

# Construction and Function of Interpenetrated Molecules Based on the Positively Charged Axle Components

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**Abstract:** Interpenetrated molecules have attracted increasing attention from chemists not only because of their intriguing architectures and topologies, but also as a result of potential applications in molecular machinery and nanotechnology. In this account we review recent efforts on the construction of interpenetrated molecules based on the molecular recognition toward some positively charged axle components in aqueous or organic medium. We mainly focus on guest molecules containing ammonium, anilinium, and pyridinium groups. The host molecules are cucurbiturils and crown ethers.

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**Key words:** self-assembly, supramolecular chemistry, crown compounds, nanotechnology, interpenetrated molecules

## 1 Introduction

To learn from the principles of natural biological system and facilitate our understanding and utilization of non-covalent interactions, supramolecular chemistry has developed for more than 30 years as a systematic discipline.<sup>1</sup> The field has involved basic research toward the synthesis and properties of host compounds and the construction of novel supramolecular assemblies with intriguing architectures and topologies. Along with the development of technology and increases in social demand, chemists have gradually paid more attention to the implementation of various functions and the application in biological and/or material science of accurately predesigned host–guest systems.

Interpenetrated molecules can be regarded as one of the most important members of the family of supramolecular assemblies. Various non-covalent interactions such as hydrogen bonding,<sup>2</sup>  $\pi$ – $\pi$  stacking,<sup>3</sup> ion-dipole,<sup>4</sup> electrostatic attraction,<sup>5</sup> or metal–ligand bonds<sup>6</sup> have been used in the construction of interpenetrated species.

Interpenetrated molecules are also applied as molecular switches and machines.<sup>7</sup> As dynamic complexes, they can give a response under specific external stimuli. The response can be read through changes in the solution color, UV/Vis, fluorescence, etc. The systems can perform specific motions such as threading/dethreading in a pseudorotaxane. The stimuli can be base/acid, red/ox, light, heat, anion, competitive agents, etc. Moreover, they can offer supramolecular assistance for the synthesis of interlocked molecules that are also important in the field of nanoscience.

A variety of macrocyclic compounds such as crown ethers, cyclodextrins, calixarenes, and cucurbiturils have been developed and applied in interpenetrated molecules. Researchers often divide the interpenetrated species based on the macrocyclic hosts and search for a suitable guest for the host. However, to realize the construction of a functional system, we also need to select a host for a specific guest. Positively charged molecules have some unique advantages, such as convenience of preparation and modification, and high complex stability through multiple interactions (hydrogen bonding, ion-dipole,  $\pi$ – $\pi$  stacking). A large number of interpenetrated molecules have been constructed based on molecular recognition toward some positively charged axle components, both in aqueous and organic medium.

Herein, we mainly focus on interpenetrated species such as pseudorotaxanes, and examine their controllable formation, thermodynamic origin, application in molecular switches, DNA condensation, radical stabilization, and the synthesis of interlocked molecules such as rotaxanes, catenane, and pretzelane. Guest molecules containing ammonium, aniline, and pyridinium groups were used in our work. Suitable host compounds were crown ethers and cucurbiturils.

## 2 Interpenetrated Molecules Based on Crown Ethers

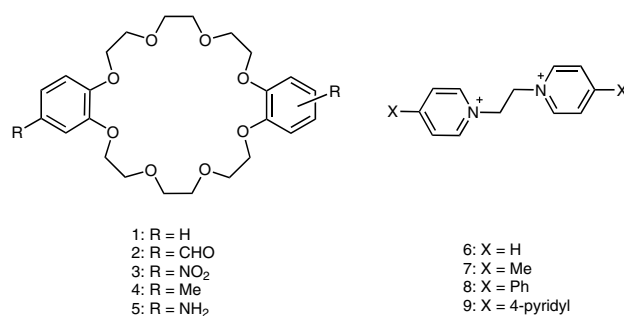
### 2.1 Thermodynamics of Resulting Complexes Between Dibenzo-24-crown-8 Derivatives and 1,2-Bis(pyridinium)ethanes

The construction of pseudorotaxanes is an important area in supramolecular chemistry. The binding behavior of pseudorotaxanes based on various host–guest pairs have been investigated widely. However, most of these studies involve  $^1\text{H}$  NMR or spectral titration. The thermodynamic origins of the behavior of pseudorotaxanes have rarely been investigated. Thus, we became interested in the binding thermodynamics of pseudorotaxanes, which were expected to help increase our understanding of assembly mechanisms during the formation of pseudorotaxanes and guide future research.

We chose the dibenzo-24-crown-8 (DB24C8) derivatives **1–5** and 1,2-bis(pyridinium)ethanes derivatives **6–9** as the target compounds (Figure 1).<sup>8</sup> 1,2-Bis(pyridinium)ethanes have been used as axle molecules to thread into the 24-crown-8 ring since Loeb et al. first reported this interesting result.<sup>9</sup> The interactions between host and guest mainly involve  $\text{N}^+\cdots\text{O}$  ion-dipole interactions,  $\text{C}\cdots\text{H}\cdots\text{O}$  hydrogen bonds between the ethylidene group and the crown ether ring, and  $\pi$ – $\pi$  stacking between the electron-deficient pyridinium and electron-rich catechol groups on the crown ether. Electron-withdrawing groups on the pyridinium ring were found to increase the stability of the pseudorotaxane. In our work, this binding behavior was comprehensively investigated by  $^1\text{H}$  NMR, UV/Vis, and isothermal titration microcalorimetry in acetonitrile. The color changes were observed only for solutions of **1–9**, **4–8**, **5–6**, and **5–7** (from colorless to light-yellow), **4–9** and **5–8** (from colorless to yellow), and **5–9** (from colorless to red),

which were consistent with the UV/Vis spectra. It can be expected that the introduction of electron-donating groups to DB24C8 and electron-withdrawing groups and/or aryl groups to 1,2-bis(pyridinium)ethane would result in efficient chromophoric behavior. Through isothermal microcalorimetric titrations, the complex stability constants were determined, which were consistent with the results obtained from the  $^1\text{H}$  NMR experiments. Moreover, the corresponding thermodynamic parameters were also obtained. Thermodynamically, the negative values of  $\Delta H^\circ$  and  $\Delta S^\circ$  in each case suggested that the formation of these complexes was an enthalpy-driven process. It was found that the nature of the substituents attached to the catechol rings in DB24C8 dramatically affected the binding thermodynamics.

Upon functionalizing **2** and **3** with electron-withdrawing groups, the binding ability was reduced. This is reasonable because the electron-cloud density of the catechol rings decreases, which weakens both the  $\pi$ -stacking and the ion-dipole interactions. Moreover, in these cases, the lower the electron-cloud density of the substituent on the



**Figure 1** Structural formulas of the DB24C8 derivatives **1–5** and *para*-substituted 1,2-bis(pyridinium)ethane hexafluorophosphate salts **6–9**

### Biographical Sketches



**Zhi-Jun Zhang** was born in Shanxi, China in 1985. He received his B.Sc. (2007) in Chemistry from Nankai University, Tianjin. He is

currently a PhD student in Professor Yu Liu's group in the Department of Chemistry at the Nankai University. His research is focused on

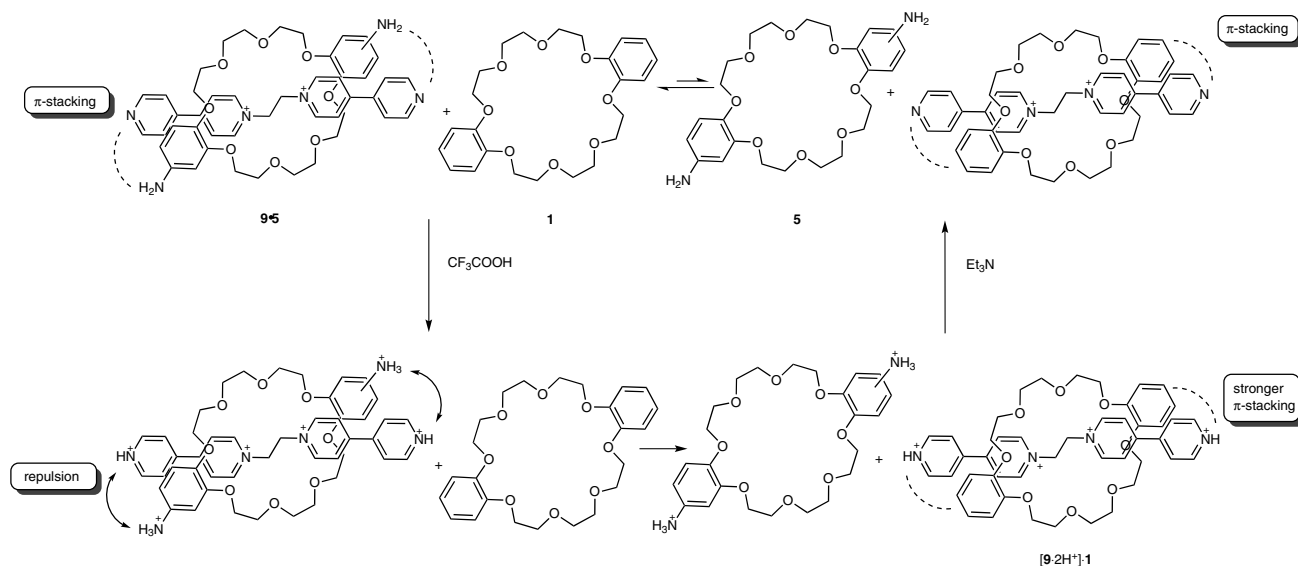
the construction of interpenetrated and interlocked molecules based on macrocyclic compounds.



**Prof. Dr. Yu Liu** graduated from the University of Science and Technology of China in 1977, and received his PhD degree from Himeji Institute of Technology, Japan, in 1991. In 1993, he

moved to Nankai University as a full professor. He is now the chairman of the Asian and Oceanian Cyclodextrin League, a member of the International Cyclodextrin League, and a spe-

cially appointed professor of the 'Cheung Kong Scholars Programme of China'. He is the author of nine books and more than 300 articles in the area of supramolecular chemistry.



**Scheme 1** The acid/base controlled dethreading and rethreading of the [2]pseudorotaxanes

guest changes, the smaller the enthalpy changes, and the larger the entropy changes, and vice versa.

