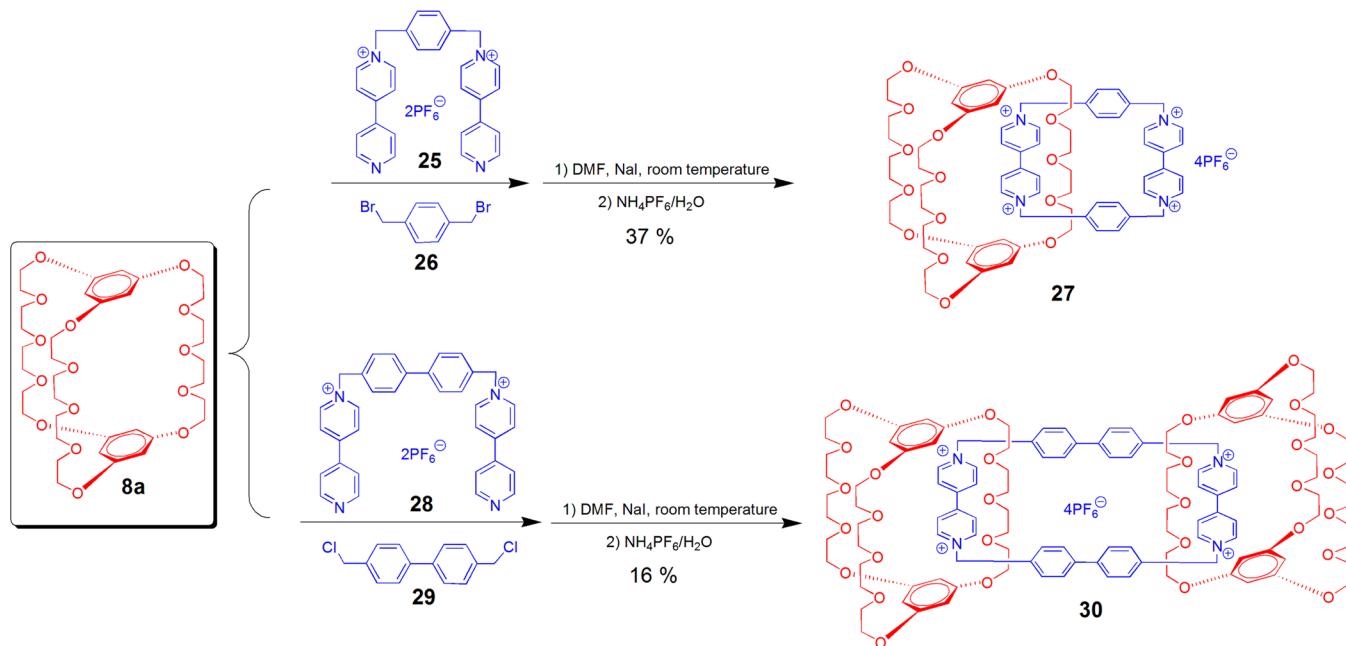
The immediate solvent evaporation method (ISEM) can be applied in the construction of [2]rotaxanes to accelerate the reaction process.<sup>61</sup> This was realized using BMP26C8-based cryptand **10b** as the host.<sup>40</sup> The yields reached 81%, which are very attractive for rotaxane syntheses. Based on the good cryptand/paraquat and cryptand/trispyridinium recognition motifs, Liu et al. developed an excellent one-pot [2 + 3] clipping method to obtain cryptands and their related [2]rotaxanes through 6-fold imine bond formation.<sup>62,63</sup>

Catenanes were also prepared based on the cryptand/paraquat recognition motifs. With **8a** as a building block, a [2]catenane (**27**) and a [3]catenane (**30**) were successfully synthesized in 37% and 16% yields, respectively, higher than those with simple cyclophanes (Scheme 2).<sup>64</sup> Similarly, two [2]catenanes were synthesized in 31% and 25% yields by using **9a** and **10b** as the host molecules, respectively.<sup>65</sup> These studies gave useful information for the future construction of polyrotaxanes and polycatenanes.

Based on the taco complex templates of BMP32C10 and paraquat derivatives, a [2]rotaxane (**31**) and a [2]catenane (**32**) were prepared by olefin metathesis in yields of 90% and 85%,<sup>66</sup> respectively. A nearly quantitative yield was achieved when the amine/aldehyde dynamic clipping methodology was used (Scheme 3).<sup>67</sup> This protocol provided an effective synthetic method to avoid the above-mentioned symmetry-based problem encountered using difunctionalized bis(*p*-phenylene) or bis(*o*-phenylene) crown ethers.

