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Stimuli-Responsive Mechanically Interlocked Molecules Constructed from Cucurbit[*n*]uril Homologues and Derivatives

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Cucurbit[*n*]uril supramolecular chemistry has developed rapidly since 2001 when different cucurbit[*n*]uril homologues (Q[*n*]) were successfully separated in pure form. The combination of Q[*n*] cavity size and various types of external stimuli has given birth to numerous types of Q[*n*]-based mechanically interlocked molecules (MIMs), including (pseudo)rotaxanes, catenanes, dendrimers and poly(pseudo)rotaxanes. In this review article, the important advances in the field of Q[*n*]-based MIMs over the past two decades are highlighted. This review also describes examples of heterowheel (pseudo)rotaxanes and poly(pseudo)rotaxanes involving Q[*n*]s, and reflects on the opportunities and challenges of constructing Q[*n*]-based stimuli-responsive MIMs.

1. Introduction

Inspired by many significant biological processes in living organisms, the design and synthesis of molecular machines has received great interest over the past few decades.¹⁻⁸ This interest stems from the scientific value of molecular machines, which has been evidenced by the award of the Nobel Prize in Chemistry in 2016 to Sauvage, Stoddart, and Feringa.⁹⁻¹¹ A machine utilized in daily life tends to be a combination of multiple mechanical devices that transform or apply power, and control motion. An analogously artificial molecular machine that operates at the molecular scale is a device composed of multiple molecular components through weak interactions such as hydrogen bonds, $\pi\cdots\pi$ stacking, charge transfer, metal coordination and hydrophobic interactions.¹²⁻¹⁸ Importantly, the relative positions of the molecular components can be changed by external stimuli (e.g. heat, light, pH changes, solvent polarity changes, metal ion coordination, electrochemical control of oxidation states etc.), resulting in relative motion between the molecular components. Various kinds of artificial

molecular machines such as molecular motors, switches, muscles, lifters, ratchets, and wires, have been reported.¹²⁻¹⁸

Mechanically interlocked molecules (MIMs), including (pseudo)rotaxanes, catenanes, dendrimers and poly(pseudo)rotaxanes, are considered as prototypes or precursors for the construction of artificial molecular machines.¹⁹⁻²² MIMs generally are comprised of a linear “axle” and a cyclic “wheel”. Intramolecular movements between the “axle” and “wheel” components of a MIM can be achieved *via* external stimuli. Among various MIMs, pseudorotaxanes are undoubtedly the simplest type which bear a linear “axle” and a macrocycle or “wheel” bound together through noncovalent interactions. In contrast to pseudorotaxanes, there are two bulky stoppers at the end of the linear “axle” of a rotaxane, which prevent the “wheel” dissociating from the “axle”. When two or more different cyclic “wheel”s are threaded onto the same “axle”, this kind of MIM is termed as heterowheel (pseudo)rotaxane. Poly(pseudo)rotaxanes are constructed by incorporating a number of (pseudo)rotaxanes into polymers.

Up to now, a large number of MIMs have been developed by employing macrocycles such as crown ethers, cyclodextrins (α -, β - and γ -CD), calix[*n*]arenes, pillar[*n*]arenes, various cyclophanes and coordination-based macrocycles.²³⁻²⁸ Our interest in this area has focused on the use of cucurbit[*n*]urils (Q[*n*]s, *n* = 5–8 and 10, Figure 1) and their derivatives. Q[*n*]s are a series of synthetic macrocyclic compounds with a

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hydrophobic cavity and two carbonyl-laced portals.²⁹⁻³⁷ Compared with their parent Q[n], common Q[n] derivatives possess substituents at their waist, while the hydrophobic cavity and carbonyl-laced portals remain unchanged.³⁸ However, their solubility, binding affinity and other properties often change. From a structural point of view, Q[n]s and their

derivatives are perfect candidates for fabricating various MIMs. This review will focus on the stimuli-responsive MIMs constructed from Q[n] homologues and their derivatives over the past two decades. Emphasis will also be given to heterowheel (pseudo)rotaxanes and poly(pseudo)rotaxanes involving the use of Q[n]s.

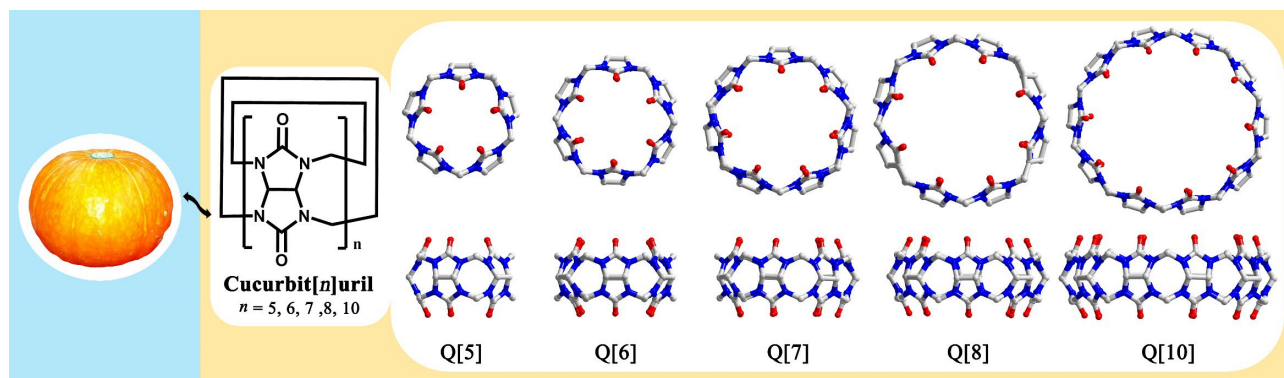


Figure 1 | X-ray crystal structures of cucurbit[n = 5-8, 10]urils.

2. Catenanes constructed from Q[5] derivatives

It is well known that Q[5] is the smallest Q[n] homologue. Previous studies have confirmed that the cavity of Q[5] and its derivatives can only accommodate gases, small anions and small solvents²⁹. Linear species are unable to thread through the cavity of Q[5] to form common MIMs. Pioneering work by Tao and co-workers developed a strategy of coordination with metal ions to construct catenanes by using alkyl-substituted Q[5] (abbreviated as SQ[5]).^{39, 40} The coordination of three kinds of SQ[5] (including 1,2,4-hexamethylcucurbit[5]uril, pentacyclopentanocucurbit[5]uril, and 1,2,4-

cyclopentanocucurbit[5]uril) with potassium ions led to three attractive catenane structures. As shown in Figure 2a, the basic structural unit of the catenanes is a trigonal-planar unit, which is constructed from three SQ[5] ligands and six K⁺ ions. Each K⁺ ion coordinates with six carbonyl groups from two portals of two neighbouring SQ[5] ligands. In such a way, adjacent trigonal-planar basic units are connected together to generate a 10-membered “bracelet” framework (Figure 2b). Interpenetration of the “bracelet” framework finally leads to the formation of a catenane structure (Figure 2c). This strategy of coordination with metal ions may lead to other interesting MIMs in the future.

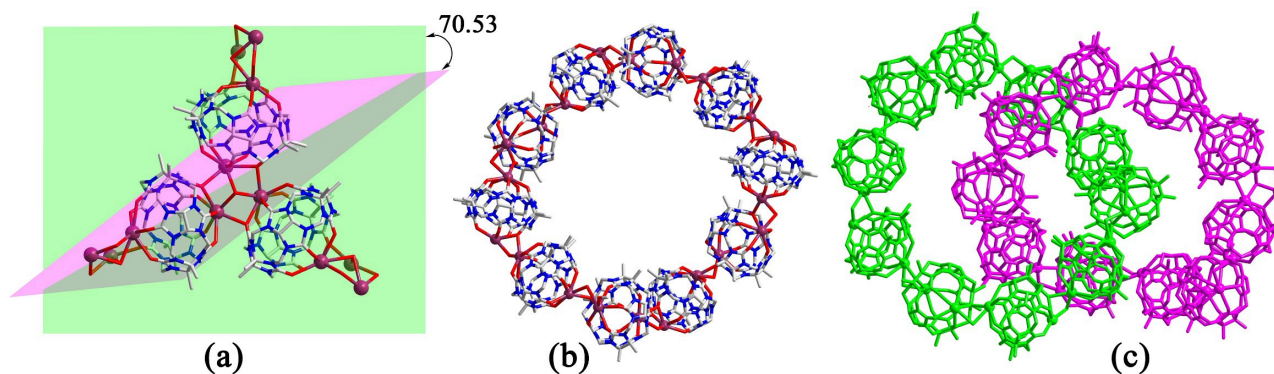


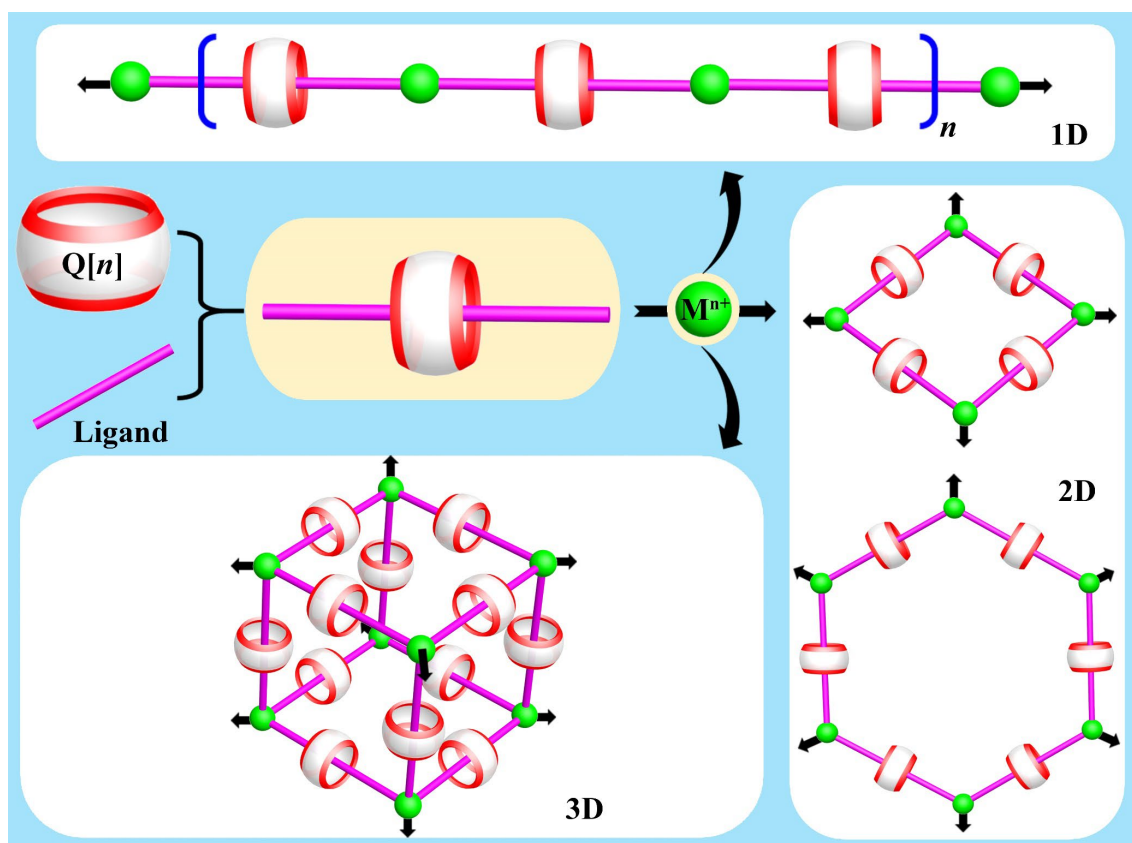
Figure 2. (a) Schematic illustrating the trigonal-planar unit and the coordination environment of the K⁺ ion; (b) A single 10-membered “bracelet” framework; (c) Interpenetration of two “bracelet” frameworks.