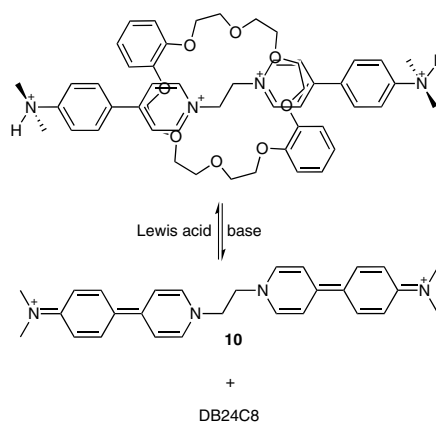
Because of the electron-donating group on the modified crown ether **4** and **5**, the binding constants are larger than **1–3** upon complexation with 1,2-bis(pyridinium) ethane derivatives. In these cases, the bigger the changes to the electron-cloud density of the substituent on the guest, the smaller the enthalpy changes and the larger the entropy changes. More generally, it should be emphasized that enhanced  $\pi$ – $\pi$  stacking and ion-dipole interactions can give more favored enthalpy change and cause a higher complex stability.

## 2.2 Molecular Switches Based on Positively Charged Molecules and Crown Ethers

We have demonstrated that modified DB24C8 with an electron-donating group can exhibit efficient chromophoric behavior with the 1,2-bis(pyridinium)ethane derivatives. Based on this result, we designed an acid/base controlled chromophoric molecular switch in which the axle molecule **9** can shuttle between different wheels (**1** and **5**) upon acid/base addition (Scheme 1),<sup>10</sup> and the switching process can be easily detected by the naked eye due to its dramatic color change. From UV/Vis absorbance and <sup>1</sup>H NMR spectra, it can be demonstrated that when three components were mixed in solution, diamino-dibenzo-24-crown-8 (**5**) exhibited a stronger binding ability toward guest **9** comparing to the parent DB24C8 (**1**). The solution became red and was accompanied by the development of a charge transfer (CT) band at 440 nm. However, after addition of 20 equivalents of acid, the solution color changed to yellow. This observation can be explained by the protonation of both the amino groups in **5** and the pyridium groups in **9** disassociating the complex **9·5**, but significantly enhancing the stability of another pseudorotaxane [9·2H<sup>+</sup>]**1** as a consequence of the resul-

tant additional hydrogen bond of C–H···O and  $\pi$ – $\pi$  stacking interactions. Consequently, the axle shuttled from the macrocycle **5** to **1**. Addition of Bu<sub>3</sub>N could quantitatively reverse the process. The thermodynamic origin was also investigated by using microcalorimetry titration. The complexation of **9** with **1** was enthalpy driven both in the absence and the presence of CF<sub>3</sub>COOH, but the increased binding abilities in the presence of the acid are governed by the entropy term. With acid and base assigned as the inputs, this process can be described as three INHIBIT (INH) logic gates.

Recently, Loeb and co-workers also reported a methodology to perform a threading/dethreading motion through switching *off/on* the intramolecular charge-transfer (ICT) in an axle with an *N,N*-dimethylaniline group on the 4-position of the pyridinium ring (Scheme 2).<sup>11</sup> Guest molecule **10** showed a much weaker binding ability with the DB24C8 ring because its resonance form increased the electron density in the pyridinium rings and decreased the ability of the axle to thread through DB24C8. Addition of a suitable Lewis acid can switch off the ICT and restore



**Scheme 2** pH-driven dethreading and rethreading of the [2]pseudorotaxanes

the ability of the axle to form a pseudorotaxane with DB24C8.

DB24C8 has a much higher association constant with dibenzylammonium hexafluorophosphate in the [2]pseudorotaxane in aprotic solvent ( $K_a = 27000 \text{ M}^{-1}$  in  $\text{CDCl}_3$  vs.  $K_a = 420 \text{ M}^{-1}$  in  $\text{CD}_3\text{CN}$ ).<sup>2a</sup> Addition of base can deprotonate the  $\text{NH}_2^+$  center on the axle component, turn off the hydrogen bonding and electrostatic interactions, and cause axle dethreading from the 24-crown-8 macrocycle. The pseudorotaxane can be reformed by protonating the amine moiety with addition of suitable acid. This process can be reversed by addition of base and repeated several times. The described system therefore represents a prototype, at the supramolecular level, for a simple molecular machine. This strategy has been exploited to construct various molecular devices and machines during the past decade.

A double plug–socket system was constructed based on bis-24-crown-8 host **11** and bis-ammoniums guest **12** (Figure 2).<sup>12</sup> Two matching rigid spacers [anthracene in **11** and 1,4,5,8-naphthalenediimide (NDI) in **12**] were selected to enhance the association between the host and the guest by increasing their complementarity and optimizing the multivalent effects. From  $^1\text{H}$  NMR, UV/Vis and ESI mass spectra, the strong multivalent interactions were confirmed and investigated thoroughly. Furthermore, after addition of  $(\text{Bu})_3\text{N}$ , the double plug–socket species disassembled, but reassembled upon the addition of  $\text{CF}_3\text{COOH}$ . Surprisingly, **11** can be photooxidized in solution to produce an endoperoxide, due to a self-sensitized process in which the substituted anthracene acts as a sensitizer after being excited. However, after addition of the NDI bis-ammonium guest, **11** can be protected from photooxidation, which can be attributed to a photo-induced

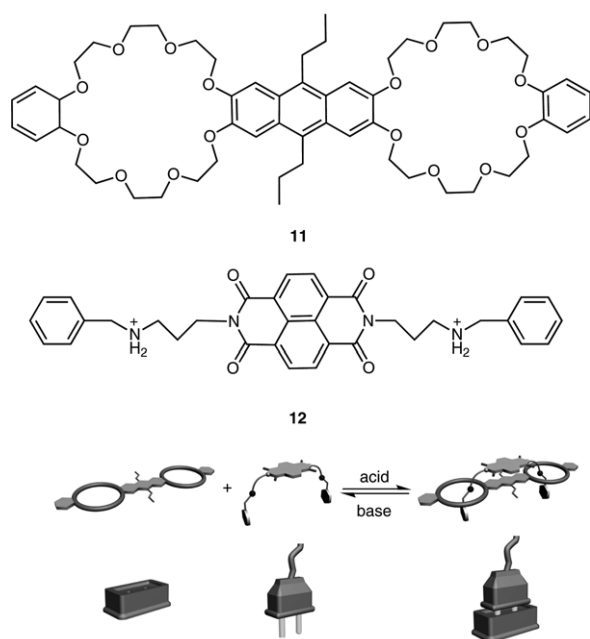


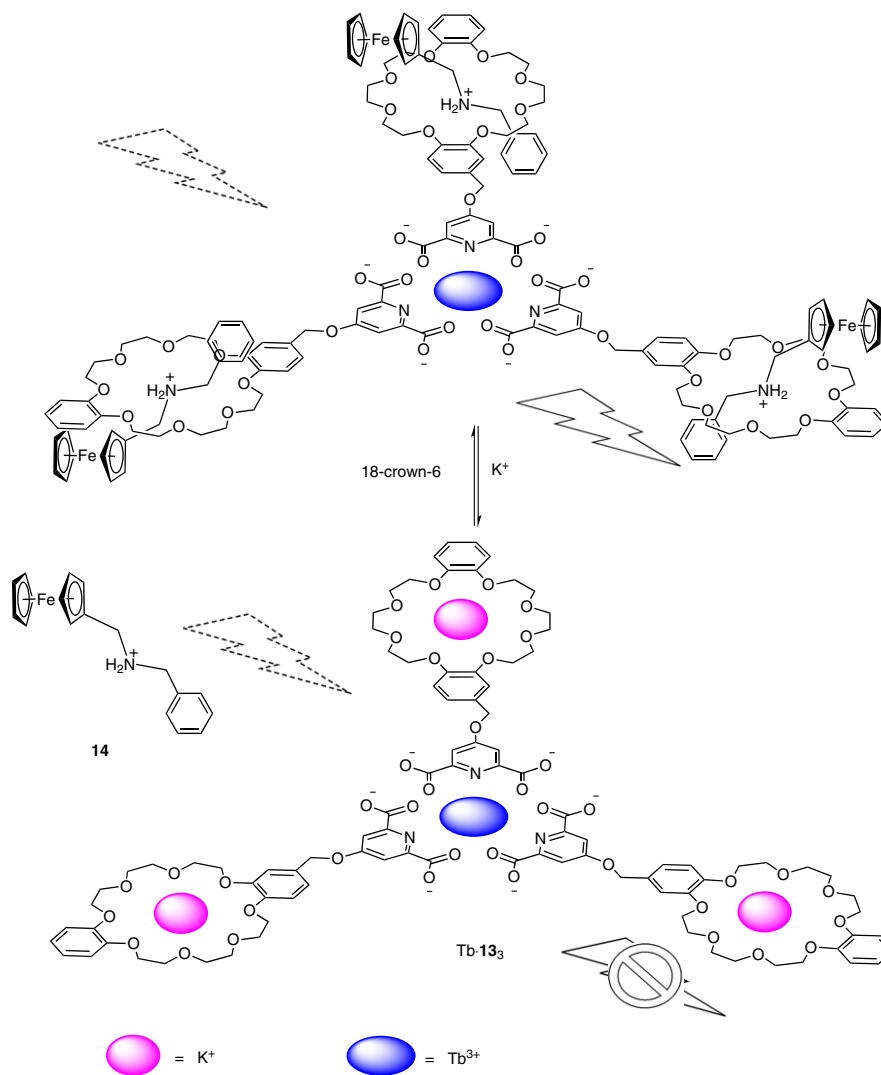
Figure 2 A double plug–socket system

electron transfer (PET) process from excited anthracene to NDI and to the high binding affinity between **11** and **12**. Upon addition of an excess of base, **11** can be released and then photooxidized. So **11**–**12** can work as base/acid switchable molecular shields. Considering fluorescence as output, and base, acid, visible light, and  $\text{O}_2$  as inputs, an input-sequence-specific NAND logic gate was constructed from **11**–**12**, which can be thought of as molecular keypad locks with alarm systems.