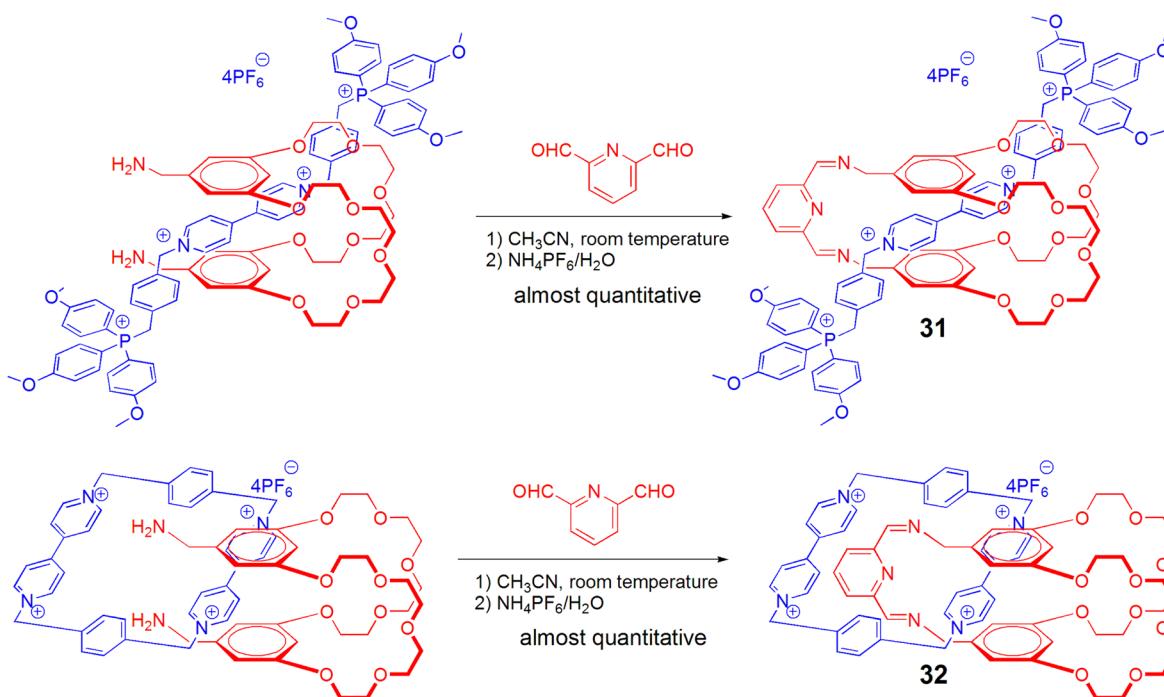
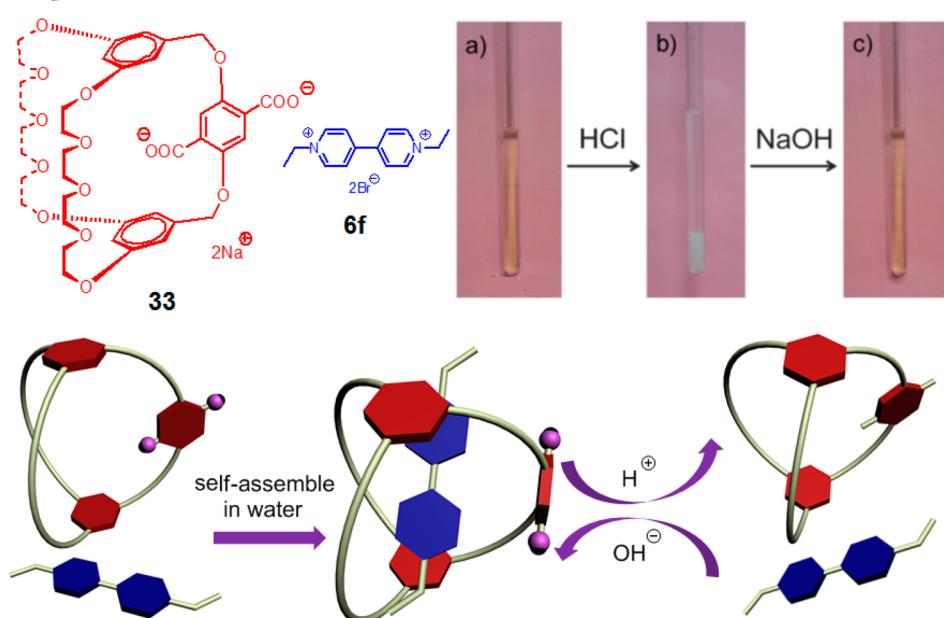
## ■ MOLECULAR SWITCHES