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3. MIMs constructed from Q[6] and its derivatives

In the early study of Q[*n*] chemistry, Q[6] was used to construct (pseudo)rotaxane-based molecular switches.⁴¹⁻⁴⁵ Afterwards, Kim *et al.* demonstrated the construction of a series of 1D, 2D and 3D polyrotaxanes and molecular necklaces by using Q[6].⁴⁶⁻⁵¹ As illustrated in Scheme 1, a pre-designed short “string” threads through the Q[6] “bead” to form a stable pseudorotaxane first, and then the pseudorotaxane is coordinated to metal ions to generate 1D, 2D and 3D polyrotaxanes. In general, the short “string” involves diaminobutane or

diaminopentane terminated with a 3/4-pyridylmethyl group or other groups with coordination ability, while the metal ion is a transition metal ion or lanthanide metal ion. Kim, Buschmann, Steinke, and others have also constructed many poly(pseudo)rotaxanes and dendrimers containing Q[6] threaded on organic polymers, wherein no metal ion coordination is involved.⁵²⁻⁵⁶ These remarkable structures incorporating Q[6] have been reviewed by Kim in 2002.⁵⁷ Here we only describe the Q[6]-based MIMs reported over the last two decades.



Scheme 1. Schematic representation of construction of 1D, 2D and 3D polyrotaxanes.

3.1 Light responsive MIMs based on Q[6]

Among various external stimuli, light is particularly attractive for controlling the movement of molecular machines because of advantages such as cleanness, stability and the ability for precise manipulation. Bispyridinium ethylene and its derivatives are a class of photoswitchable molecules. Under light irradiation, they can undergo a *Z* to *E* isomerization process. In 2011, Sindelar and co-workers found that the binding interaction of Q[6] with bispyridinium ethylene results in the formation of a stable inclusion complex. By attaching bulky dinitrobenzene stoppers on both sides of the dipyrindyl ethylene of the inclusion complex, they obtained a rotaxane in which the Q[6] wheel shuttles along the bispyridinium axle (Figure 3a).⁵⁸ Very recently,

we have synthesized an interesting guest, namely 1-(4-carboxybenzyl)-4-[2-(4-pyridyl)-vinyl]-pyridinium chloride, by using bispyridinium ethylene. By interchanging heat and light irradiation, the guest is encapsulated and released by the symmetrical tetramethylcucurbit[6]uril (TMeQ[6]) in its *trans*- and *cis*-forms (Figure 3b).⁵⁹

By utilizing the ring-opening and ring-closing photoisomerization of dithienylethene, Yin, Liu *et al.* designed and synthesized a [3]pseudorotaxane based on Q[6].⁶⁰ Upon irradiation with UV light ($\lambda = 302$ nm) and visible light ($\lambda > 402$ nm), the axle with a dithienylethene backbone underwent photoisomerization, as illustrated in Figure 4.

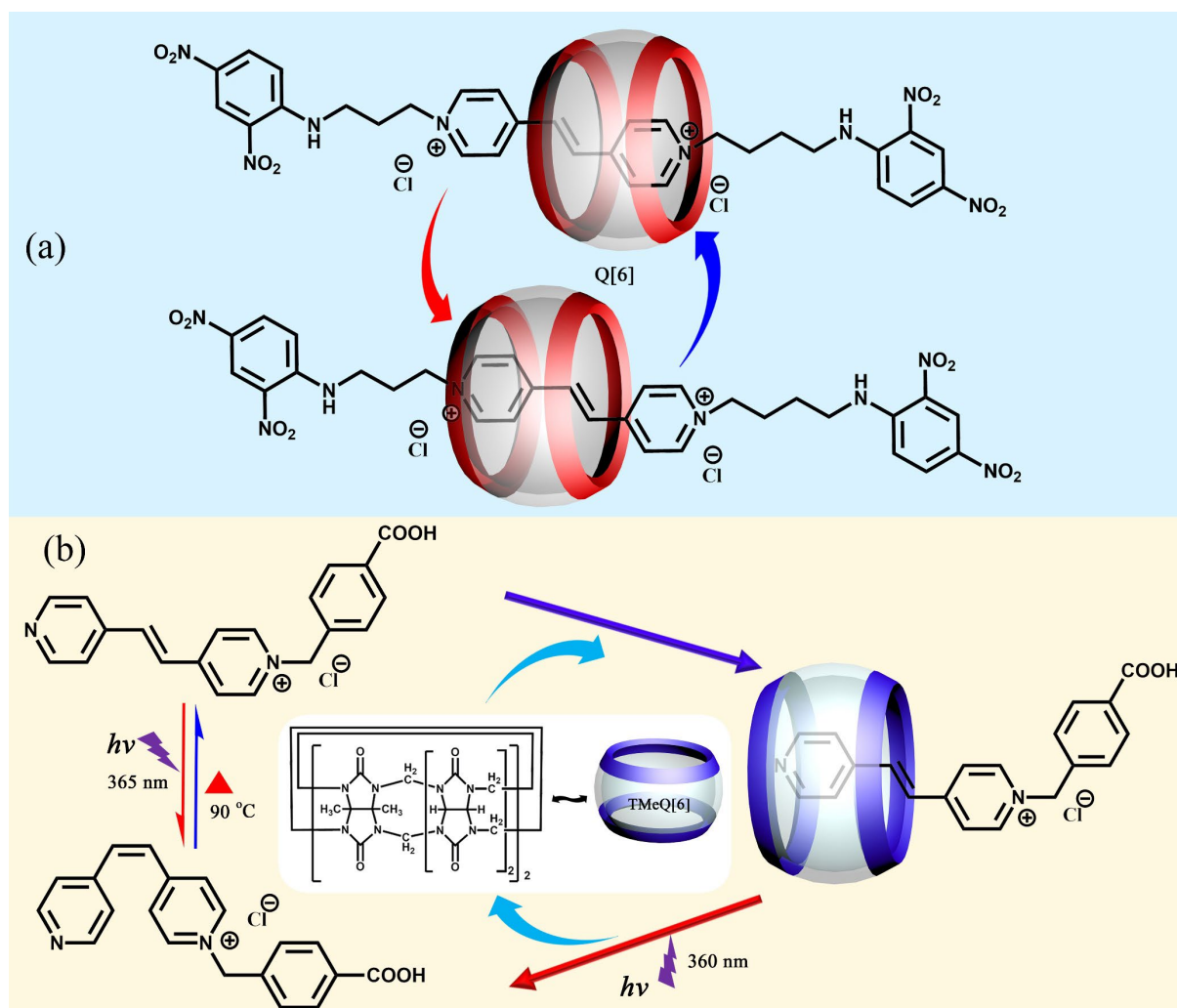


Figure 3. (a) Molecular shuttle based on Q[6] and bispyridinium ethylene; (b) Guest encapsulation and release by TMeQ[6] under light irradiation and heating.

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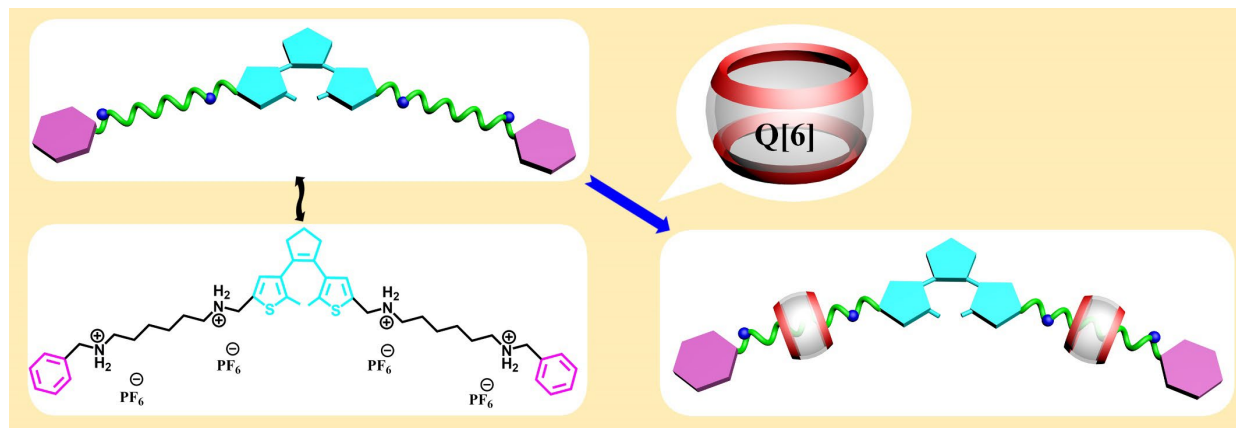


Figure 4. Photoisomerization behaviour of [3]pseudorotaxane based on Q[6] and a dithienylethene derivative.

3.2 pH responsive MIMs based on Q[6]

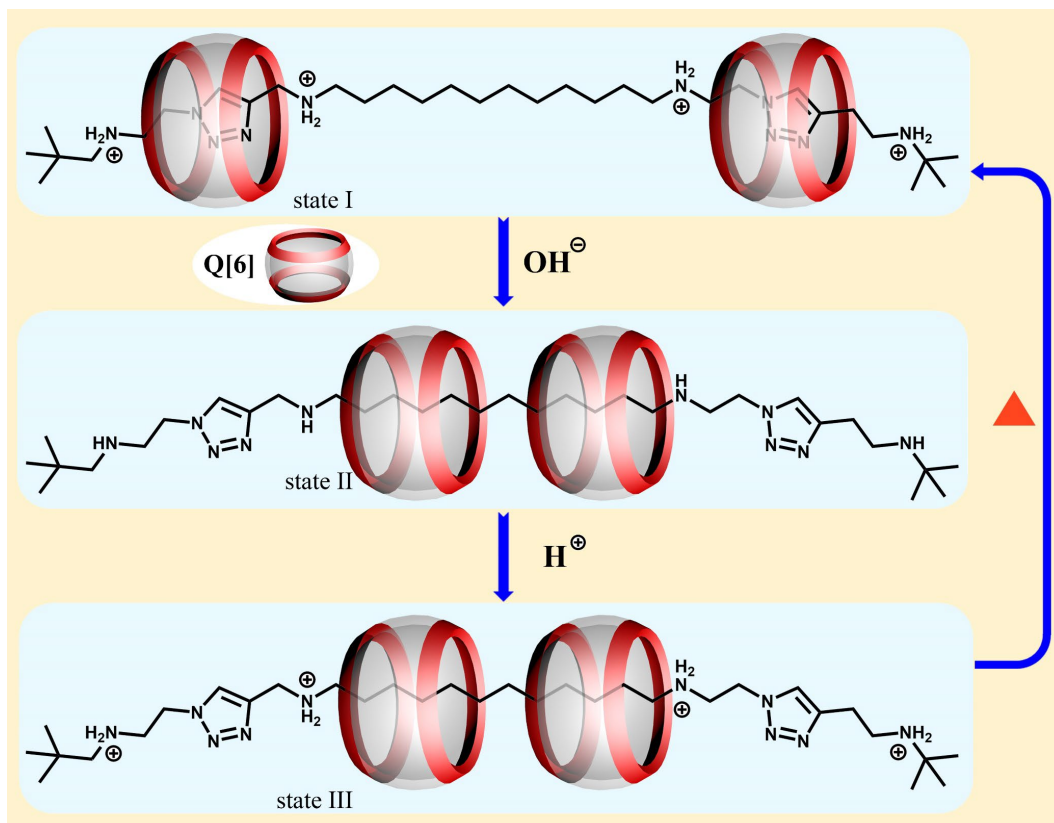
Through a 1,3-dipolar cycloaddition reaction catalyzed by Q[6], Tuncel and Katterle in 2008 prepared a pH- and heat-responsive [3]rotaxane.⁶¹ As shown in Scheme 2, at low pH values, the Q[6] “wheels” are located on the diaminothiazole moieties because of ion-dipole interactions (state I). Upon addition of base, the Q[6] “wheels” move onto the hydrophobic dodecyl spacer (state II). Surprisingly, the Q[6] “wheels” prefer to remain on the dodecyl spacer (state III) after re-protonation of the axle. They can shuttle back to state I upon heating. In 2011, by taking advantages of ESR and NMR spectroscopy, Lucarini *et al.* demonstrated a paramagnetic rotaxane containing Q[6] as a wheel.⁶²

In 2015, Liu *et al.* reported a pseudorotaxane-based molecular switch which functioned in response to pH stimuli.⁶³ As shown in Scheme 3, the antioxidant selenoenzyme compound can be encapsulated into the Q[6] cavity to form a pseudorotaxane when the pH is below 6. If the pH value is increased to 7, the pseudorotaxane of the selenoenzyme compound with