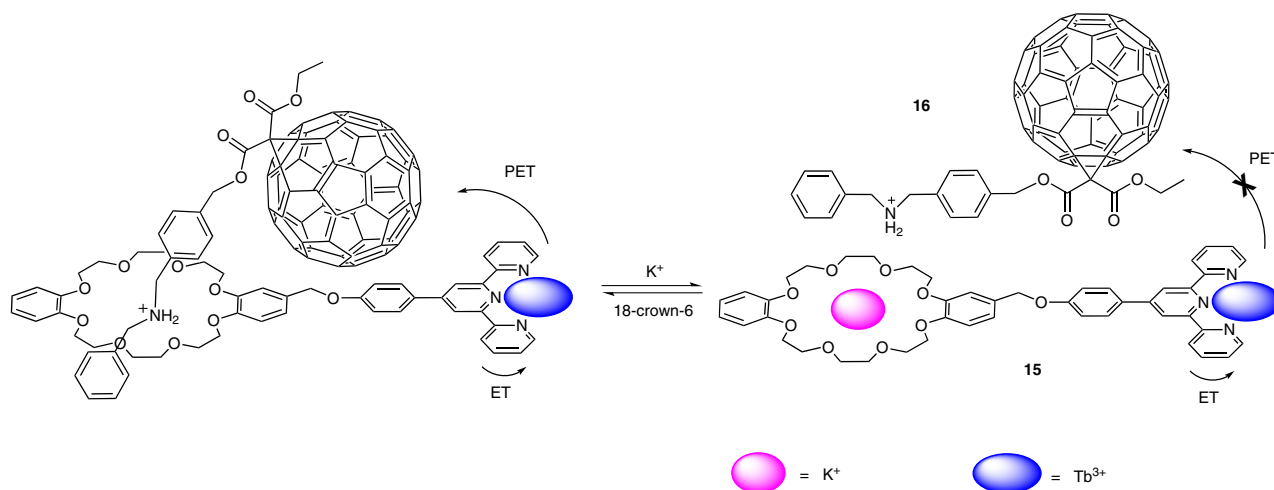
Some alkali metal cations such as  $\text{Na}^+$  and  $\text{K}^+$  can be used as competitive guests to disassemble the pseudorotaxanes by shifting the complexation equilibrium. Utilizing this property, a reversible luminescent lanthanide switch was constructed (Scheme 3).<sup>13</sup> Combining the DB24C8 macrocycle with pyridine-2, 6-dicarboxylic acid (DPA) as an excellent chelator and antenna for  $\text{Tb}^{3+}$ , the obtained ligand **13** can form a stable 3:1 complex  $\text{Tb}^{3+}\cdot\mathbf{13}_3$ . Meanwhile, this complex can bind the alkyl(ferrocenylmethyl)ammonium guest **14** because of its 24-crown-8 macrocycles. When 3.0 equivalents of **14**, bearing the ferrocene moiety, was added, the lanthanide luminescence of the complex was significantly quenched (ca. 94% at 544 nm). This phenomenon can be explained by considering a PET from the ferrocene moiety to DPA. Moreover, after addition of  $\text{KPF}_6$ , with the **14** replaced by metal cations, the quenched lanthanide emission was restored as a consequence of suppressed PET. It was found that addition of 18-crown-6 can reproduce luminescence quenching. This process can be repeated several times; addition of  $\text{K}^+$  caused the restoration of luminescence, while addition of 18-crown-6 led to its quenching.

We further prepared a [2]pseudorotaxane comprised of the DB24C8 derivative **15** bearing a terpyridine unit as a chelator for lanthanide ions and the fullerene-containing ammonium salt **16** (Scheme 4).<sup>14</sup> Upon titration with  $\text{Tb}^{3+}$ , **15** was found to form a stable 1:1 complex with a stability constant of  $(1.8 \pm 0.7) \times 10^5 \text{ M}^{-1}$ . The complex  $\mathbf{15}\cdot\text{Tb}$  showed characteristic emission bands at 491, 544, 586, and 622 nm as a result of energy transfer (ET) from ligand to lanthanide ions. Through  $^1\text{H}$  NMR spectroscopic experiments, the formation of [2]pseudorotaxane between **15** and **16** could be confirmed. Upon addition of 1.3 equivalents of guest **16**, bearing the  $\text{C}_{60}$  moiety, to the solution of  $\mathbf{15}\cdot\text{Tb}$ , approximately 90% of the fluorescence intensity of  $\text{Tb}^{3+}$  complex was quenched at 544 nm with a quantum yield of 0.005. Considering that fullerenes are good electron acceptors, these results indicated that there should be an intramolecular PET process in [2]pseudorotaxane  $\text{Tb}\cdot\mathbf{15}\cdot\mathbf{16}$  from the excited singlet state of  $\mathbf{15}\cdot\text{Tb}$  complex to the  $\text{C}_{60}$  moiety in solution. The assembling/disassembling processes of [2]pseudorotaxane can also be reversibly governed by adding  $\text{K}^+$  and 18-crown-6 in series; the PET process could be reversibly controlled by the binding and release of the cationic guests.

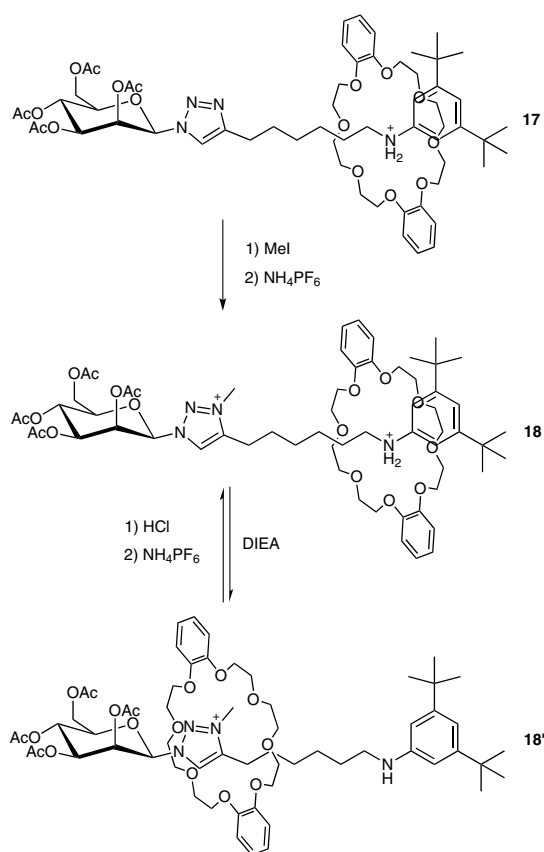
We also evaluated the Gibbs free energy ( $\Delta G_{\text{PET}}$ ) of the electron-transfer reaction based on cyclic voltammetry experiments. Using the Rehm–Weller equation, the  $\Delta G_{\text{PET}}$



**Scheme 3** Schematic representation of the presumed coordination mode for the [Tb·13<sub>3</sub>·14<sub>3</sub>] system



**Scheme 4** Schematic representation of the presumed coordination mode for the Tb·15·16 system



**Scheme 5** An acid/base driven molecular shuttle based on [2]rotaxane **18**

value was calculated to be negative enough to drive the PET reaction in a thermodynamically favorable way.

### 2.3 Interlocked Molecules Based on Positively Charged Molecules and Crown Ethers

Mechanically interlocked molecules based on the 24-crown-8 system possessing switchable capabilities have been exploited as prototypes for molecular-level nanomachines such as molecular shuttles,<sup>15</sup> molecular muscles,<sup>16</sup> and molecular elevators.<sup>17</sup> It has always attracted the interest of chemists to construct novel interlocked molecules and explore their applications.

Recently, a method to effectively prepare the rotaxane of 24-crown-8 was developed by using the copper(I)-catalyzed Huisgen alkyne-azide 1,3-dipolar cycloaddition (CuAAC ‘click’ reaction).<sup>18</sup> After methylation of [2]rotaxane **17**, a pH-controlled two-station rotaxane **18** was obtained (Scheme 5). The *N*-methyltriazolium moiety was first introduced and investigated as a binding site of 24-crown-8. From the <sup>1</sup>H NMR spectra it was found that, upon deprotonation/protonation, the DB24C8 ring can make shuttling movements between the benzylianium station and the triazolium station.

The bistable rotaxane with two kinds of binding site offers a method to adjust the spacial distance between the components in the system. We chose an electron-rich pyrene

moiety at the DB24C8 wheel and an electron-deficient NDI unit in the middle of the bis-ammonium axle. Upon CuAAC ‘click’ reaction followed by *N*-methylation of two triazoles, bistable [3]rotaxane **19** was obtained (Scheme 6).<sup>19</sup> Through <sup>1</sup>H NMR spectroscopic experiments, the acid/base controlled motion in the rotaxane system could be confirmed. Furthermore, we performed photophysical experiments on the rotaxane before and after deprotonation. When DB24C8 rings were located at the ammonium sites, a weak ICT process existed between the pyrene and NDI unit. Upon deprotonation, the secondary amines had no affinity with the macrocycles, which moved to the triazolium sites and accompanied efficient enhancement of the ICT intensity. This observation can be attributed to more suitable spatial arrangement when the macrocycles move away from the central part. This bistable [3]rotaxane offers a new prototype of a molecular shuttle that could perform photophysical functions by adjusting the spacial distance between donor and acceptor in mechanically interlocked molecules.