Molecular switches are molecules that can be reversibly shifted between two or more stable states.<sup>2</sup> Threaded structures, such as pseudorotaxanes, rotaxanes, and catenanes, are excellent candidates to construct molecular switches, because the interactions between components in these systems are easily broken and recreated by external stimuli, causing relative movement of the components. We synthesized a water-soluble cryptand **33** by attaching two carboxylate groups to the third arm.<sup>68</sup> Cryptand **33** forms a stable complex with paraquat derivative **6f** in water (Scheme 4, panel a). When the carboxylate groups were converted to their neutral form by adding aqueous HCl, the cryptand precipitated, and the complex was disassembled (Scheme 4, panel b). The reverse process was induced by adding 1 equiv of NaOH (Scheme 4, panel c). This molecular switch can be monitored visually since the yellow color of the complex disappeared and reappeared repeatedly upon addition of acid and then base, demonstrating a functional aqueous supramolecular system.

Scheme 1. Syntheses of Cryptand-Based [2]Rotaxane 22 and [3]Rotaxane 24<sup>57,58</sup>Scheme 2. Syntheses of [2]Catenane 27 and [3]Catenane 30 Based on the Cryptand/Paraquat Recognition Motif<sup>64</sup>

A dual-responsive host–guest system based on a complex between a bis(1,2,3-phenylene) cryptand **34** and paraquat **6a** (Scheme 5) was developed.<sup>69</sup> This complex exhibits taco complex geometry, different from the pseudorotaxanes formed by other cryptands.<sup>30,32–41</sup> Due to the rigidity of the third arm, proper organization of the cryptand is difficult to achieve, so the association constant of complex **34**–**6a** ( $2.2 \times 10^3 \text{ M}^{-1}$ ) is only a little higher than that of **3a**–**6a** ( $9.2 \times 10^2 \text{ M}^{-1}$ ) in chloroform/acetonitrile (v/v = 1:1), benefiting from the introduction of additional binding sites. The complex **34**–**6a** exhibits pH-responsiveness due to the protonation (by adding

trifluoroacetic acid) and deprotonation (by adding triethylamine) of the pyridyl nitrogen on the third arm. In addition, the introduction of a seven-atom third chain divides the BMP32C10 cavity into two asymmetric 24-crown-8 cavities, endowing the complex **34**–**6a** with K<sup>+</sup>-responsive ability (upon adding and removing KPF<sub>6</sub>). Although the association constant of complex **34**–**6a** is not very high, this dual-responsive binding system informs the design of advanced functional supramolecular systems such as molecular logic gates and molecular machines. The K<sup>+</sup>-responsiveness was also found in other

Scheme 3. Taco Complex Templated Dynamic Clipping Syntheses of [2]Rotaxane 31 and [2]Catenane 32<sup>67</sup>Scheme 4. Cartoon Representation of a Water-Soluble Molecular Switch<sup>68a</sup>