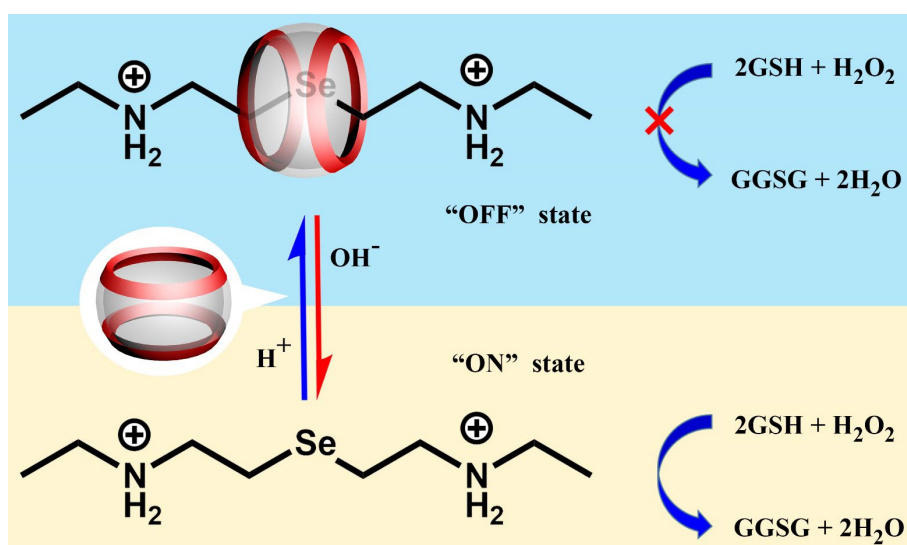
the Q[6] is dissociated and the active site of the selenoenzyme compound was exposed to solution. As a result, the glutathione peroxidase (GPx) activity is switched on. According to the same strategy, other pH-responsive pseudorotaxanes were also developed by the same group.⁶⁴

Modification of material surfaces by organic molecules is an effective method to introduce new functions at the surface of materials. As an early example, Kim *et al.* designed and constructed a self-assembled monolayer, whose prototype is a Q[6]-based pseudorotaxane, on a gold surface (Scheme 4).⁶⁵ Firstly, the “strings” containing butanediammonium and 1,2-dithiolane groups are attached at the gold surface, and then the Q[6] “beads” are threaded on the “strings”. The reversible de-threading and re-threading of the Q[6] “bead” on the “string” is controlled by the pH value. In 2008, Stoddart and co-workers developed a pH-controllable nanovalve, the mesoporous silica nanoparticle surface of which is attached by Q[6] pseudorotaxanes (Scheme 5).⁶⁶ The nanovalves are able to encapsulate and release guest molecules (rhodamine

B) on command via modulating the pH values. On the basis of this achievement, Stoddart, Zink and co-workers further developed dual-controlled nanoparticles exhibiting AND logic.⁶⁷ In the dual-controlled nanoparticle systems, the release of encapsulated guest molecules requires both light and pH change, which are operated in tandem to one another. At the same time, they also designed and synthesized a pH clock-operated mechanized nanoparticle system for biological applications.⁶⁸

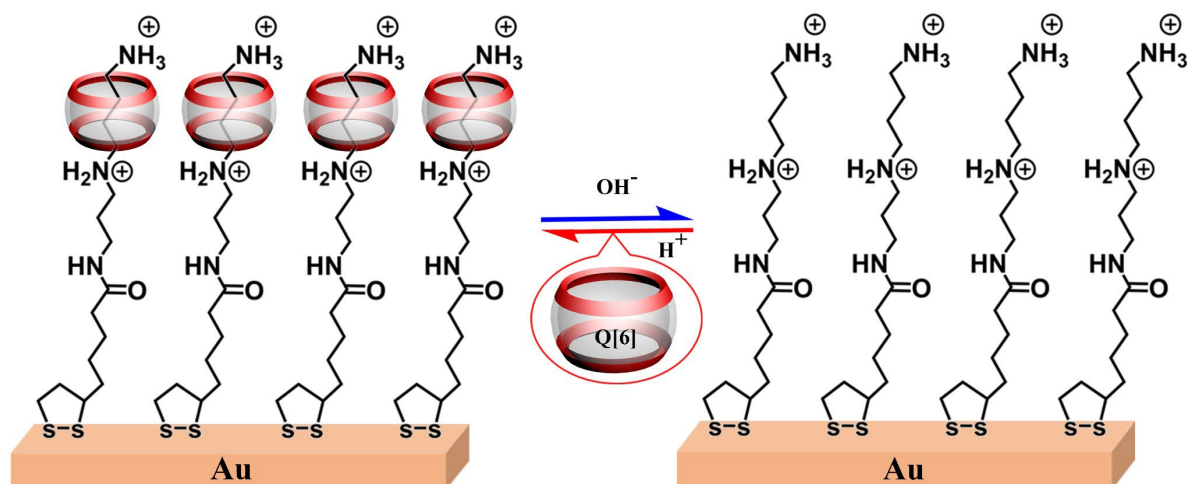


Scheme 2. pH and heat-triggered switching of Q[6] on an axle.

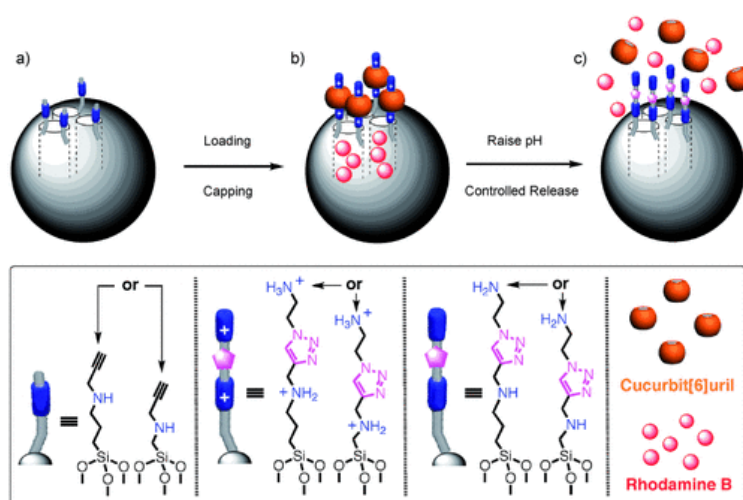


Scheme 3. Schematic representation of the pH-controlled switching of the artificial antioxidant selenoenzyme.

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Scheme 4. Schematic illustrating the de-threading and re-threading of the Q[6] "bead" under pH control.



Scheme 5. Graphical representations show the operations of the nanovalve based on a Q[6] pseudorotaxane. Reproduced from reference[66]. Copyright 2008 John Wiley & Sons.

3.3 Polypseudorotaxanes constructed from Q[6]

Using a Q[6] catalyzed 1,3-dipolar cycloaddition, Tuncel and co-workers synthesized a Q[6]-based polypseudorotaxane. As illustrated in Figure 5, this polypseudorotaxane behaves as a pH-driven polymeric switch. At an appropriate pH ($\text{pH} < 9$), the amine groups of the linear axle are protonated and the Q[6] "beads" are

located on the triazole rings *via* ion-dipole interactions. When the pH value is greater than 9, the Q[6] "beads" move onto the hydrophobic aliphatic spacer *via* hydrophobic interactions.⁶⁹

According to the strategy of Kim⁵⁷, our group synthesized a chiral helical polyrotaxane by using a TMeQ[6] "bead" and the achiral *N,N'*-bis(2-pyridylmethyl)-1,6-hexanediamine "string".⁷⁰ In aqueous

solution, the TMeQ[6] “bead” docks at the middle position of the “string”, forming a pseudorotaxane.⁷¹ When AgNO₃ was added to the solution of this pseudorotaxane, the achiral “string” can coordinate to Ag⁺ metal ions to form a helical coordination polymer (Figure 6), while TMeQ[6] “beads” are threaded on this coordination polymer, thereby generating a helical

polyrotaxane. Most interestingly, the crystal of this helical polyrotaxane is a racemic compound, which contains equal amounts of left-handed and right-handed helices. We and others have also reported other poly(pseudo)rotaxanes by using Q[6] and its derivatives.⁷²⁻⁷⁷

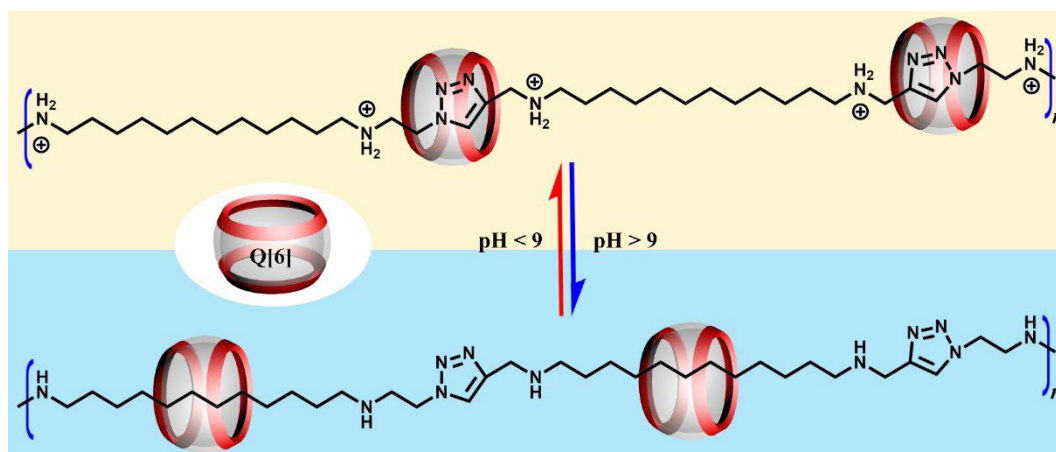


Figure 5. pH-responsive polypseudorotaxane based on Q[6].

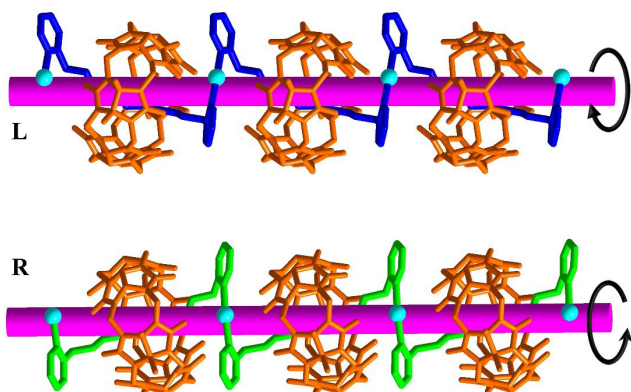


Figure 6. X-ray crystal structure of helical polyrotaxanes of TMeQ[6] with *N,N'*-bis(2-pyridylmethyl)-1,6-hexanediamine and Ag⁺.

4. MIMs constructed from Q[7].

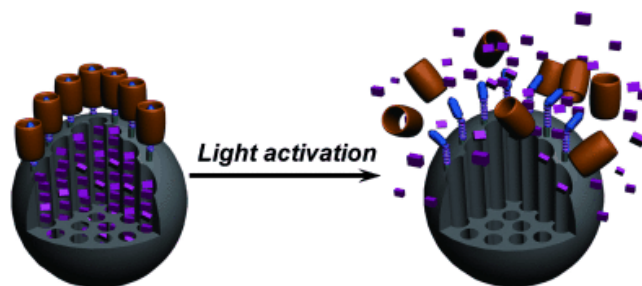
The synthesis and isolation of Q[7] and Q[8] by Kim, Day and co-workers opened up many new research avenues in supramolecular chemistry.^{78, 79} Compared with Q[6], the cavity of Q[7] is much larger, and thus can accommodate a wide range of guests such as adamantane, viologen, *o*-carborane, ferrocene and naphthalene derivatives. On the other hand, among the

Q[*n*] homologues, Q[7] exhibits the best solubility in aqueous solution. Therefore, Q[7] is a useful ‘bead’ for the construction of various MIMs. Here, we describe light-, pH-, redox-, and metal ion coordination-responsive molecular switches based on Q[7], plus poly(pseudo)rotaxanes and dendrimers constructed from Q[7].