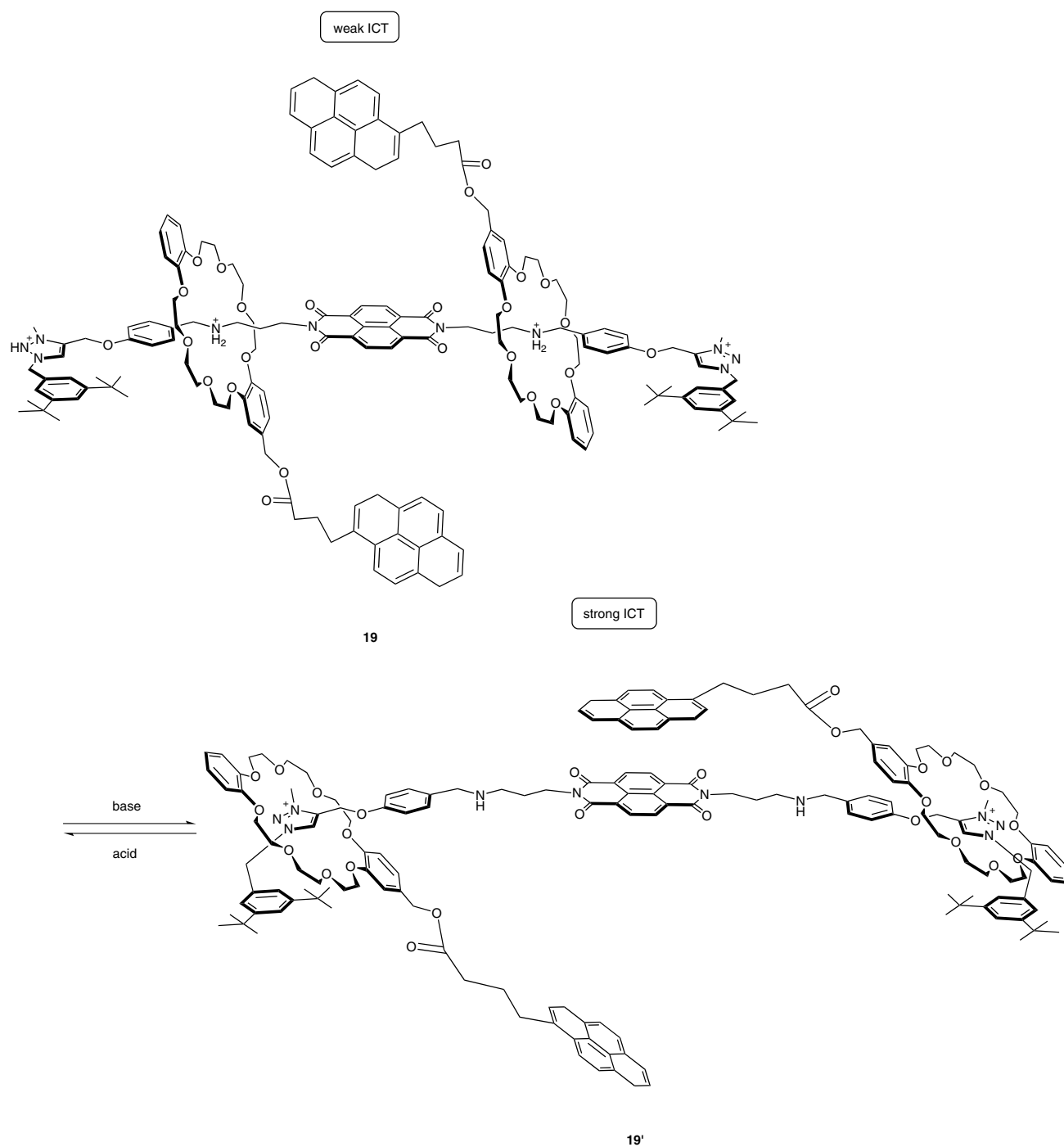
To realize more efficient syntheses of rotaxanes, template synthetic approaches have been widely used, and various protocols have been employed including ‘threading-followed-by-stoppering’, ‘slippage’, and ‘clipping’ approaches.<sup>20</sup> Recently, some novel protocols were reported. One was ‘threading-followed-by-shrinking’, in which a specific reaction was performed to reduce the ring size so that the ring cannot slip over the stopper, and interlock the axle component. A number of prerequisites must be met to realize this protocol: (1) the specific shrinking reaction should not disrupt the stability of pseudorotaxane, and its rate should be faster than the disassociation rate of the host–guest complex; (2) the reaction conditions should be mild to prevent disassociation, and (3) the change of the ring size should be suitable for the size of stopper to achieve the transformation from pseudorotaxane to rotaxane. In 2004, Asakawa and co-workers first reported this protocol.<sup>21</sup> They synthesized a crown-ether-like macrocyclic unit incorporating a salophen moiety and reduced the free space of the macrocycle upon chelating Pd<sup>2+</sup> ion to realize ‘shrinking’. Recently, Chiu and co-workers presented a more intuitive approach (Scheme 7)<sup>22</sup> in which a crown-ether-like macrocyclic unit **20**, with an arylmethyl sulfone motif, was chosen to complex with the cycloheptyl-terminated dialkylammonium ion **21**. Under photochemical conditions, the arylmethyl sulfone unit could extrude SO<sub>2</sub>, thereby decreasing the number of atoms in the ring skeleton to form [2]rotaxane **22**.

The other protocol was termed ‘threading-followed-by-swelling’ (Scheme 8). Chiu and co-workers proposed such an approach<sup>23</sup> for which, again, a number of requirements must be met: (1) the terminal group should undergo an enlargement process under controllable conditions without additional atoms or groups; (2) the reaction rate should be faster than the disassociation rate of the pseudorotaxane-like complex, and (3) the change of the terminal group size should be precisely suitable for the ring component to slip out of the axle component prior to swelling,

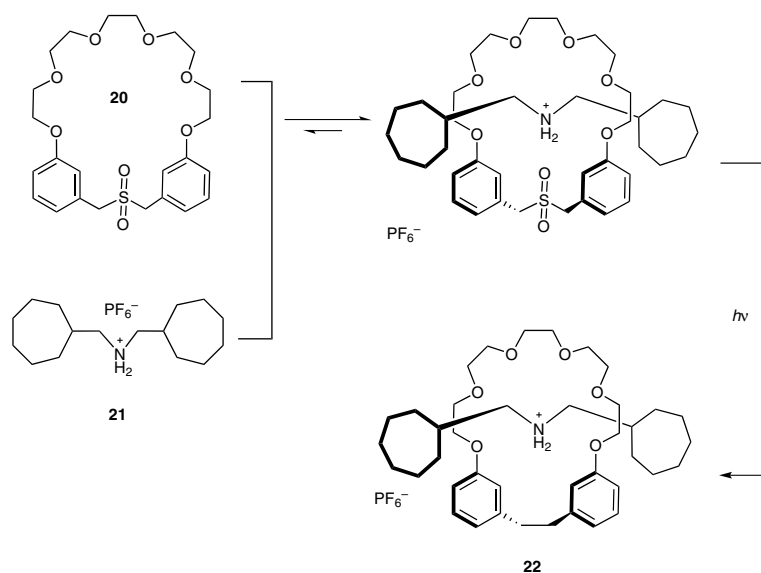
but not afterward. The *cis*-1-[(*Z*)-alk-1'-enyl]-2-vinylcyclopropane group in **23** was chosen as the terminal group; this group can be converted into a bulkier cycloheptadiene unit through a Cope rearrangement under heating. The [2]rotaxane **24** could then be obtained in a clean and efficient way. Moreover, a [c2]daisy chain was also constructed by the same group by using this approach.<sup>24</sup>

Although various synthetic protocols have been developed, the construction of high-order rotaxanes still remains a challenge for chemists. In particular, it seems much more difficult to obtain heterorotaxanes containing

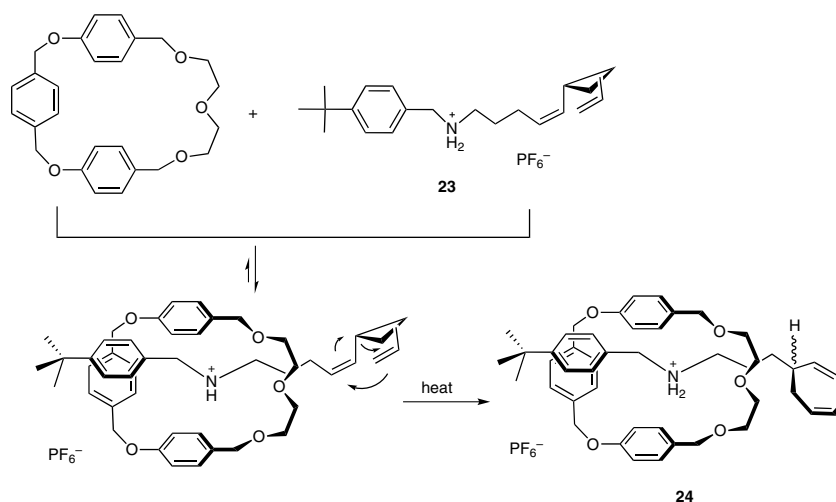
two or more similar ring components, as well as [n]rotaxanes with more than one axle molecule threaded through the same ring. We designed a four-component self-assembly strategy to construct a novel hetero[7]rotaxane **27** (Scheme 9),<sup>25</sup> which contains two axles and five ring components in its structure. One bis(*p*-phenylene-34-crown-10) (BPP34C10) was located in the center by a twin-axial rotaxanation. Four benzo-21-crown-7 (B21C7) rings were located around the terminals by a single-axial rotaxanation. Using the common 'threading-followed-by-stoppering' approach to synthesize high-order [n]rotaxanes, a



**Scheme 6** pH-Controlled intramolecular charge-transfer behavior in bistable [3]rotaxane



**Scheme 7** Chemical representation of the concept of the metal-free ‘threading-followed-by-shrinking’ protocol



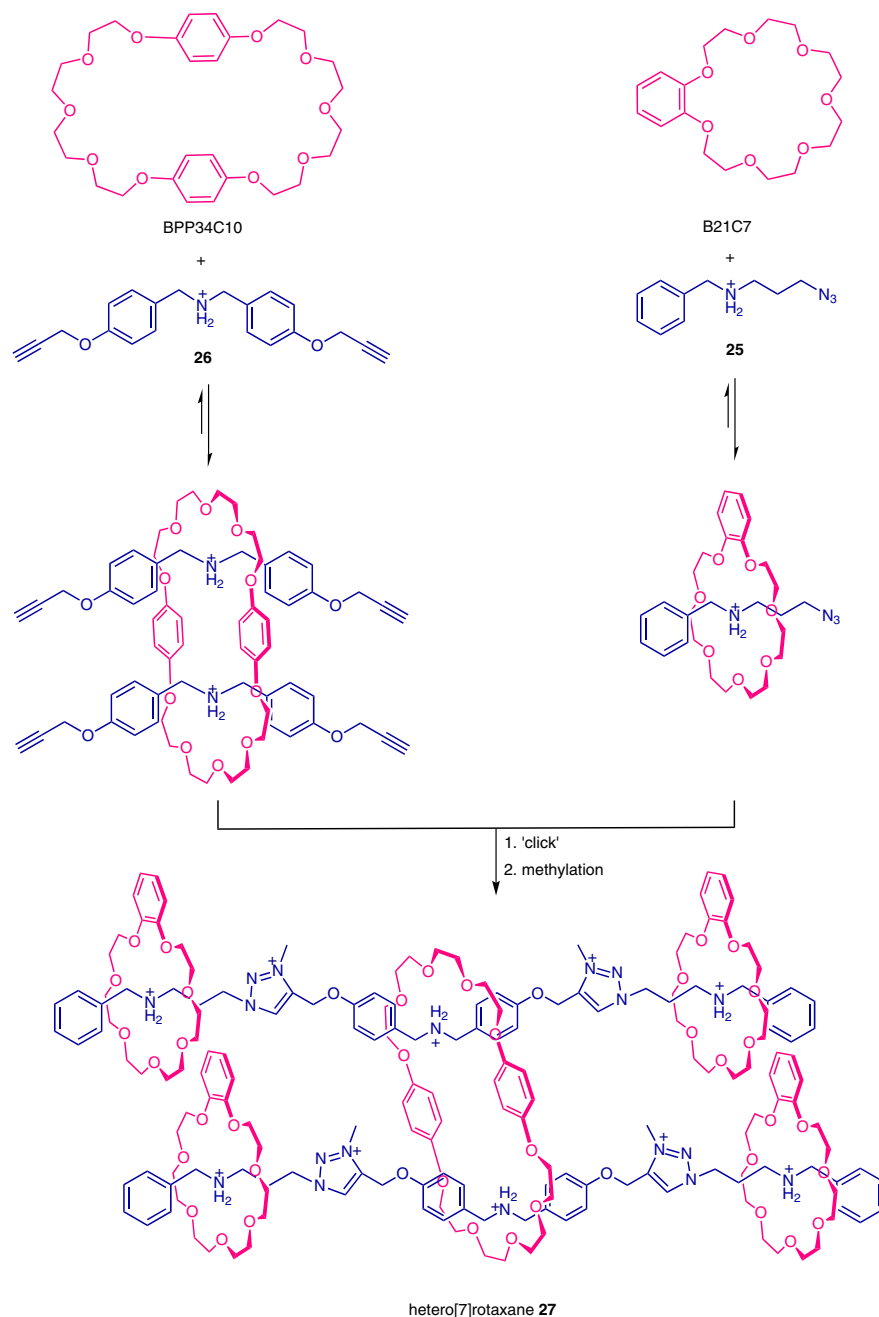
**Scheme 8** Chemical representation of the concept of the ‘threading-followed-by-swelling’ protocol

high association constant is needed to maintain the dynamic multi-component complex. Moreover, the synthesis of higher-order rotaxanes often needs the corresponding components to contain more binding sites, which increases the synthetic difficulty. Our strategy connected two kinds of pseudorotaxanes without additional reactants to realize ‘stopping’. We chose two macrocyclic units, BPP34C10 and B21C7, and two secondary ammonium compounds, **25** and **26**. When they were mixed, the [3]pseudorotaxane based on BPP34C10 and [2]pseudorotaxane based on B21C7 could be formed exclusively. The CuAAC ‘click’ reaction was chosen because it was very efficacious in rotaxane synthesis, and the reactive azide and alkyne groups could be introduced into the two pseudorotaxanes respectively. In the [7]rotaxane, we also employed the ‘cascade-stopping’ concept, which was introduced by Jiang et al. in 2008.<sup>26</sup> Four B21C7 rings can be stoppered by the outer phenyl groups, while the central BPP34C10 was ‘cascade-stoppered’ by the B21C7 rings.