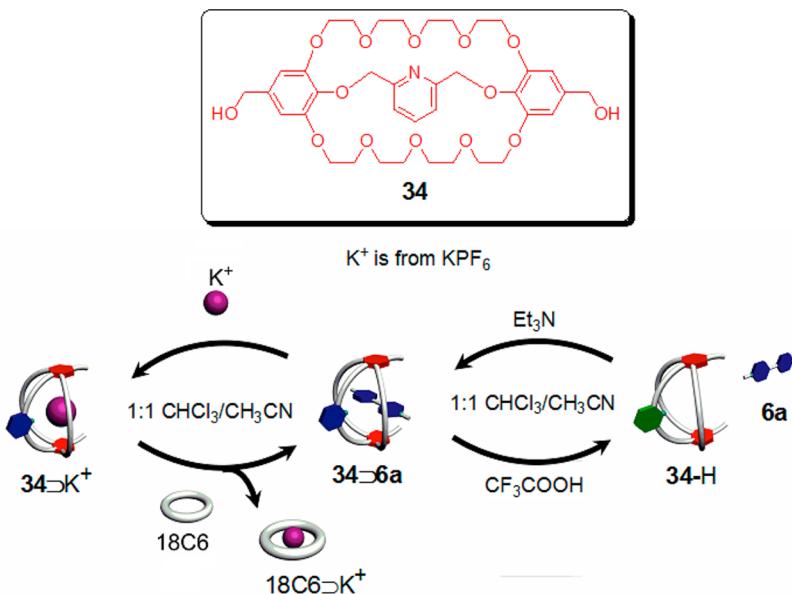
Adapted with permission from ref 68. Copyright 2013 Royal Society of Chemistry. <sup>a</sup>The precipitate (panel b) was the insoluble protonated cryptand.

cryptand-based host–guest systems when different guests were used.<sup>37,50,51</sup>

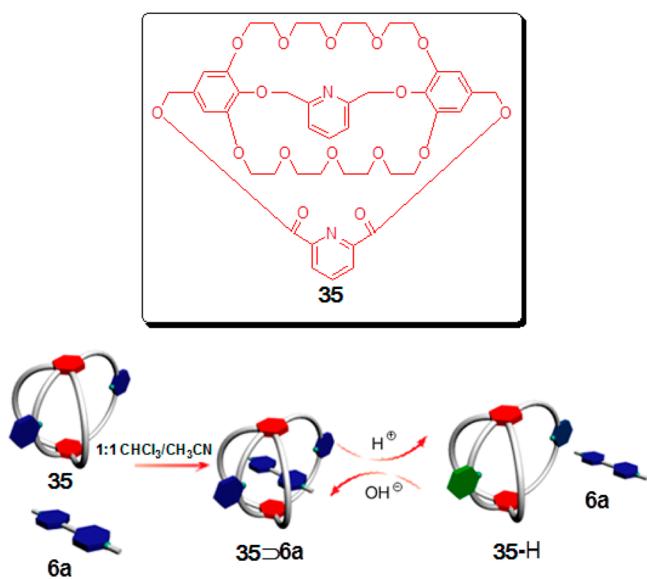
A four-armed cage molecule (**35**)<sup>70</sup> (Scheme 6) was also synthesized. We studied the association constant differences from crown ethers to cryptands and then to the four-armed cage molecule and found that binding sites and proper host cavity size are both very important to produce macrocyclic hosts with high binding affinities. For the BMP32C10-based cage molecules, a fourth arm with more than seven atoms was required to get better binding affinities with paraquat **6a** than that of **8b**–**6a**, with the highest reported association constant for cryptand/paraquat-based systems so far.<sup>30,33</sup> More

importantly, the complex **35**–**6a** can be easily disassembled/reassembled by acid/base, making this recognition motif useful in the construction of molecular machines and stimuli-responsive supramolecular polymers.

By introduction of an azobenzene moiety in the third arm of a BMP32C10-based cryptand, photoresponsive cryptand **36** was synthesized and a photodriven molecular switch was constructed (Scheme 7).<sup>71</sup> The azobenzene exhibits a *trans*-conformation initially, and the cryptand does not bind the 2,7-diazapyrenium salt **12** due to its relatively small cavity size. However, the azobenzene changes its conformation to *cis* upon irradiation with UV light, and then the cryptand exhibits good

Scheme 5. Cartoon Representations of a Dual-Responsive Molecular Switch<sup>69</sup>

Adapted with permission from ref 69. Copyright 2010 John Wiley and Sons, Inc.

Scheme 6. Chemical Structure of Four-Armed Cage Molecule 35 and Its Acid/Base Controllable Complexation with Paraquat 6a<sup>70</sup>

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binding affinity for guest 12. The reverse process can be induced by irradiation with visible light or by heat, causing the dissociation of complex *cis*-36 $\supset$ 12. This photoresponsive host-guest recognition motif can be used in the fabrication of more complicated photodriven molecular machines, which can be monitored by the change in fluorescence intensity of guest 12. The smaller paraquat guest 6a forms complexes with both the *cis*- and *trans*-azobenzene isomers of cryptand host 36.