4.1 Light responsive MIMs based on Q[7].

In an early report, Tian and co-workers presented a light-driven pseudo[4]rotaxane,⁸⁰ which was constructed via the insertion of Q[7] and α -CD onto a dumbbell axle consisting an azobenzene unit and two viologen moieties (Figure 7). The α -CD macrocycle shuttling on the azobenzene unit of the pseudo[4]rotaxane can be achieved upon irradiation with 430 and 360 nm light, which leads to different induced circular dichroism (ICD) signals.

In 2012, Zhao⁸¹ *et al.* presented a photoresponsive [3]rotaxane based on Q[7] and a dumbbell molecule (Figure 8). The dumbbell molecule consists of one *trans*-azobenzene unit and two viologen units. Two viologen units of the dumbbell molecule can be encircled by two shuttling Q[7] rings to form a [3]rotaxane. Under different light irradiation, the azobenzene unit of the dumbbell molecule undergoes *trans-cis* isomerization, resulting in different shuttling ranges of the Q[7] rings. In the same year, the Yang group developed a photoresponsive supramolecular nanovalve, in which the Q[7]-cinnamamide [2]pseudorotaxanes were installed on the outer rim of mesoporous silica nanoparticles.⁸² As shown in Scheme 6, this nanovalve can trap cargo molecules within its nanopores in biological media. When irradiated with light of a suitable wavelength, the cinnamamide stalks undergo a *trans*- to *cis*-conformational change, leading to the de-threading of Q[7], and the trapped cargo molecules are released.



Scheme 6. Schematic representation of light-responsive nanovalves based on Q[7]-cinnamamide [2]pseudorotaxane. Reproduced from reference [82]. Copyright 2012 John Wiley & Sons.

Very recently, Basílio, Palora, McClenaghan, and co-workers have prepared a guest axle comprising a central *trans*-chalcone moiety and two terminal pyridinium units.⁸³ As can be seen in Figure 9, the guest axle complexes with the Q[7] wheel in water to form a pseudorotaxane, in which the Q[7] wheel shuttles along the axle. Upon irradiation under slightly acidic conditions, the *trans*-chalcone moiety of the pseudorotaxane transforms into a fluorescent cationic flavylum moiety and the Q[7] wheel translocate to a flavylum moiety, resulting in the formation of another kind of pseudorotaxane. Interestingly, translocation of the Q[7] wheel leads to a dramatic increase in the fluorescence quantum yield.

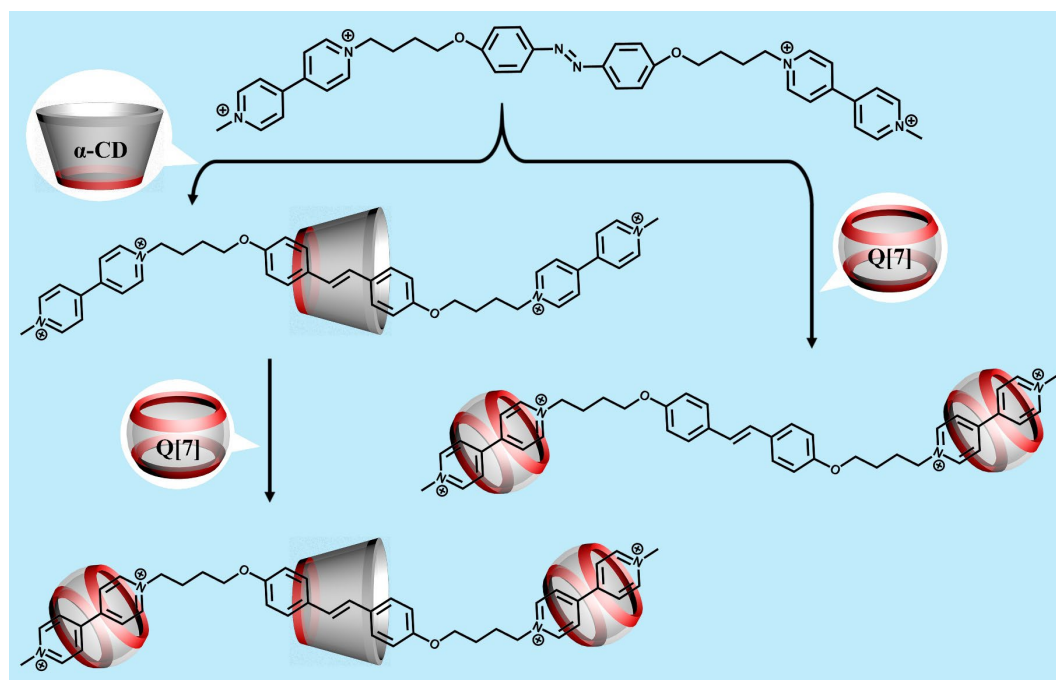


Figure 7. Schematic representation showing the synthesis of a pseudo[4]rotaxane.

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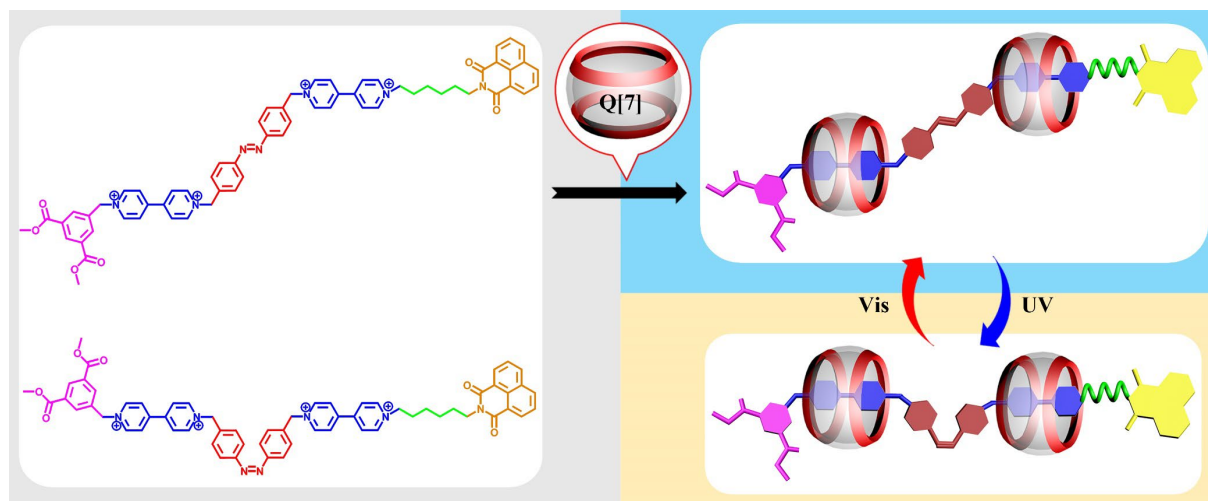


Figure 8. Light-controllable Q[7]-based molecular shuttle.

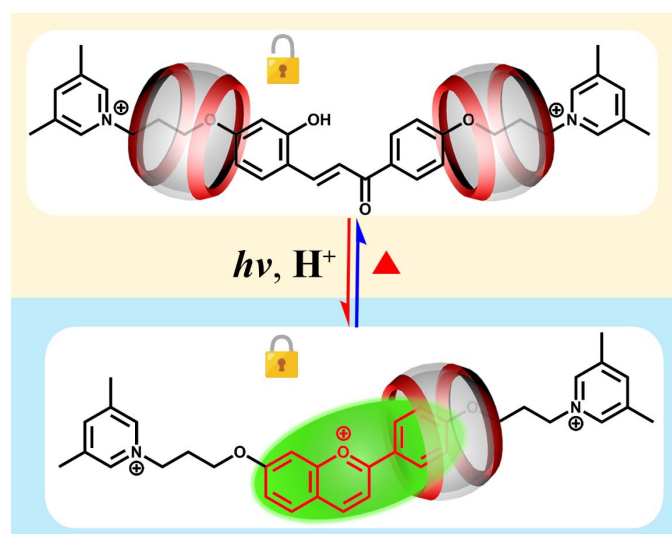
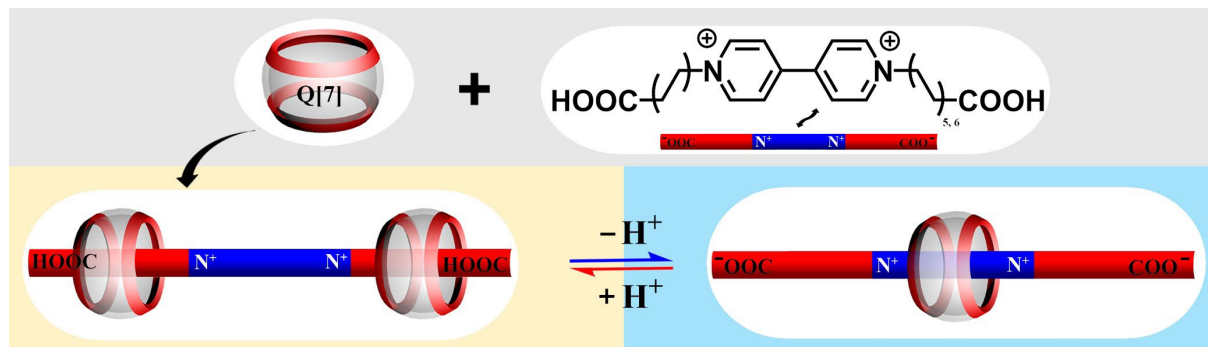


Figure 9. Schematic representation showing the transformation of two different pseudorotaxanes under light irradiation.

In an early study, the Kaifer group demonstrated a pH-controlled [2]pseudorotaxane based on a Q[7] wheel and an axle, which contains a central viologen unit, two aliphatic *N*-substituents and two terminal COOH groups.⁸⁴ The Q[7] wheel shuttles between two terminal COOH groups of the axle at low pH (~ 2.6), while it docks on the central viologen unit at neutral pH (Scheme 7). A few years later, the same group explored the pH effects on the kinetics of this [2]pseudorotaxane formation and dissociation.⁸⁵ By using the Q[7] wheel and an axle containing one viologen nucleus and two *p*-toluic acid arms, the Liu group constructed a multiple interconvertible system, in which the formation and interconversion of different MIMs are controlled by pH.⁸⁶

4.2 pH responsive MIMs based on Q[7]

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Scheme 7. pH control on the location of the Q[7] wheel in the pseudorotaxanes.

In 2009, Tian and co-workers designed and synthesized a V-type molecule comprising a cyanine branch and a *p*-aminophenoxy ethyl side arm.⁸⁷ The Q[7] macrocycle can form quite different [2]pseudorotaxanes with this V-type molecule by encapsulating the cyanine branch or the aminophenoxy ethyl side arm in aqueous solution at different pH (Figure 10). The different types of [2]pseudorotaxane display different colours in solution. Two years later, Tian *et al.* synthesized another V-type molecule comprising a cyanine dye unit as a threading unit and a [Ru(bpy)₃]²⁺ as a stopper moiety on the other arm.⁸⁸ The cyanine dye unit prefers to thread into the Q[7] rather than the β -CD cavity.

In 2013, Akkaya and co-workers demonstrated a pH-mediated molecular shuttle system based on a Q[7] wheel (Figure 11).⁸⁹ The axle consists of a substituted Bodipy fluorophore, a viologen unit, an aliphatic *N*-substituent and a terminal COOH group, which can provide two alternative stations for the Q[7] wheel. The docking location of the Q[7] wheel is controlled by

changing the pH of the aqueous solution. That is, oscillating pH values lead to a switching of the Q[7] from one station to another. Interestingly, this switching is accompanied by a change of fluorescence spectroscopy.