The good combination of self-assembly and synthetic strategy ensures the correct position of two kinds of rings in the [7]rotaxane.

Besides the rotaxanes, we also constructed a porphyrin-based [2]catenane and a pretzelane based on the molecular recognition toward secondary ammonium ion by DB24C8 (Figure 3).<sup>27</sup> Catenanes are composed of two or more interlocked macrocyclic components that are not linked covalently to each other. Pretzelanes are bridged [2]catenanes that are connected by covalent bonds. After Vögtle et al. reported the first pretzelane,<sup>28</sup> Stoddart and co-workers synthesized a number of donor–acceptor pretzelanes that comprised an electron-deficient tetracationic cyclophane tethered to and mechanically interlocked with an electron-rich macrocyclic polyether.<sup>29</sup> To the best of our knowledge, only the two examples of pretzelanes mentioned above have been reported. We used Sn-porphyrin phenolates to achieve the ring-closing and obtain the desired interlocked structure; Sn-porphyrin phenolates





**Scheme 9** Construction of hetero[7]rotaxane **27** by the modularized four-component self-assembly strategy with **25**, **26**, B21C7, and BPP34C10

are the stable products of the equilibrium-based condensation reaction of substituted phenols with Sn-porphyrin dihydroxide in an organic medium. Through the axial ligation of Sn-porphyrin dihydroxide **28** with two resorcinol moieties of the termini of the aromatic dibenzylammonium spacer **29**, macrocycle **30** can be obtained. When using DB24C8 to thread the dibenzylammonium spacer to form a [2]pseudorotaxane, the final product was the [2]catenane **31**. When **28** was replaced with the Sn-porphyrin dihydroxide–crown ether conjugate **32**, pretzelane **33** was obtained.

### 3 Interpenetrated Molecules Based on Cucurbiturils

When changing the counter anions with halide ions, the positively charged molecules can be dissolved in water. We mainly chose to use cucurbiturils (CBs) as the host molecules. The controlled assembly behavior, application in DNA condensation, and stabilization of radical cation in the interpenetrated molecules are discussed.

Cucurbiturils are a class of pumpkin-shaped cyclic glycoluril oligomers with 5–10 glycoluril units linked by methylene groups.<sup>4,30</sup> They have hydrophobic cavities and

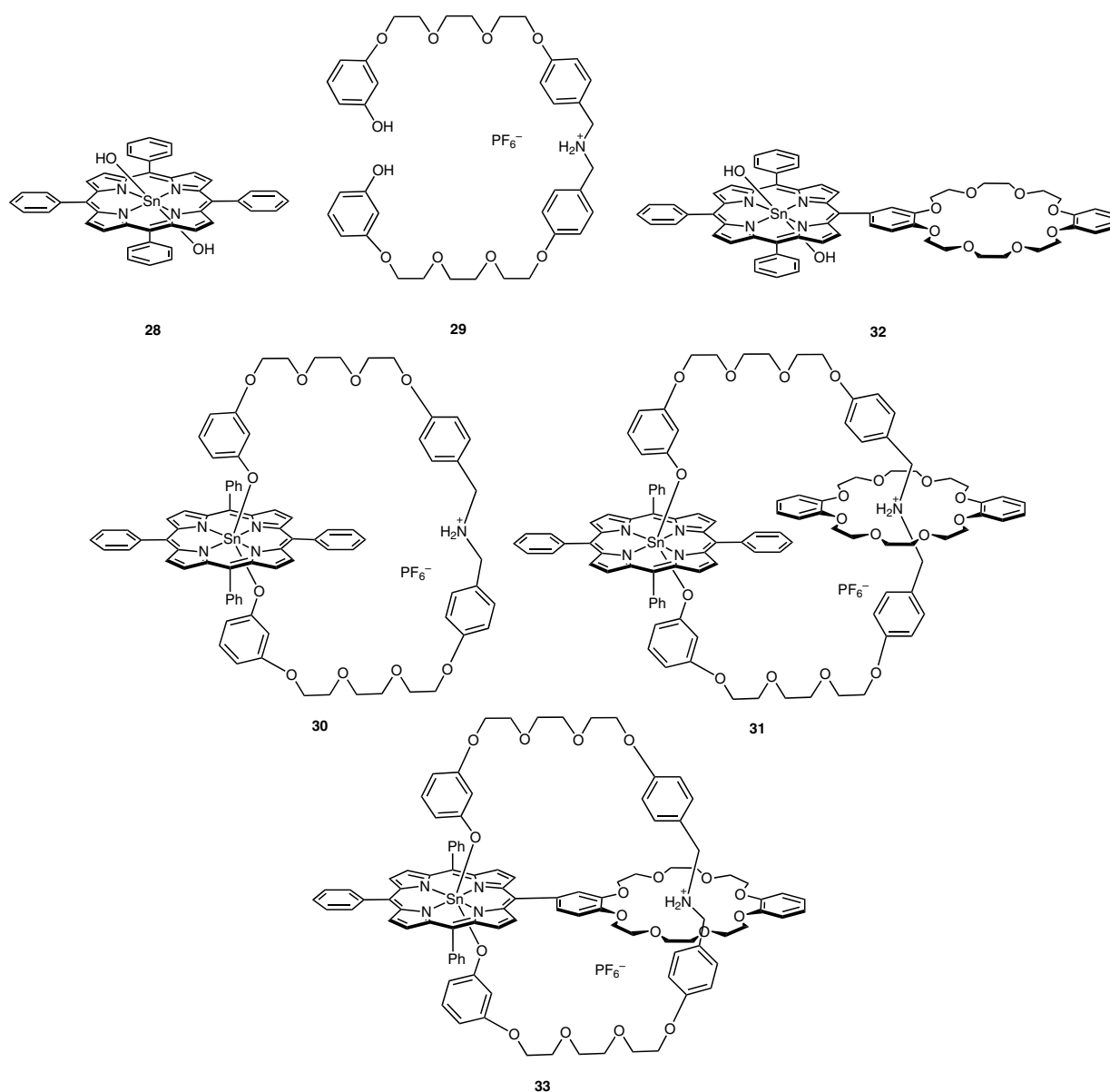
carbonyl-laced portals, resulting in strong binding affinity with positively charged guests through ion-dipole and hydrophobic interactions. The complexation is also partially affected by the size of the host and guest. The most widely used members are CB[6], CB[7], and CB[8].

### 3.1 Reversible 2D Pseudopolyrotaxanes and their Application in DNA Condensation

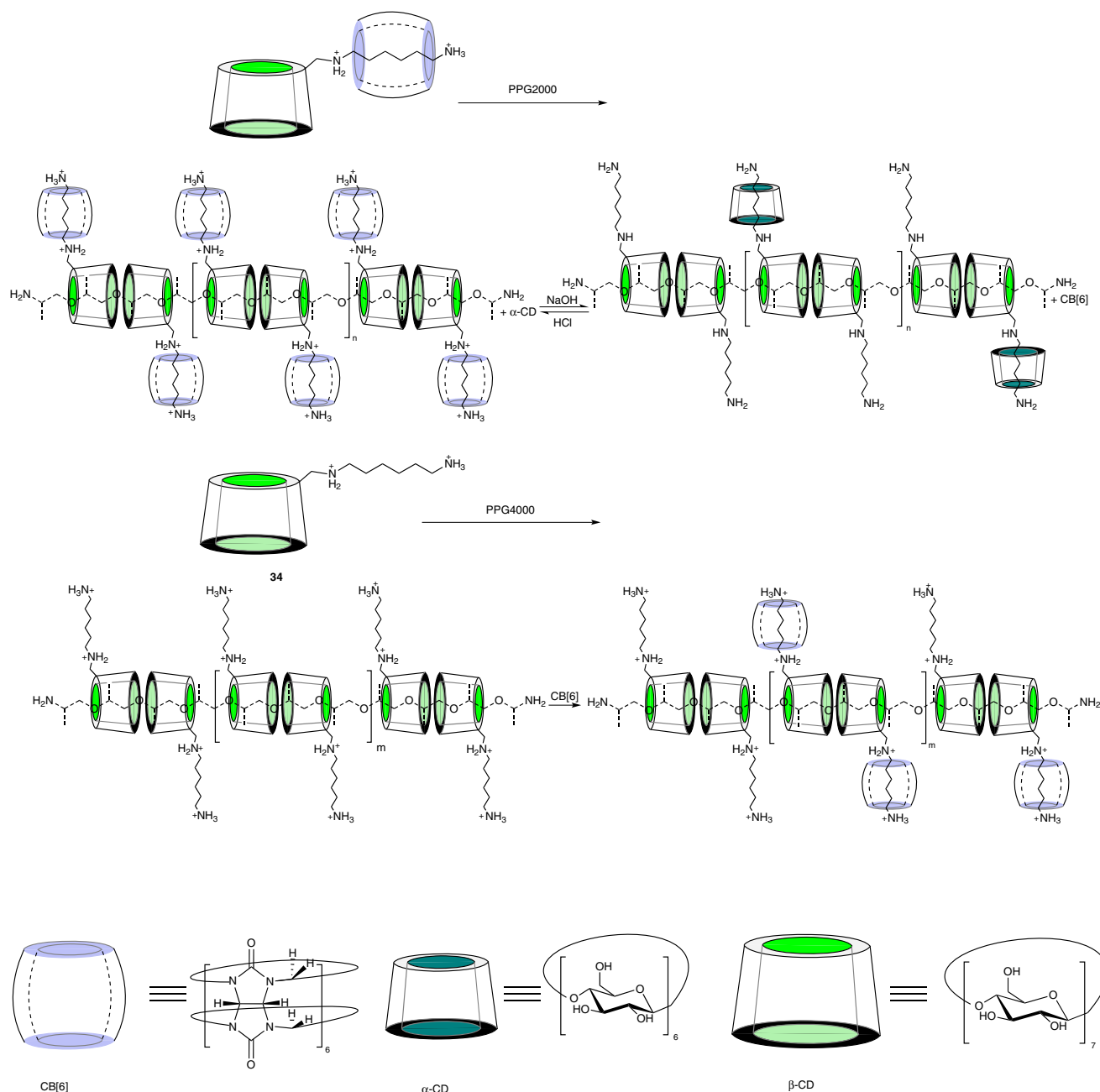
Cyclodextrins (CDs), a class of cyclic oligosaccharides with six to eight D-glucose units, possess a hydrophobic cavity that can bind various neutral and anionic species; in contrast to CBs, which often bind cationic guests. Based on their different recognition behavior, we designed a novel 2D pseudopolyrotaxane (Scheme 10),<sup>31</sup> in which the cyclic molecules of  $\beta$ -CDs were threaded onto the polymeric main chain and CB[6]s were threaded onto its side chains. For the main chain, we chose amino-terminat-