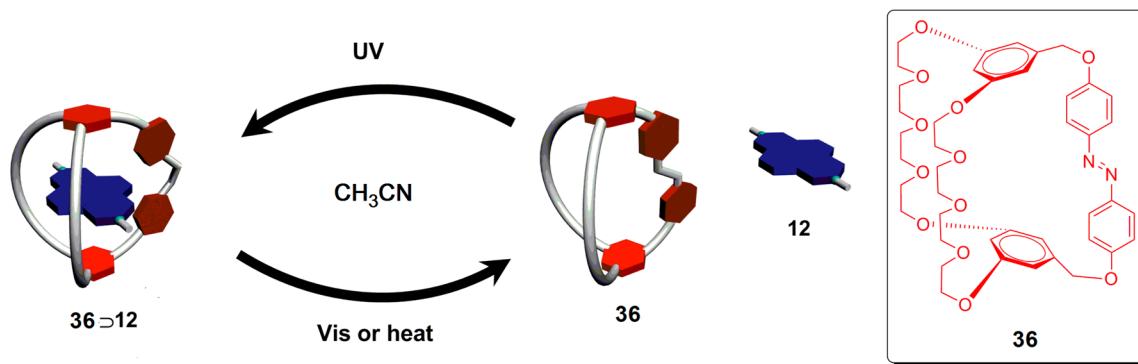
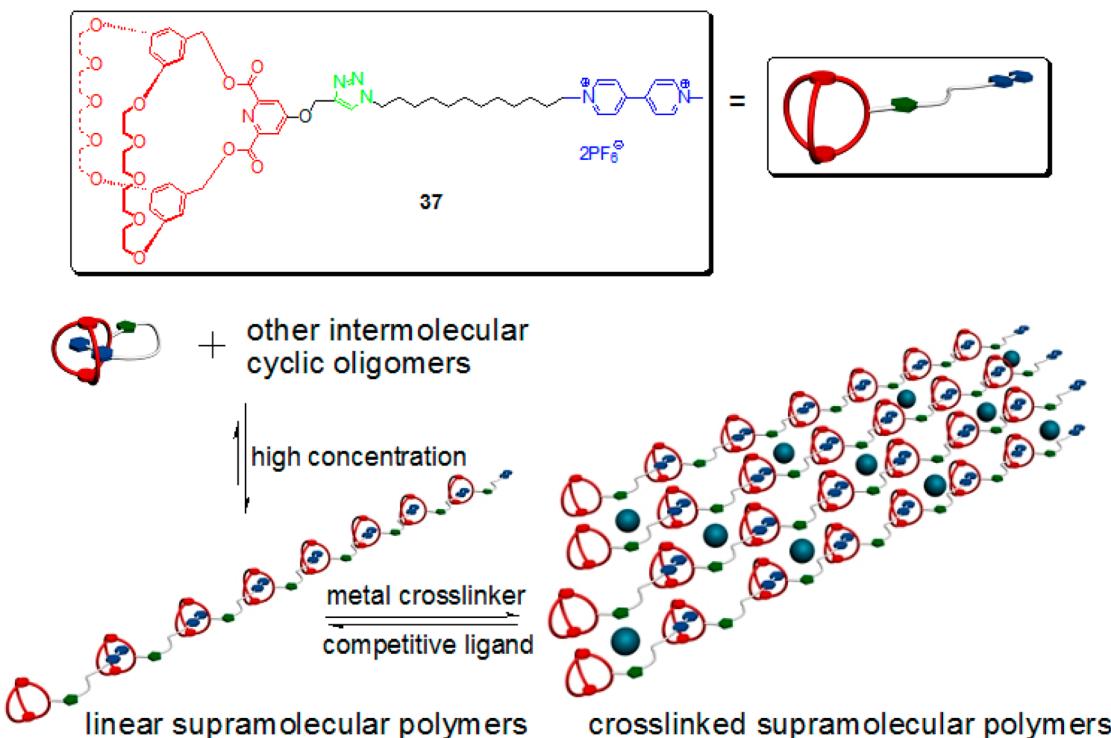
## SUPRAMOLECULAR POLYMERS

Supramolecular polymers are polymeric arrays of low molecular weight monomeric units held together by reversible non-

covalent interactions.<sup>72</sup> They combine good material properties with low-viscosity melts, providing them with some interesting properties that conventional polymers can not reach, such as stimuli-responsiveness, self-healing, and shape memory. The advantages of cryptand-based pseudorotaxane supramolecular polymers include (1) high binding constants that result in high degrees of polymerization and (2) the ability to be converted to rotaxane units, mechanically locking in the molecular recognition sites and producing a stimuli-responsive macromolecule. While other hydrogen bonding-based systems can achieve high degrees of polymerization, they cannot be converted to permanently linked structures. Other host-guest systems do not generally possess high enough binding constants to produce high degrees of polymerization.