Based on Q[7] pseudorotaxanes, the Yang group in 2014 designed and constructed a biocompatible layer-by-layer coated mesoporous silica nanoparticles. By changing the pH values or by adding competitive agents, the cargo molecules, e.g., doxorubicin hydrochloride (DOX) or propidium iodide (PI) were released from the crafted mesoporous silica nanoparticles.⁹⁰ In the following year, the Yang group reported another kind of mesoporous silica nanoparticle, on which dynamic cross-linked supramolecular network of polymer chains is attached via disulfide bond and ion-dipole interactions between Q[7]s and protonated diamines in the polymer chains. Lowering the pH value or addition of glutathione results in the disassembly of the cross-linked polymer network and the release of anticancer drugs.⁹¹

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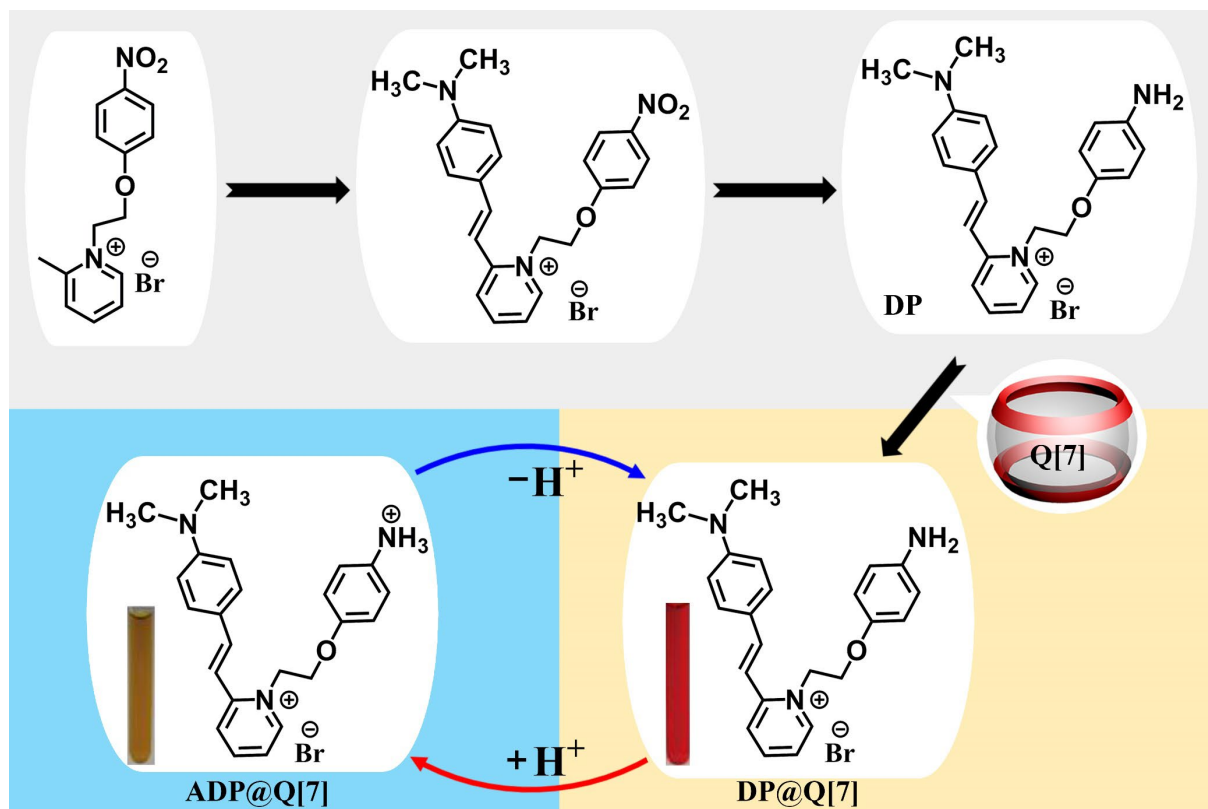


Figure 10. pH-controlled V-type molecular switch based on Q[7].

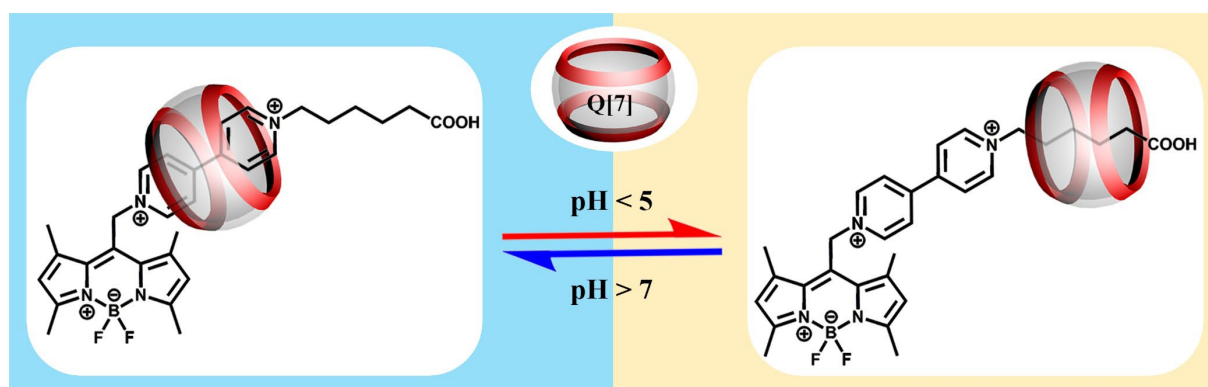


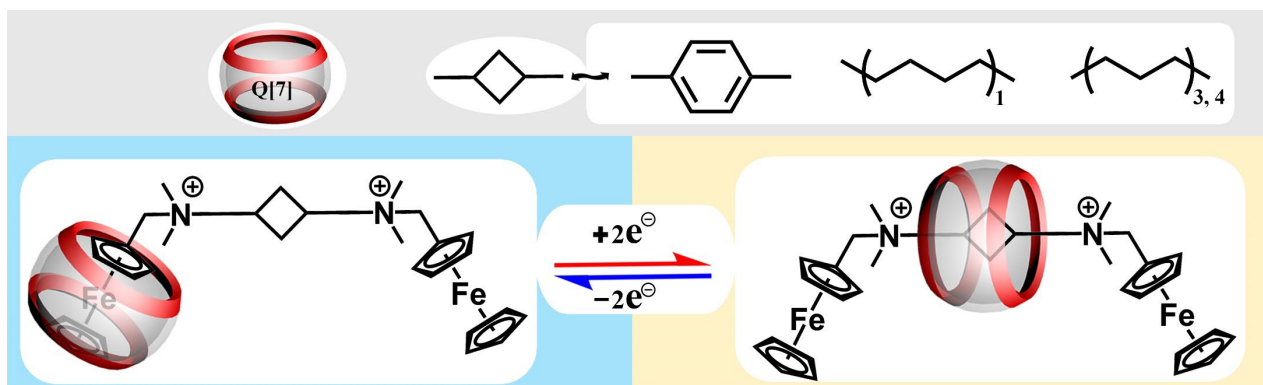
Figure 11. pH-controlled molecular shuttle based on Q[7].

4.3 Redox responsive molecular switches based on Q[7].

Both viologen and ferrocene are important redox active groups and they have been widely used to construct electrochemically driven molecular machines. For instance, Kaifer *et al.* demonstrated electrochemically

driven pseudorotaxanes constructed from a Q[7] wheel and a ferrocenyl-containing axle (Scheme 8).⁹² The designed axle guests contain two terminal ferrocenyl units and hexylene or xylylene units. Whether the binding

location of Q[7] is at the central binding site or at two terminal binding sites, can be controlled via the redox process of the ferrocenyl units of the axle guests.



Scheme 8. Schematic representation showing that the Q[7] binding location is electrochemically controlled.

In a follow-up study, the Liu group constructed an electrochemically driven molecular selector by using Q[7] and cyclohexanocucurbit[6]uril (CyH₆Q[6]).⁹³ As illustrated in Figure 12, Q[7] and CyH₆Q[6] can selectively bind with different moieties of the axle guest

hexyldimethyl(ferrocenylmethyl)ammonium to form different stable [2]pseudorotaxanes. Interestingly, the formation and dissociation of the [2]pseudorotaxanes as well as the binding location is controlled by the redox states of the guest.

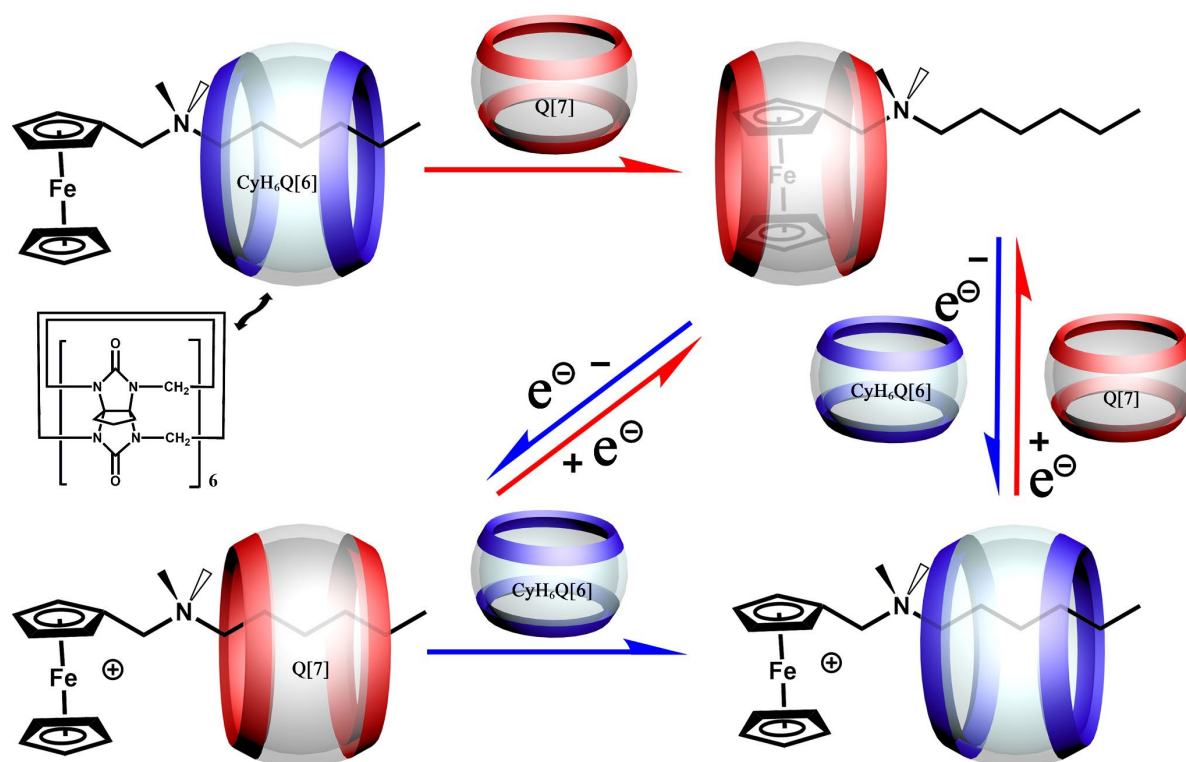


Figure 12. Electrochemically driven molecular selector constructed by Q[7] and CyH₆Q[6].

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4.4 Metal ion coordination-responsive MIMs based on Q[7]

In 2018, Wang, Kermagoret, Bardelang *et al.* reported a Q[7]-based molecular switch controlled by metal ion coordination⁹⁴. As can be seen from Figure 13, the complexation of the Q[7] wheel with the rigid Viologen–Phenylene–Imidazole (*V–P–I*) axle in aqueous solution reveals that the Q[7] wheel prefers to locate at the *V* station. The addition of Ag^+ results in the Q[7] sliding from station *V* to station *P* of the axle because of the formation of $\text{Ag}^+\cdots\text{N}$ and $\text{Ag}^+\cdots\text{O}$ coordinating bonds.

4.5 Polypseudorotaxanes and Dendrimers constructed from Q[7]

In an early study performed by Kaifer and Ling, Q[7] was demonstrated to form highly stable inclusion complexes with two monomers bis(diethylsulfonium)-*p*-xylylene and

bis(tetrahydrothiophenium)-*p*-xylylene.⁹⁵ Based on these findings, Garcia *et al.* synthesized a pseudopolyrotaxane PPV@nQ[7] (Figure 14) in which the polymer poly(phenylene vinylene) threaded through numerous Q[7] cavities under basic conditions, and then studied its enhanced luminescence properties.⁹⁶ The pseudopolyrotaxane material PPV@nQ[7] may be useful in nanotechnology. By condensation of aniline in the presence of Q[7] in hydrochloride acid solution, Liu and co-workers constructed a pseudopolyrotaxane PANI@nQ[7], in which many Q[7] macrocycles thread on a one-dimensional polyaniline PANI chain.⁹⁷ Zhang and co-workers fabricated a polypseudorotaxane based on the cationic polymer ϵ -poly-*L*-lysine and the macrocyclic host Q[7].⁹⁸ The antibacterial efficiency of the polypseudorotaxane can be tuned by altering the ratio of the macrocyclic host to the cationic polymer.