ed PPG2000, which has been used in the construction of various CD-based pseudopolyrotaxanes.<sup>32</sup> For the side chain, protonated hexane-1,6-diamine was chosen because it exhibits a strong binding ability with CB[6] ( $K = 4.49 \times 10^8 \text{ M}^{-1}$ ) in aqueous solution.<sup>33</sup> Firstly, 6-[(6-aminohexyl)amino]-6-deoxy- $\beta$ -CD chloride (**34**) was prepared and found to form a stable [2]pseudorotaxane with CB[6]. Assembly of the [2]pseudorotaxanes was realized through threading of their  $\beta$ -CD cavity onto the  $\alpha,\omega$ -PPG2000 diamino polymer. When an excess of  $\alpha$ -CD was present in solution, the CB[6]s would dethread off the neutral side chains through deprotonation with NaOH, and the  $\alpha$ -CDs could thread on to the side chains to form a new 2D pseudopolyrotaxane. The reversible interconversion between these two 2D pseudopolyrotaxanes can be realized by base/acid control.

We further designed another way to prepare the 2D pseudopolyrotaxane in which the diamine modified  $\beta$ -CDs



**Figure 3** [2]Catenane **31** and pretzelane **33**



**Scheme 10** Preparation of 2D pseudopolyrotaxanes through two different pathways

were first threaded onto the PPG4000 polymer. The  $\text{CB}[6]$ s were then quantitatively threaded onto the positively charged side chains. By using this approach it was possible to control the degree of substitution of  $\text{CB}[6]$ s in the obtained 2D pseudopolyrotaxane. Interestingly, it was found that the pseudopolyrotaxane containing 70%  $\text{CB}[6]$ s could form the largest particles with DNA, resulting in the most efficient DNA condensation. The binding interaction between DNA and the series of pseudopolyrotaxanes and the ability to condense DNA did not grow linearly with the percentage of  $\text{CB}[6]$ s. This surprising observation could be explained by an increase in rigidity with the addition of  $\text{CB}[6]$ s, which progressively dominates the interaction; conversely, the effective charges of

pseudopolyrotaxanes decreased with increasing numbers of  $\text{CB}[6]$  units.

### 3.2 Pseudorotaxanes Based on Bipyridinium Derivatives and Cucurbiturils

Through modification of the N-terminal of 4,4-bipyridine, the bispyridinium derivatives become a suitable guest for CBs because (1) the 4,4-bipyridinium unit has a positively charged terminal and a hydrophobic part, resulting in a high affinity with  $\text{CB}[7]$ <sup>34</sup> and  $\text{CB}[8]$ ,<sup>35</sup> (2) the preparation of such derivatives is convenient; (3) the 4,4-bipyridinium unit is electrochemically active, which is a property that could be used in switchable systems.<sup>36</sup>

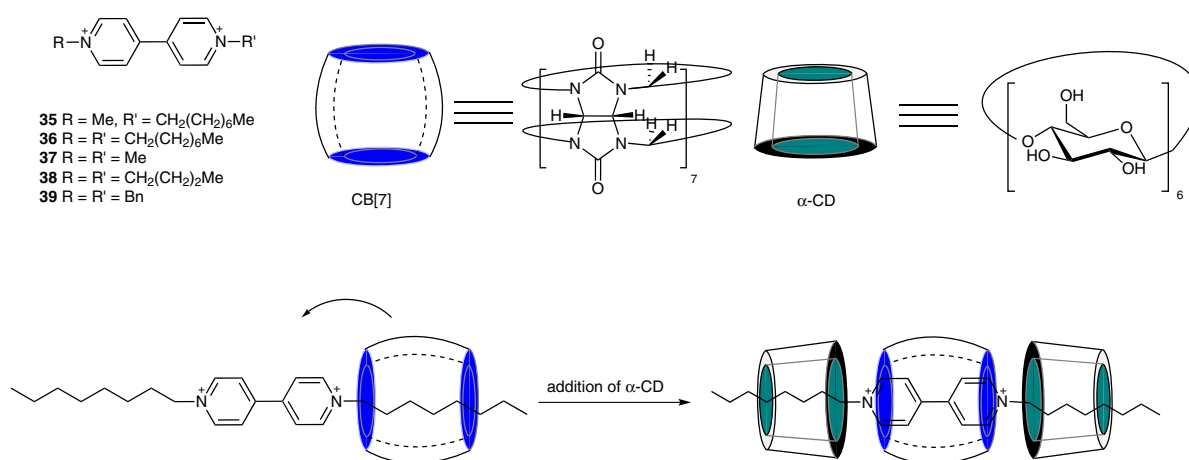
When the 4,4'-bipyridinium unit is modified with a hydrophobic group, the location of CBs may be affected. Kaifer and co-workers reported that when the *N*-substituted aliphatic chain was longer than four carbon atoms, the CB[7] host binds more favorably with aliphatic substituents.<sup>37</sup> We mainly focused on the movement of CB[7] along the axle molecule upon the addition of external  $\alpha$ -CD (Scheme 11).<sup>38</sup>

One asymmetric *N*-methyl-*N'*-octyl-4,4'-bipyridinium dication (**35**) and one symmetrical *N,N'*-dioctyl-4,4'-bipyridinium dication (**36**) were chosen to bind with CB[7]. It was found that CB[7] shuttled between the octyl and bipyridinium moiety in **35**, but was mainly located at the octyl moiety. In the case of **36**, CB[7] docked on the octyl moiety. However, upon stepwise addition of  $\alpha$ -CD, CB[7] was found to move to the bipyridinium moiety, leaving the octyl moiety for the  $\alpha$ -CD. This process presumably results from collaborative contributions of the molecular recognition behavior of the two macrocycles, and is dependent on the structures of the guest molecules. We performed similar experiments on other symmetrical axle molecules such as **37**, *N,N'*-dibutyl-4,4'-bipyridinium (**38**), and *N,N'*-dibenzyl-4,4'-bipyridinium (**39**), but no such movement was observed. CB[7] was found to bind with the bipyridinium unit of **37** directly, leaving no more binding site for the external  $\alpha$ -CD. Although CB[7] could locate on the butyl or benzyl group of **38** and **39**, these *N*-substituents were not long enough to be included by  $\alpha$ -CD.

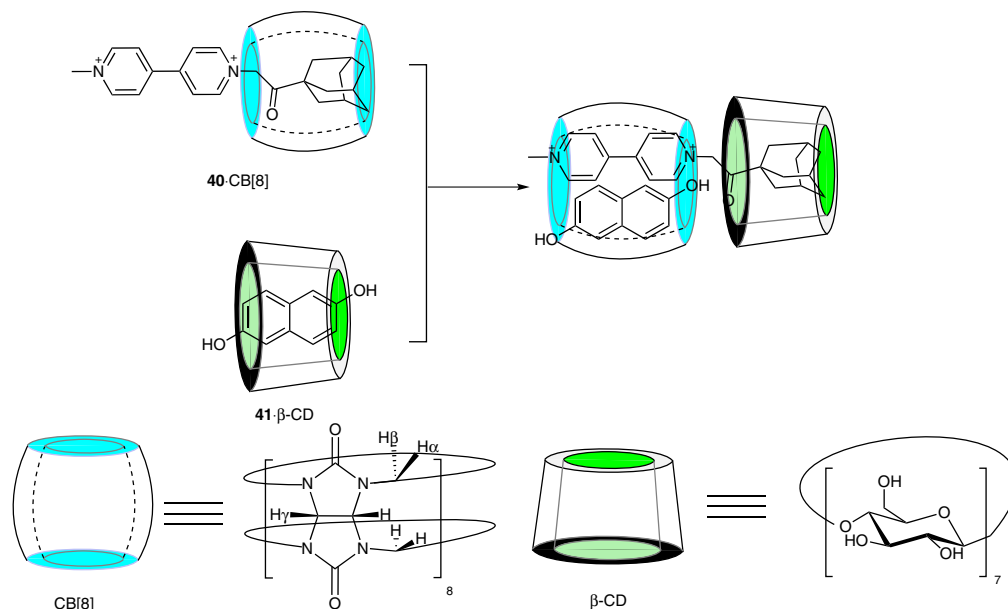
To investigate the thermodynamic origins of the movement of CB[7] driven by  $\alpha$ -CD, isothermal titration calorimetry (ITC) experiments were performed. The complexation of  $\alpha$ -CD with **35**·CB[7] was attributed to both favored enthalpy and entropy changes. The favored enthalpy change for the formation of [**35**·CB[7]· $\alpha$ -CD] should come not only from the complexation of the octyl moiety with  $\alpha$ -CD but also from hydrogen-bonding interactions between CB[7] and  $\alpha$ -CD. Furthermore, the binding constant for the formation of the 1:1 complex of  $\alpha$ -CD and **36**·CB[7] was larger than that of  $\alpha$ -CD and **36**, which

should be ascribed to the charge density on **36** decreasing upon binding of CB[7], resulting in  $\alpha$ -CD easily binding at the octyl moiety. The affinity of CB[7] toward the octyl moiety of **36** was slightly stronger than that toward its bipyridinium moiety. Therefore, the exothermic enthalpy changes of the complexation between the axle molecules and  $\alpha$ -CD afforded an impetus to compete with the very strong binding of CB[7] to push it from the octyl moiety to the bipyridinium moiety.