Complementary host 8b and guest 6a were linked together by a copper(I)-catalyzed 1,3-dipolar click cycloaddition reaction, forming heteroditopic monomer 37 (Scheme 8).<sup>73</sup> A linear supramolecular polymer resulted from the self-organization of 37 in acetonitrile when the concentration exceeded its critical polymerization concentration (75 mM); below that concentration cyclic oligomers, primarily the dimer, predominate. Moreover, the topology of the supramolecular polymer can be altered from linear to cross-linked by adding PdCl<sub>2</sub>(PhCN)<sub>2</sub> to link the 1,2,3-trizole units, which can be reversed by adding a competitive PPh<sub>3</sub> ligand. Cryptand-based monomer 37 formed larger polymeric aggregates than the corresponding crown ether-based monomer owing to its higher association constant. This study provided an alternative method for topological control and stimuli-responsiveness of macromolecules, enabling the construction of smart materials.

We also designed two cryptand-based monomers, 38a and 38b, one with a covalent linkage and the other with a metal-complex linkage. By self-assembly of these cryptand AA monomers with a bisparaquat BB monomer (39), linear supramolecular polymers were prepared with relatively high molecular weights (Scheme 9).<sup>74</sup> For example, at 290 mM of 38a and 39, the degree of polymerization (*n*) was calculated to be  $93 \pm 47$ , indicating a number-average molecular weight

Scheme 7. Chemical Structure of Cryptand 36 and Cartoon Representation of a Photoresponsive Molecular Switch<sup>71</sup>Scheme 8. Chemical Structure and Cartoon Representation of Heteroditopic Monomer 37 (above) and Topology Control (below)<sup>73</sup>

Adapted with permission from ref 73. Copyright 2010 John Wiley and Sons, Inc.

( $M_n$ ) of 241 kDa, much higher than that of the similar crown ether-based systems. Because of entanglements resulting from the large macromolecules, long thin fibers were easily drawn and films were cast from concentrated solutions of monomers 38 and 39. These concepts are now being extended to biscryptands based on analogues of hosts 11 and 8b, which have been functionalized and linked via the 4-positions of the pyridyl moieties.

## ■ CONCLUSIONS AND OUTLOOK

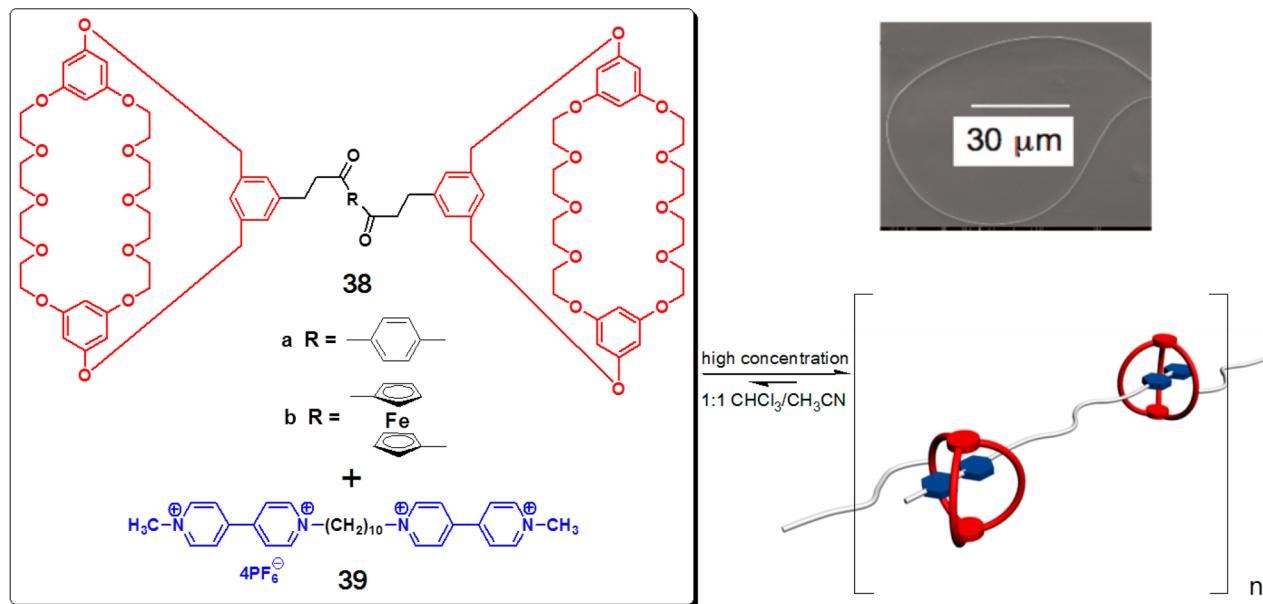
We have devoted more than 10 years to the study of recognition of crown ethers by organic guests and developed cryptands as a new type of hosts, greatly increasing the host–guest association constants. Various self-assembled structures such as pseudorotaxanes, rotaxanes, catenanes, molecular switches, and supramolecular polymers with different functions have been constructed efficiently using the cryptand-based