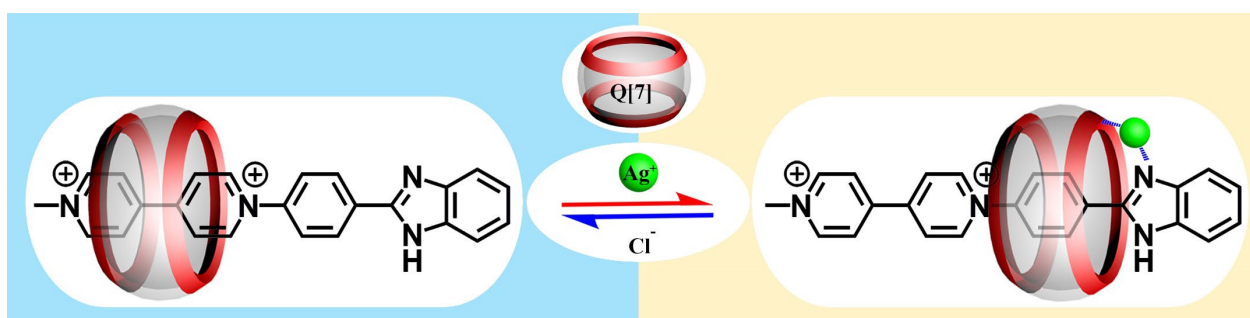


Figure 13. Metal coordination induced molecular switch.

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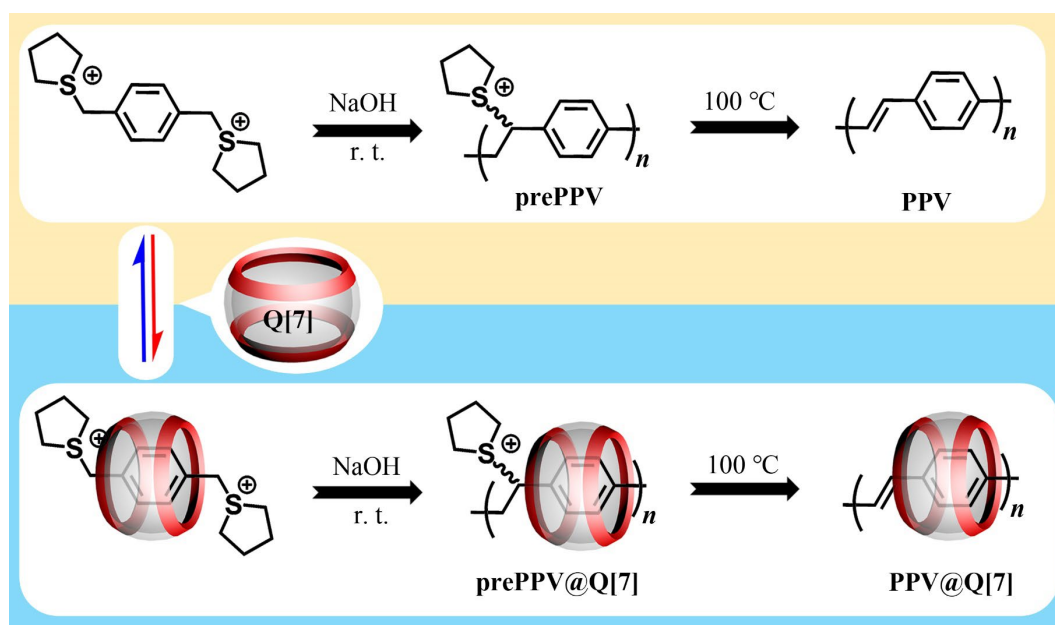


Figure 14. Formation of pseudopolyrotaxane PPV@nQ[7] by polymerisation of bis(tetrahydrothiophenium)-*p*-xylylene under basic conditions.

In 2019, Saleh *et al.* synthesized a bioactive supramolecular carbohydrate polymer by the grafting of Q[7]-encapsulated dequalinium chloride hydrate (DCH) onto alginic acid carbohydrates (ALG).⁹⁹ By changing the polymer temperature and adding 2-anilinonaphthalene-6-sulfonic acid (ANS), controlled shuttling of the Q[7] wheels along the DCH stalk was possible, accompanied by a change in the Förster resonance energy transfer (FRET) signals (Figure 15).

By using host-guest interactions, Q[7] macrocycles can be attached on dendrimers through the formation of

pseudorotaxanes.¹⁰⁰⁻¹⁰² For example, Kaifer and Ong in 2003 reported the host-guest molecular encapsulation of Newkome-Type dendrimers containing a 4,4'-bipyridinium residue by Q[7] (Scheme 9).¹⁰⁰ Li, Yang *et al.* demonstrated a series of dendrimers, in which the terminal naphthyl groups can be threaded through Q[7] cavities to form pseudorotaxanes.¹⁰² By modifying with Q[7], the dendrimers showed a significant increase in fluorescence quantum yields because the energy dissipation of the terminal naphthyl groups was entirely suppressed.

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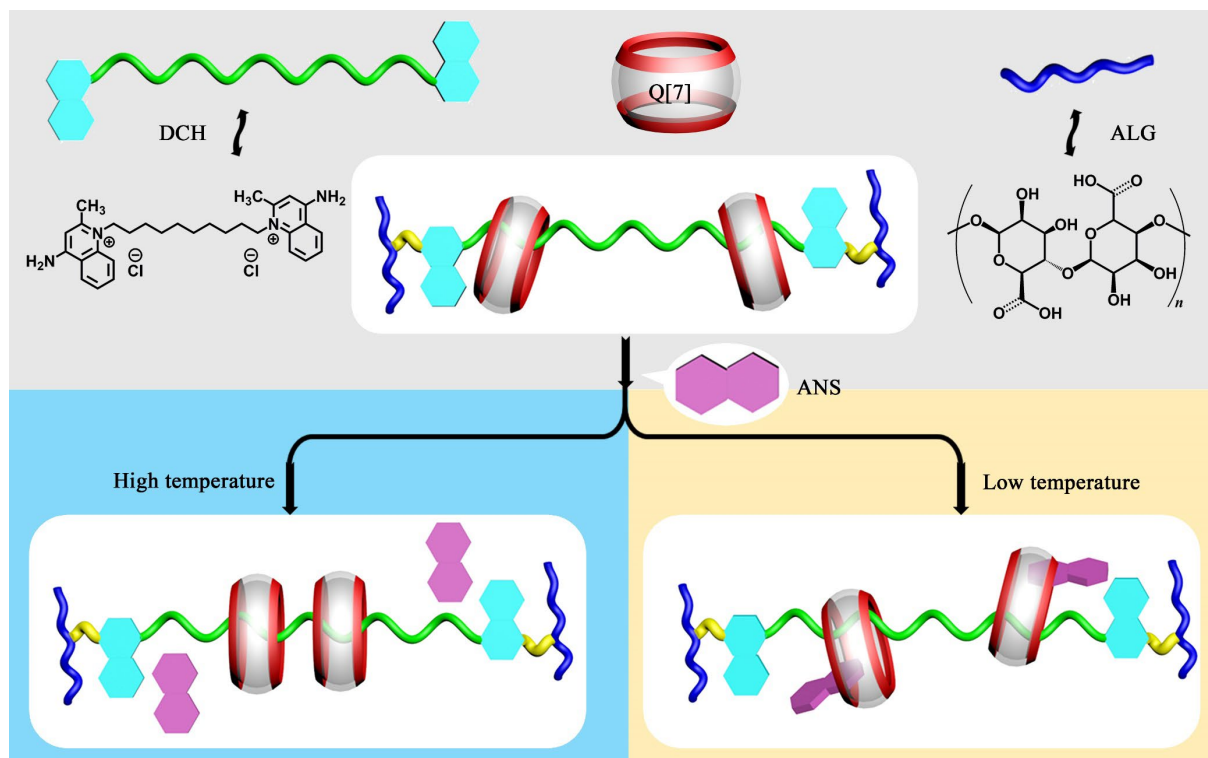
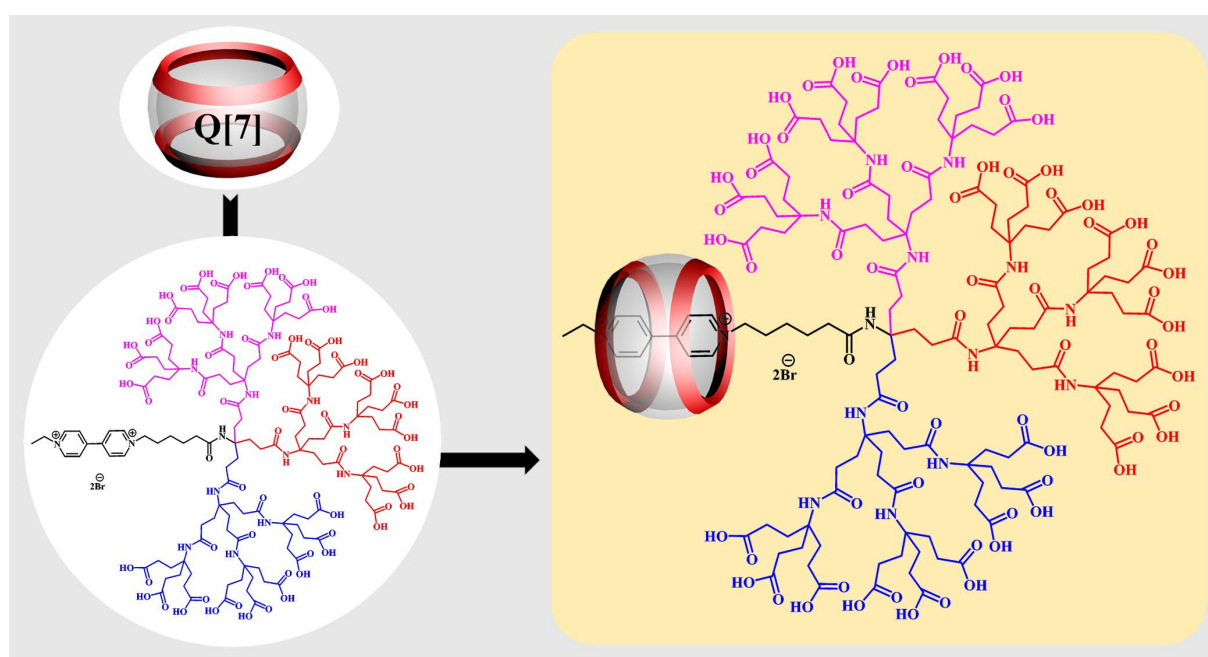


Figure 15. Illustration of the movement of Q[7] wheels upon the temperature changes.



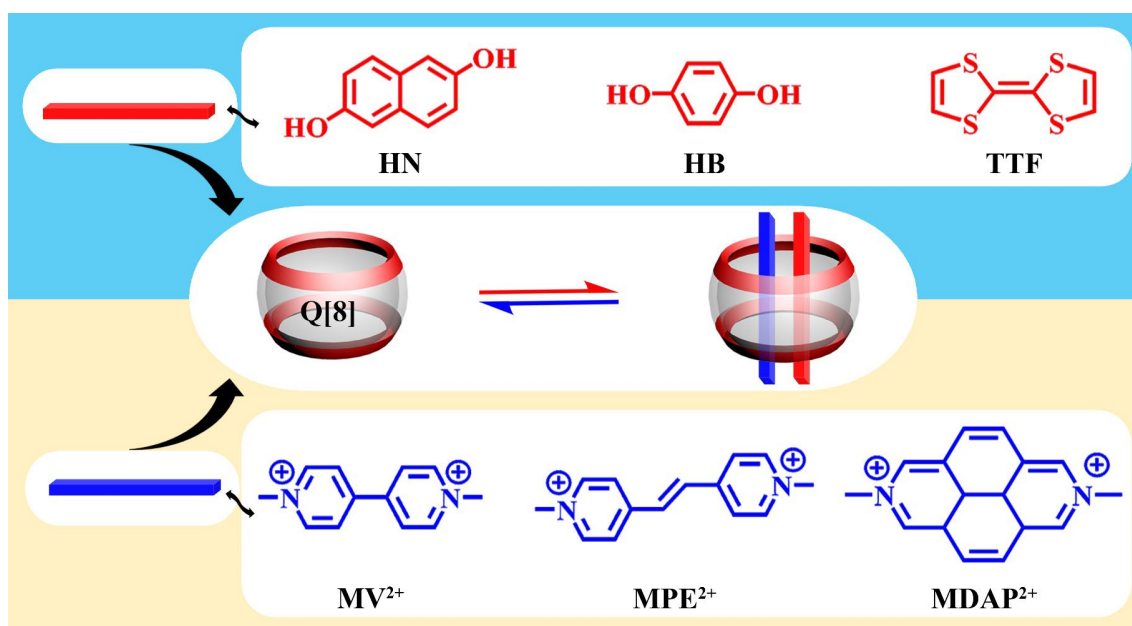
Scheme 9. Schematic representation of Q[7] binding with dendrimers.