In above work, we prepared two hetero-wheel pseudorotaxanes based on the cooperative effect of the ion-dipole interactions of viologen guests with CB[7] and hydrophobic interactions of that with CB[7]/ $\alpha$ -CD. Based on the binding behavior of CB[8] and  $\beta$ -CD, a hetero-wheel [4]pseudorotaxane was designed and prepared (Scheme 12).<sup>39</sup> The adamantane-modified viologen **40** was found to form a stable [2]pseudorotaxane with CB[8]. From <sup>1</sup>H NMR experiments, CB[8] was found to dock on the adamantane moiety but not at the viologen nucleus, which was understandable because the adamantane group can offer a much larger binding constant with CB[8] when it has a positively charged terminal.<sup>40</sup> When the inclusion complex of hydroxynaphthalene **41** and  $\beta$ -CD was added into a solution of **40**·CB[8], a quaternary complex formed in which the CB[8] moved to the viologen nucleus to form a CT complex with **41**, while  $\beta$ -CD included the adamantane moiety. To understand the formation of the hetero-wheel [4]pseudorotaxane, **41** was added to a solution of **40**·CB[8]. However, without  $\beta$ -CD, the CT complex barely existed. To form such a CB[8]-stabilized CT complex, the first step is the inclusion of CB[8] at the viologen moiety.<sup>41</sup> But CB[8] preferred to bind the adamantane moiety in **40**·CB[8], thus the hydroxynaphthalene cannot be included into the cavity of CB[8] to form the CT complex. Upon addition of  $\beta$ -CD into a mixture of **40**, **41** and CB[8],  $\beta$ -CD would bind competitively at the adamantane moiety of **40**, making partial CB[8] molecules move onto the viologen nucleus of **40**. This not only led to the formation of a stable CT complex between **40** and **41** but also greatly facilitated the movement of more CB[8] onto the



**Scheme 11** Structures of guests and the movement of CB[7] driven by  $\alpha$ -CD



**Scheme 12** Formation of hetero-wheel [4]pseudorotaxanes

viologen moiety. In such a quaternary complex, the ion-dipole interactions between positively charged terminals and CB[8], the hydrophobic interactions of aromatic parts with  $\beta$ -CD/CB[8], and the CT interaction were the main driving forces.

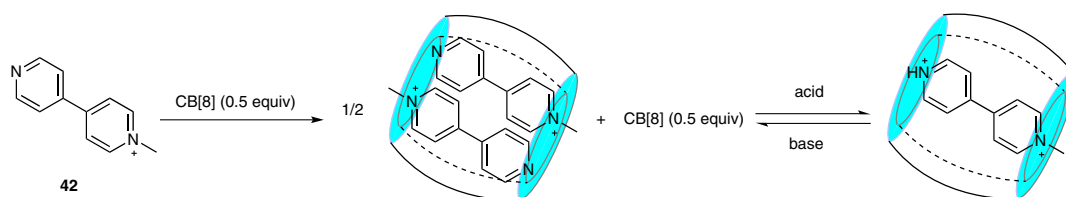
In addition to the bipyridinium dication guests, we also became interested in monocharged viologen (MCV), which could be prepared through a modification of one of the N-terminals on 4,4-bipyridine. Compared with double charged viologen, the obtained singly charged bipyridinium moiety has a similar ability to bind with CB[7].<sup>42</sup> The bare N-terminal can be easily protonated to obtain a second positive charge, which endows the MCV-based system with acid-base switchable properties.

Furthermore, we found that MCV can be included in CB[8] as a homo-guest pair in a head-to-tail stacking mode (Scheme 13). Even upon adding more CB[8], the 2:1 guest-host complex still existed, which was more stable than the 1:1 complex. Upon protonation, the MCV unit was found to form a 1:1 complex with CB[8], which was similar to the doubly charged viologen. In the presence of excess CB[8], the interconversion between 2:1 and 1:1 guest-host complex can be realized by acid/base control.

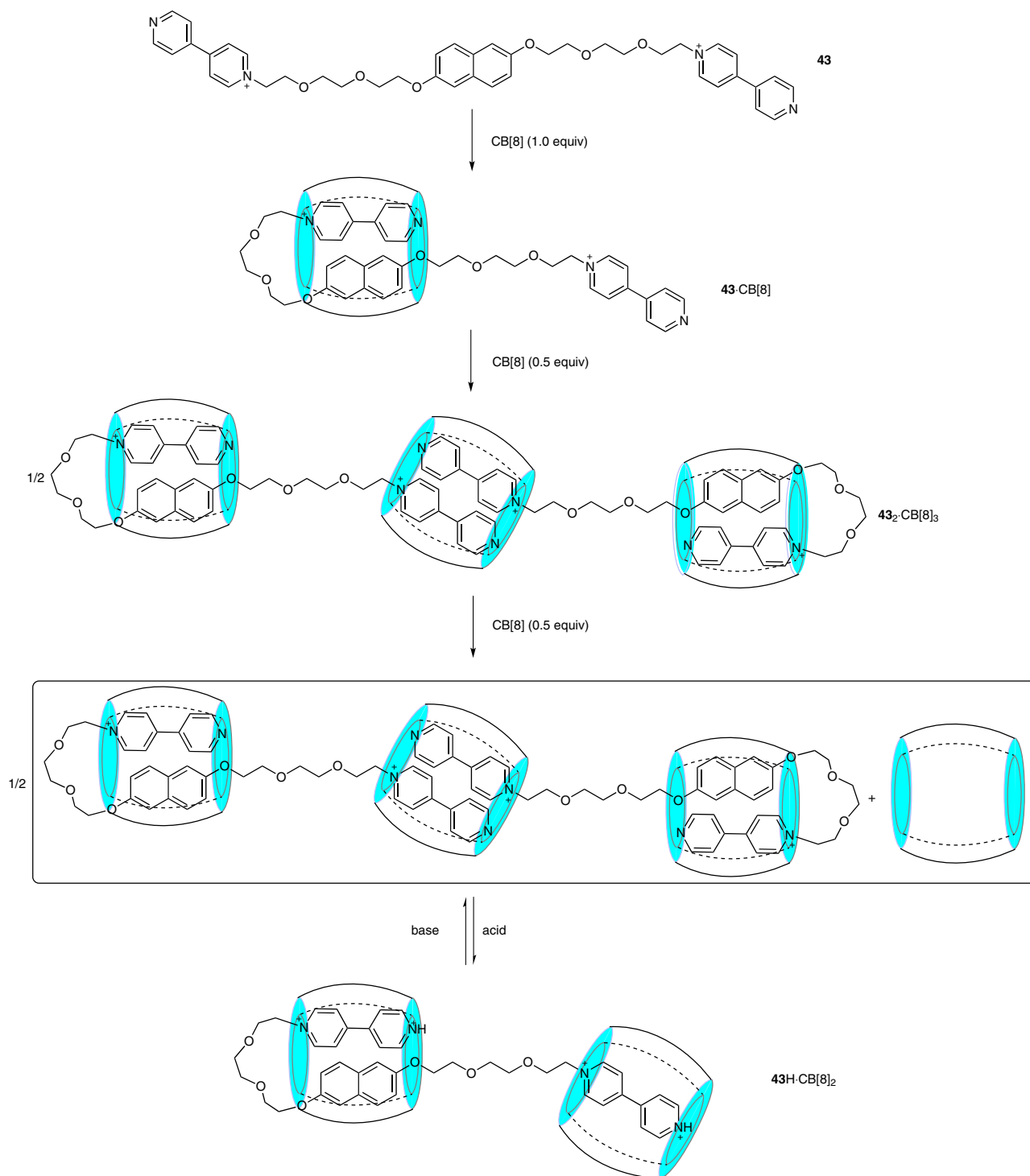
Based on this property, we designed and synthesized axle molecule **43** in which two MCV units were located at its two ends and one naphthoxy (NP) group was positioned in

the middle (Scheme 14).<sup>43</sup> Upon addition of 1.0 equivalent of CB[8], the electron-rich NP and the electron-deficient MCV unit were included into the cavity of CB[8] to form a host-stabilized CT complex **43**·CB[8]. The [2]pseudorotaxane **43**·CB[8] had a bare MCV unit, which could be used to form a 2:1 complex with CB[8]. Thus, through addition of new CB[8], two [2]pseudorotaxanes can be connected through the CB[8]·MCV<sub>2</sub> 1:2 complex. The newly formed [5]pseudorotaxane **43**<sub>2</sub>·CB[8]<sub>3</sub> was confirmed through UV/Vis, 2D NMR, and ESI-MS analyses. Upon addition of acid, the connection was broken and, in the presence of excess CB[8], **43**<sub>2</sub>·CB[8]<sub>3</sub> was transformed into a [3]pseudorotaxane. The addition of base resulted in a reversible switch between the two different pseudorotaxanes. We also performed a diffusion-ordered spectroscopy (DOSY) experiment to investigate the acid/base controlled interconversion process. When acid was added to the solution of [5]pseudorotaxane, the measured diffusion coefficients increased considerably from  $1.73 \times 10^{-10}$  to  $2.29 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ . This result suggested that the average aggregation size decreases by 2.3 times upon acidification, which was consistent with the size change observed between the two supramolecular species.

When we connected two MCV units using a hexyl linker, **44** was found to form a loop structure with 1.0 equivalents of CB[8] (Scheme 15).<sup>44</sup> From the <sup>1</sup>H NMR spectra, it was



**Scheme 13** Binding modes and the interconversion process involved with MCV



**Scheme 14** Schematic representation of the binding modes and the interconversion process between [5]pseudorotaxane and [3]pseudorotaxanes

seen that  $H_\alpha$  and  $H_\beta$  of CB[8] on the exterior portals were also shifted upfield and split into two groups, which was different to that in the  $\text{MCV}_2 \cdot \text{CB}[8]$  2:1 complex. This result indicated that the two portals of CB[8] were located in magnetically different environments brought about by the unsymmetrical structure of the guest-pair inside the cavity. The water molecules bridged between the two positively charged terminals may play a role of overcoming the charge repulsion in the uncommon head-to-head

stacking of two MCV units. Moreover, if the two linked MCV units stacked in a common head-to-tail mode, the two linkers would be placed in the opposite direction and cause polymerization of the guests. Such a polymeric state would be unfavorable, which can also be explained why the formation of the 1:1 host-guest complex with a loop structure should be more favorable.

The stability of the loop structure was also due to the strong hydrophobic interactions between the aromatic



parts of the two MCVs and CB[8], however, it was still dependent on the property of the linker. When the linker used was triethylene glycol, which is less hydrophobic, the loop structure could also be formed. When the linker was replaced by an octyl group, CB[8] tended to locate on the aliphatic chain, which may offer stronger hydrophobic and ion-dipole interactions.