recognition motifs, indicating the unmatched advantages of this family of versatile hosts.

The development of molecular self-assembly is one of the most important topics in chemistry. It benefits greatly from research on host–guest recognition motifs, since different binding properties and different interaction mechanisms enrich the scope of supramolecular chemistry and can be applied in various fields, not only in chemistry but also in biology, computing, materials, and so on. Cryptand-based host–guest recognition motifs play a significant role in advancing supramolecular chemistry and stimuli-responsive self-assembly research.

We have made significant progress in the use of cryptand-based self-assembly, but we are still in the early days, and there are still challenges, such as the development of a broader range of organic molecules as guests and the design of even more effective cryptand and pseudocryptand hosts, the design of

**Scheme 9. Chemical Structures and Cartoon Representation of Self-Assembly of Homoditopic Monomeric Hosts 38a and 38b with Homoditopic Guest 39 To Form Linear Supramolecular Polymers and SEM micrograph of a Fiber Drawn from a Concentrated Solution of Equimolar 38a and 39<sup>74</sup>**



biologically compatible structures, and the applications of these systems in the construction of molecular devices and smart materials. For us, it is a continuing and exciting journey, but for this Account, it represents the end of our summary of the situation as it currently exists.

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### Funding

The work described herein was supported by the National Science Foundation (USA, Grants CHE-0521738, DMR-DMR-0097126, and DMR-0704076), the Petroleum Research Fund administered by the American Chemical Society (Grants 33518-AC7, 40223-AC7 and 47644-AC7), National Basic Research Program (Grant 2013CB834502), and the National Natural Science Foundation of China (Grant 21125417).

### Notes

The authors declare no competing financial interest.

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**Feihe Huang** was born in China in 1973. He obtained his Ph.D. in Chemistry from Virginia Polytechnic Institute and State University (VT) under the guidance of Prof. Harry W. Gibson in March 2005. Then he joined in Prof. Peter J. Stang's group at University of Utah as a postdoctoral researcher. He became a Professor of Chemistry at Zhejiang University in December 2005. His current research interests are supramolecular polymers and pillararene supramolecular chemistry.

**Zhenbin Niu** was born in China in 1980. In 2005 he enrolled at VT and joined the group of Harry W. Gibson to pursue his Ph.D. In 2011, he joined Prof. Stephen L. Craig's group at Duke University as a postdoctoral researcher. His current interests include mechanically responsive polymer materials, medical hydrogels, and the syntheses and applications of cryptands and pseudocryptands in self-assembly processes.

**Harry W. Gibson** (b. Syracuse, NY, USA, 1941) obtained his B.S. in Chemistry (1962) and his Ph.D. in Organic Chemistry (1965), both at Clarkson University, under the supervision of Prof. Frank D. Popp. After a postdoctoral experience with Prof. Ernest L. Eliel at the University of Notre Dame, in 1966 he joined Union Carbide Corporation. In 1969 he moved to the Xerox Corporation. He left in 1984 to join the Signal Corporation. He has been Professor of Chemistry at Virginia Tech since 1986. Since 2006, he has been a Guest Professor at Zhejiang University. His research interests include self-assembly processes of small molecules and polymers and ionic liquids as components of functional polymers.

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