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5. MIMs constructed from Q[8].

Compare to its smaller homologues Q[6] and Q[7], the most significant feature of Q[8] is that its cavity is large enough to accommodate two different aromatic guest molecules, an electron-deficient molecule (electron-Acceptor) and an electron-rich molecule (electron-Donor), to form a stable 1:1:1 ternary inclusion complex (Scheme 10).¹⁰³ The Donor-Acceptor interaction or charge-transfer interaction between π -systems is stabilized by the Q[8] host, which is commonly known as

a host-stabilized charge-transfer interaction. By taking advantage of the host-stabilized charge-transfer interactions between the guest pair inside the hydrophobic cavity of Q[8], a variety of MIMs and supramolecular polymers based on Q[8] have been synthesized. The work in this area has been reviewed by Kim¹⁰³, Tian¹⁰⁴, and Kaifer¹⁰⁵, and so will not be considered here. The host-stabilized charge-transfer interaction is also used to selectively bind with the target guest. A good example of this utility is the Q[8] rotaxane synthesized by Urbach *et al*¹⁰⁶.



Scheme 10. Formation of Q[8]-based 1:1:1 ternary inclusion complex.

5.1 Light responsive MIMs based on Q[8].

Very recently, Yang and co-workers constructed a 2D supramolecular organic framework (SOF) based on Q[8] by using two organic monomers, TPE-4MV and AZO, which contain multiple viologen and azobenzene functional groups, as shown in Figure 16.¹⁰⁷ The

reversible formation and dissociation of the 2D SOF was triggered by light through the *trans* – *cis* isomerization of the azobenzene group in AZO. Most importantly, by monitoring the fluorescence intensity, the 2D SOF is capable of detecting azoreductase activity, accompanied by the growth process of *Escherichia coli*.

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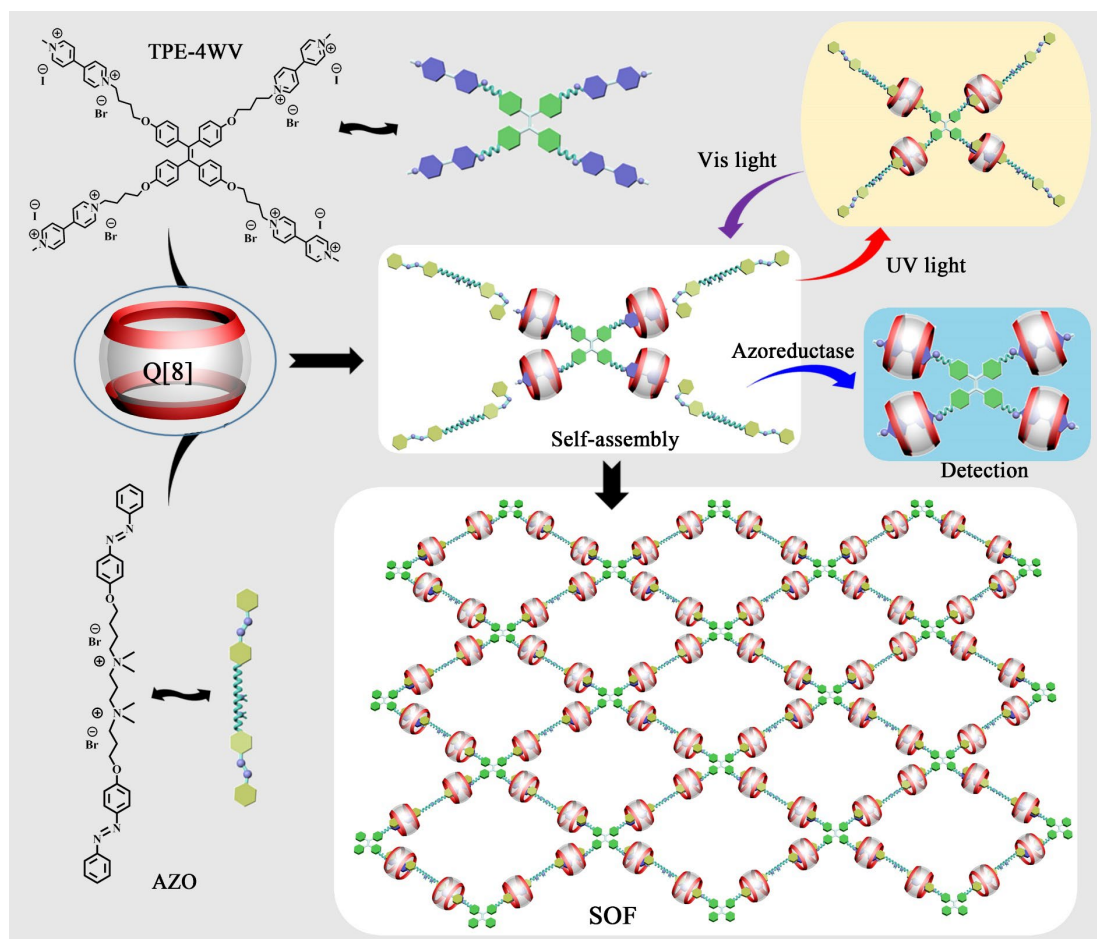


Figure 16. Schematic representation of the formation of a 2D supramolecular organic framework (SOF) by the self-assembly of TPE-4MV, AZO, and CB[8], reversible formation and dissociation realized through light-mediated isomerization, and azoreductase detection in *Escherichia coli* by the enzymatic reduction of AZO.

5.2 pH responsive MIMs based on Q[8].

In 2011, Liu¹⁰⁸ and co-workers reported a pH controlled molecular device. They first synthesized an acceptor–donor–acceptor-type linear molecule **1**²⁺ containing one electron-rich naphthoxy (NP) unit and two electron-deficient monocharged viologen (MCV) units. As can be seen in Figure 17, through the noncovalent interactions of Q[8] with the NP or MCV units and the host-stabilized charge-transfer interactions between the NP and MCV units, two **1**²⁺ axles were encapsulated into

three Q[8] hosts, forming a [5]pseudorotaxane. Upon addition of acid, the [5]pseudorotaxane dissociated to [3]pseudorotaxane. The transformation between these two pseudorotaxanes can be achieved by pH control. Bhasikuttan *et al.*¹⁰⁹ presented a pH-mediated stoichiometric switching process based on the Q[8] complexes with the H33258, a drug with antitumor and antimicrobial properties. Importantly, the distinct pH-mediated stoichiometric switching of Q[8] – H33258 complexes demonstrated contrasting fluorescence properties.

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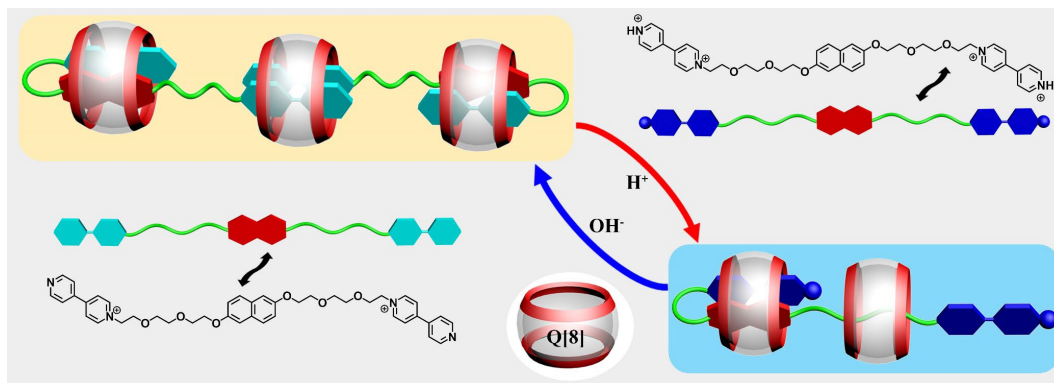


Figure 17. Schematic representation of the transformation between two pseudorotaxanes.

5.3 Redox responsive MIMs based on Q[8].

In their pioneering work, Stoddart *et al.*¹¹⁰ incorporated viologen (V^{2+}) units and 1,5-dihydroxynaphthalene (DNP) stations into thread-like compounds, which formed pseudorotaxanes with a Q[8] host. The switching behaviour of the threads within their pseudorotaxanes is redox responsive, as shown in Figure 18. In 2012, Credi,

Venturi, Tian, and co-workers synthesized tweezer-like molecules consisting of chiral binaphthol units as hinge and two bipyridinium moieties as arms. In aqueous solution, the dihedral angle of the hinge could be reversibly modulated through chemical or photochemical reduction upon association and disassociation of the Q[8] hosts.^{111, 112}