Upon addition of acid, the splitting of  $H_\alpha$  and  $H_\beta$  of CB[8] could not be observed in the  $^1\text{H}$  NMR spectrum. The characteristic peaks for the protons on the linker of the axle molecules were shifted to higher field, which indicated CB[8] moved onto the linker to form a [2]pseudorotaxane. This acid/base controlled interconversion process was also investigated by DOSY experiments. When acid was added to a solution of  $44\cdot\text{CB}[8]$ , the measured diffusion coefficient decreased from  $2.67 \times 10^{-10}$  to  $2.47 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ , indicating that the average size increased by 1.3 times upon acidification. Moreover, the hydrodynamic volumes of  $44\cdot\text{CB}[8]$  and  $44\text{H}\cdot\text{CB}[8]$  were estimated to be 1.7 and 2.2 times larger than that of free CB[8], respectively. These results reasonably excluded the possibility of polymeric species being formed and confirmed the interconversion of two supramolecular species (loop and [2]pseudorotaxane) by acid/base stimulation.

### 3.3 Stabilization of Radical Cations in Pseudopolyrotaxanes Based on Cucurbituril and Polyaniline

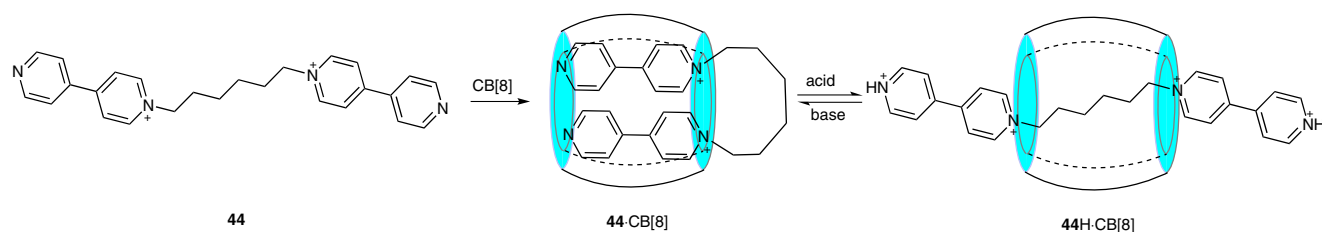
CB[7] has been shown to have a strong binding ability toward the radical cation of methyl viologen,<sup>34</sup> as well as the tetrathiafulvalene.<sup>45</sup> Kim and co-workers reported that CB[8] can include the radical dimer of methyl viologen<sup>35</sup> or tetrathiafulvalene.<sup>46</sup> Polyaniline (PANI), as a conjugated polymer, has been widely applied in electronic and optical materials.<sup>47</sup> Its high conductivity (up to  $1000 \text{ S cm}^{-1}$ )<sup>48</sup> comes from the presence of numerous radical cations in the emeraldine state, that is, the conductive doped form of PANI. Anderson and co-workers synthesized a cucurbituril/oligoaniline [2]rotaxane  $45\cdot\text{CB}[7]$  and found that the radical cation of oligoaniline could be stabilized upon complexation with CB[7] (Scheme 16).<sup>49</sup> The rotaxane was obtained through reductive amination reaction of **46** with stopper **47** in the presence of CB[7]. The rotaxane has one CB[7] located near one of the terminal ammonium centers and is soluble in most polar organic solvents. Comparison of the absorption spectra of

$45\cdot\text{CB}[7]$  and its dumbbell-shape axle component **45** with chemical oxidation by  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in water, showed that the radical cation of rotaxane persisted for much longer than that of **45**. Furthermore, square wave voltammetry showed that the first oxidation potential of rotaxane was 570 mV lower than that of dumbbell **45**.

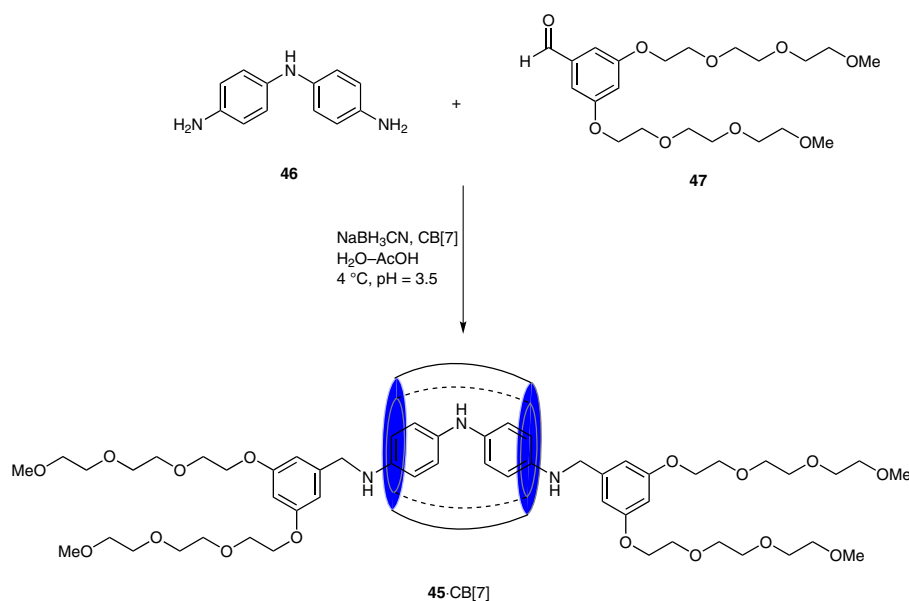
However, the investigation was performed on the oligoaniline; to examine the stabilization effect of CB[7] for radical cations on the long PANI polymers, we constructed pseudopolyrotaxane **48** through polycondensation of aniline in the presence of CB[7]<sup>50</sup> (Scheme 17) by using a method similar to that used for the preparation of PANI. Through the characteristic complexation-induced shifts in the  $^1\text{H}$  NMR spectra, together with the FTIR and NOESY results, it could be confirmed that the CB[7] units were mainly located on the doped units of the PANI chain. From an integration of the proton signals in the  $^1\text{H}$  NMR spectrum of **48**, we calculated that two doped phenyl units could thread through a CB[7] unit, which was consistent with the elemental analysis. The morphology of **48** was investigated by TEM and AFM experiments. The AFM image of a highly dilute solution of **48** showed a curved fiber structure, which was different to the small particles of PANI. Interestingly, the water solubility of **48** was improved to approximately  $1.4 \text{ mg mL}^{-1}$ , compared to  $0.3 \text{ mg mL}^{-1}$  for PANI. Upon gradual addition of 1 M NaOH, the solution of **48** changed from green to blue. Meanwhile, the UV/Vis/NIR spectrum of **48** showed that two characteristic bands at 345 and 828 nm shifted to 323 and 585 nm, respectively. This phenomenon indicated conversion of the doped form of the PANI chain into the undoped form, which could be reversed by the addition of HCl. These results demonstrate that the PANI chain maintained its reversible redox ability upon complexation with CB[7]. However, it was found that pseudopolyrotaxane **48** exhibited a pronounced delay in its redox process compared with free PANI.

EPR experiments showed a clear broadening of the signals for **48** compared to those of free PANI. Moreover, the EPR signals of **48** also exhibited a slower attenuation rate and a smaller attenuation ratio of the signal intensity than PANI.

From cyclic voltammetry experiments, free PANI showed the two typical oxidation processes at 0.23 and 0.80 V, which shifted to 0.20 and 0.82 V in the cyclic voltammogram of polypseudorotaxane **48**. The first, more negative,



**Scheme 15** Schematic representation of the interconversion process between the loop  $44\cdot\text{CB}[8]$  and the corresponding [2]pseudorotaxane  $44\text{H}\cdot\text{CB}[8]$



**Scheme 16** Synthesis of [2]rotaxane **45**·CB[7]

anodic peak of **48** indicated that the formation of radical cations in **48** was easier than in free PANI, which is consistent with the electrochemistry of the CB[7]/oligoaniline rotaxane **45**·CB[7]. The more negative cathodic peak of **48** compared with that of free PANI suggested that one electron reduction of radical cations in **48** was more difficult than that in PANI. These phenomena also confirmed the effective stabilization of radical cations of PANI upon complexation with CB[7].

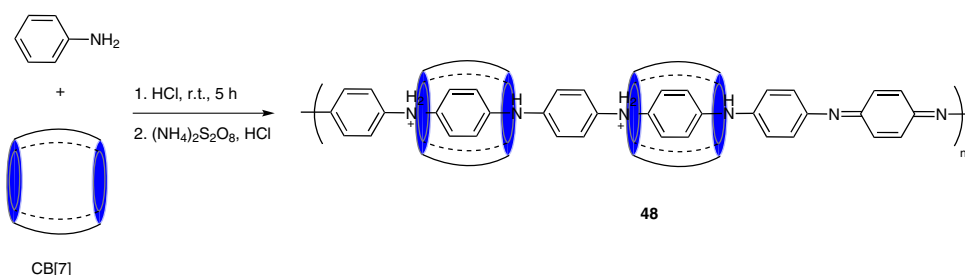
#### 4 Conclusion and Outlook

We have summarized some recent efforts on the construction of interpenetrated molecules based on the molecular recognition of positively charged axle molecules including the ammonium, pyridinium, and aniline moieties. When the positively charged guests were dissolved in organic solvents, crown ethers were selected as the hosts. The pseudorotaxanes can be maintained through hydrogen bonding and  $\pi$ - $\pi$  stacking. Both the crown ethers and the axle molecules can be modified with functional groups, which endowed these systems with more flexibility in their application in molecular machinery and nanotechnology. Based on the obtained rotaxanes and pseudorotaxanes, their switchable properties and control-

lable assembly behavior can be realized through the input of acid/base, heat, light, red/ox, etc. Moreover, based on the interpenetrated molecules, interlocked molecules such as rotaxanes, catenane, and pretzelane could be synthesized.

The positively charged axle molecules can be easily dissolved in water upon changing the counter anions. The cucurbiturils family possess a strong binding affinity toward such axle molecules based on ion-dipole and hydrophobic interactions. Although the cucurbiturils are difficult to functionalize, the axles can still offer many choices in the construction of interpenetrated molecules. Moreover, when the axle molecules have both positively charged and neutral parts, it is possible to introduce cyclodextrins into the systems. By combining the two different binding behaviors of cucurbiturils and cyclodextrins, novel interpenetrated species such as 2D pseudopolyrotaxanes and hetero-wheel pseudorotaxanes can be generated. Some unique material and biological properties have been developed in the CB-based pseudopolyrotaxanes.

In summary, through the use of accurately predesigned hosts and positively charged axle molecules, well-defined interpenetrated structures can be established; these have been applied in the construction of complex [n]rotaxanes and molecular switches, as well as systems with interest-



**Scheme 17** Preparation of pseudopolyrotaxane **48**



ing biological and material properties. We believe that the development of new functional axle molecules and the expanded use of known host-guest pairs will continue to energize the exciting findings and potential of interpenetrated molecules in the fields of molecular devices and machines, and their application in biological and material science.

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