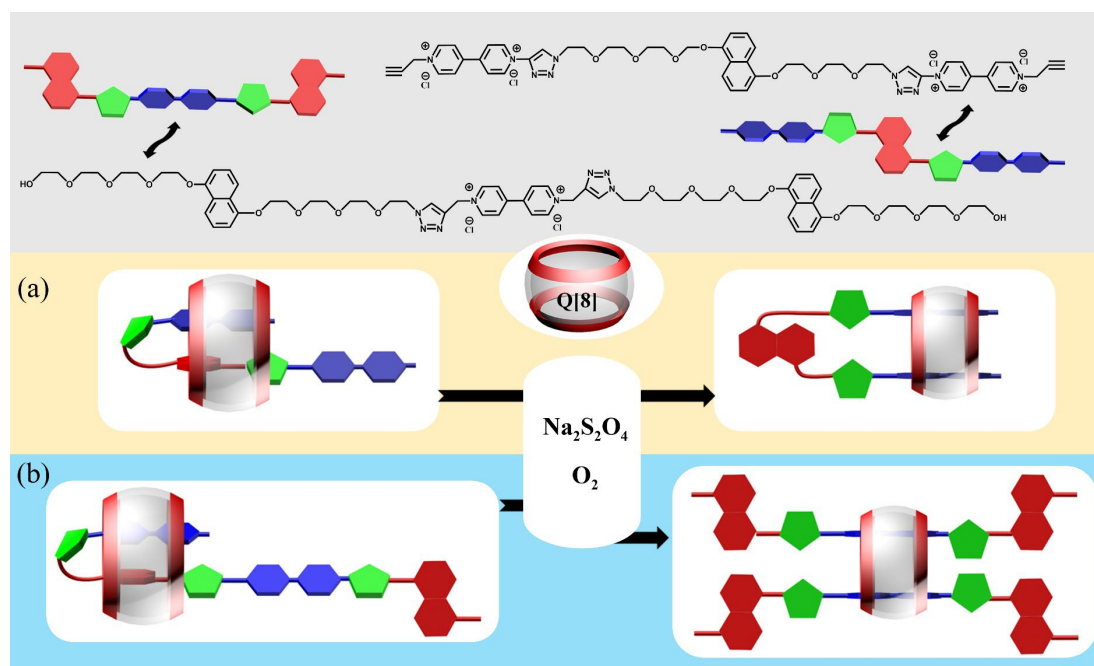


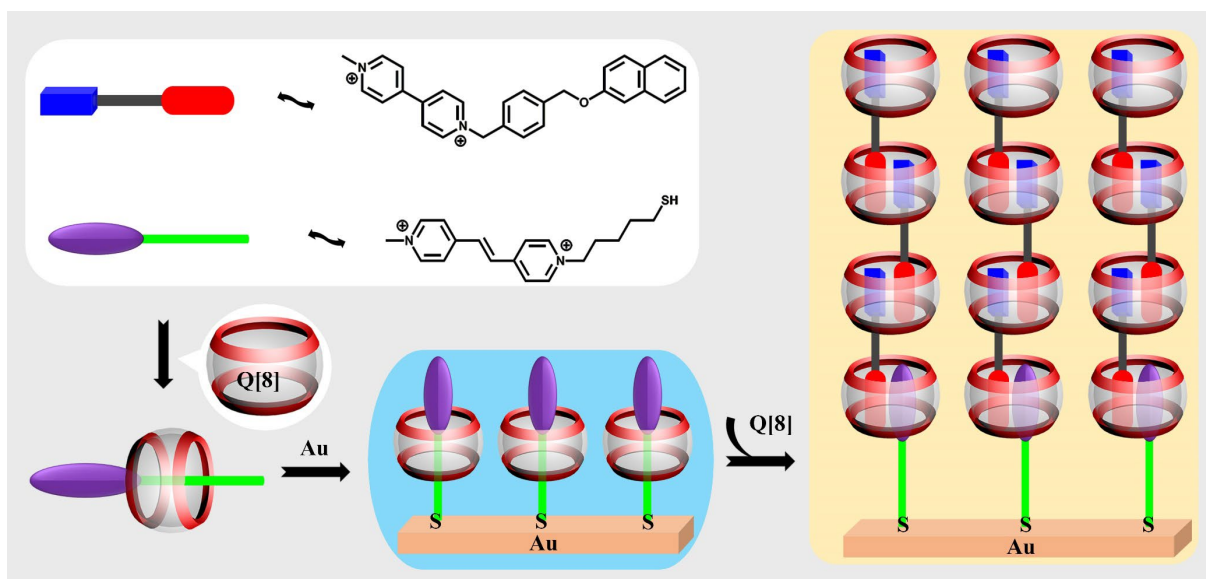
Figure 18. Chemically-triggered interconversions in host-guest complexes: (a) reduction of "end-to-interior loop" superstructure to form an "end-to-end loop" superstructure and (b) reduction of "end-to-interior loop" superstructure leads to the formation of a [3]pseudorotaxane superstructure.

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5.4 Polypseudorotaxanes and supramolecular polymers constructed from Q[8]

Much excellent work involving the use of Q[8]-stabilized charge-transfer (CT) interactions to construct rotaxanes, polypseudorotaxanes, and supramolecular polymers has been reported by Kim,^{113, 114} Zhang,^{115, 116} Scherman¹¹⁷⁻¹¹⁹ *et al.* Back in 2004, Kim and co-workers demonstrated the growth of Q[8]-based poly(pseudorotaxane) on a gold surface using Q[8]-stabilized charge-transfer interactions.¹¹³ As illustrated in Scheme 11, the

dipyridiniummethylene-Q[8] pseudorotaxanes were first anchored on the gold surface by immersing a gold substrate in an aqueous solution of dipyridiniummethylene-Q[8] pseudorotaxane. Then the poly(pseudorotaxane) could be obtained by soaking the substrate in an aqueous solution of Q[8] and D-A monomer. In the same year, Kim and co-workers designed and synthesized a Q[8]-based cyclic oligomer (molecular necklace) via host-stabilized intermolecular charge-transfer interactions.¹¹⁴

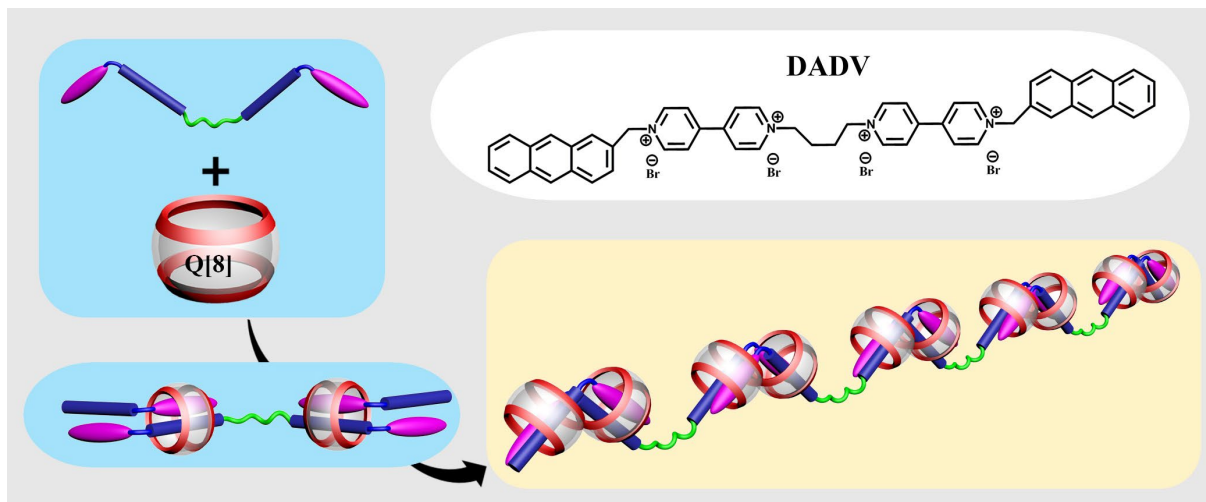


Scheme 11. Construction of a poly(pseudorotaxane) on a gold surface.

By taking advantage of multiple host-stabilized intermolecular charge-transfer interactions, the Zhang group constructed a series of supramolecular polymers with a high degree of polymerization.^{115, 116} For example, they synthesized a linear monomer bearing two viologen moieties as electron acceptors and two anthracene moieties as electron donors, as shown in Scheme 12.¹¹⁵ When encapsulated in Q[8] hosts, the monomers can be

joined together in head-to-tail fashion through multiple host-stabilized intermolecular charge-transfer interactions, forming chain-like supramolecular polymers. By using host-enhanced $\pi \cdots \pi$ interactions, Zhang,¹²⁰⁻¹²⁷ Scherman,¹²⁸ Pang¹²⁹ *et al.* also constructed many other kinds of supramolecular polymers.

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Scheme 12. Schematic representation of the formation of the supramolecular polymer based on multiple host-stabilized charge-transfer interactions.

6 MIMs constructed from Q[10]

As the Q[*n*] homologue with the largest cavity size, Q[10] was first discovered as its Q[5]@Q[10] inclusion complex by Day, Blanch, *et al.* in 2002.¹³⁰ Three years later, the Isaac group successfully isolated free Q[10],¹³¹ making it possible to study the supramolecular chemistry of Q[10]. However, only a few MIMs involving Q[10] have been reported to date.¹³²⁻¹³⁶

In 2017, Cao, Liu and co-workers¹³² designed and synthesized a dumbbell-like guest, 1,1'-

ditetraphenylethenyl-4,4'-bipyridine-1,1'-dium dichloride, containing a viologen unit in the central and two TPE units at both terminals. This nonfluorescent dumbbell-like guest can form a fluorescent [2]rotaxane with Q[10] (Figure 19) via the slipping method under heating at 95 °C in DMSO. In the past few years, many Q[10]-based supramolecular polymers with strong fluorescence have also been reported by Liu,¹³³ Xiao^{134, 135} *et al.*

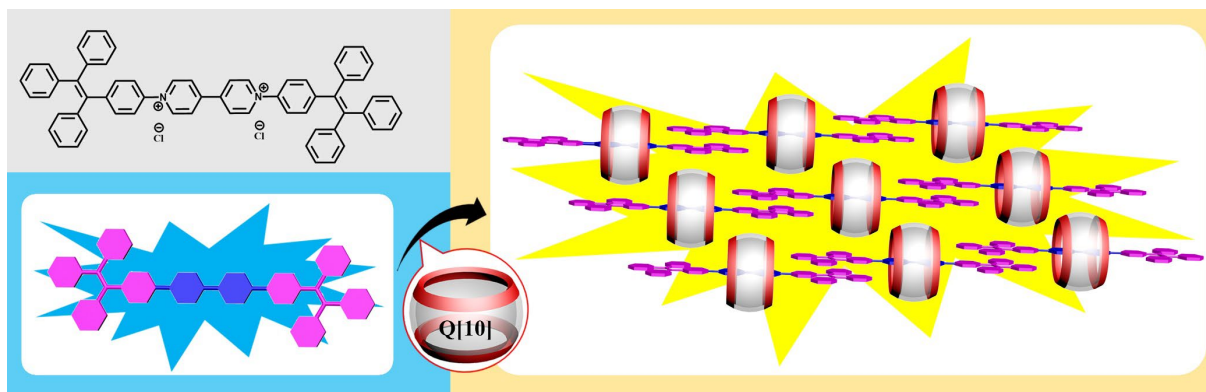


Figure 19. The formation of a fluorescent [2]rotaxane based on Q[10].

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Recently, Hannon, Bardelang, Liu and co-workers reported a class of pseudo-rotaxane, which is constructed by wrapping a Q[10] about cylindrical metallo-supramolecular helicates as the axle.¹³⁶ The constructed pseudo-rotaxane is readily converted into a proper [2]rotaxane by introducing branch points onto the

cylinder surface (Figure 20). The number of introduced branch points controlled the ability of the cylinder to de-thread from the [2]rotaxane, which finally affected the biomolecular recognition and biological properties of the metallo-supramolecular cylinders.

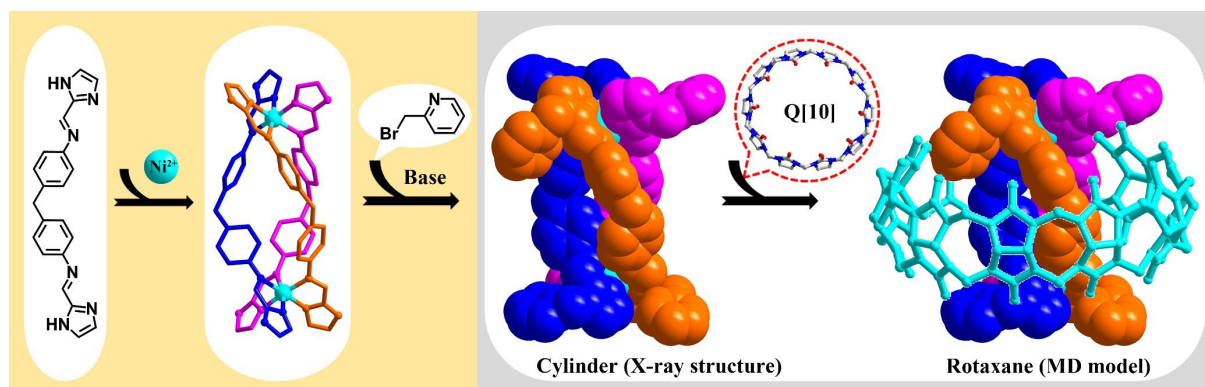


Figure 20. Synthetic strategy to create a rotaxanated cylinder.

7 Heterowheel (pseudo)rotaxanes and poly(pseudo)rotaxanes

7.1 Heterowheel (pseudo)rotaxanes

Heterowheel (pseudo)rotaxanes threading two or more different macrocycles on an axle are currently of interest because of their novel topologies and potential applications in constructing complicated molecular devices. Generally, the axles for the heterowheel (pseudo)rotaxane are long and consist of multiple recognition groups. Liu and co-workers constructed a series of heterowheel pseudorotaxanes by using

cyclodextrins and cucurbiturils.^{137, 138} For example, they found that the Q[7] docks at one of the octyl moieties in *N,N'*-dioctyl-4,4'-bipyridinium (Figure 21). Upon addition of α -CD, the Q[7] moves to the bipyridinium moiety while the α -CD docks at the octyl moieties, forming a heterowheel [4]rotaxane.¹³⁷ Similarly, other groups such as Kim¹³⁹, Sun¹⁴⁰, and Schmitzer¹⁴¹ also contributed to the construction of heterowheel pseudorotaxanes based on cyclodextrins and cucurbiturils. Stoddart *et al.* demonstrated how to incorporate pillar[5]arene and Q[6] into a viologen derivative to form heterowheel [4]rotaxanes and [5]rotaxane (Figure 22).^{142, 143}

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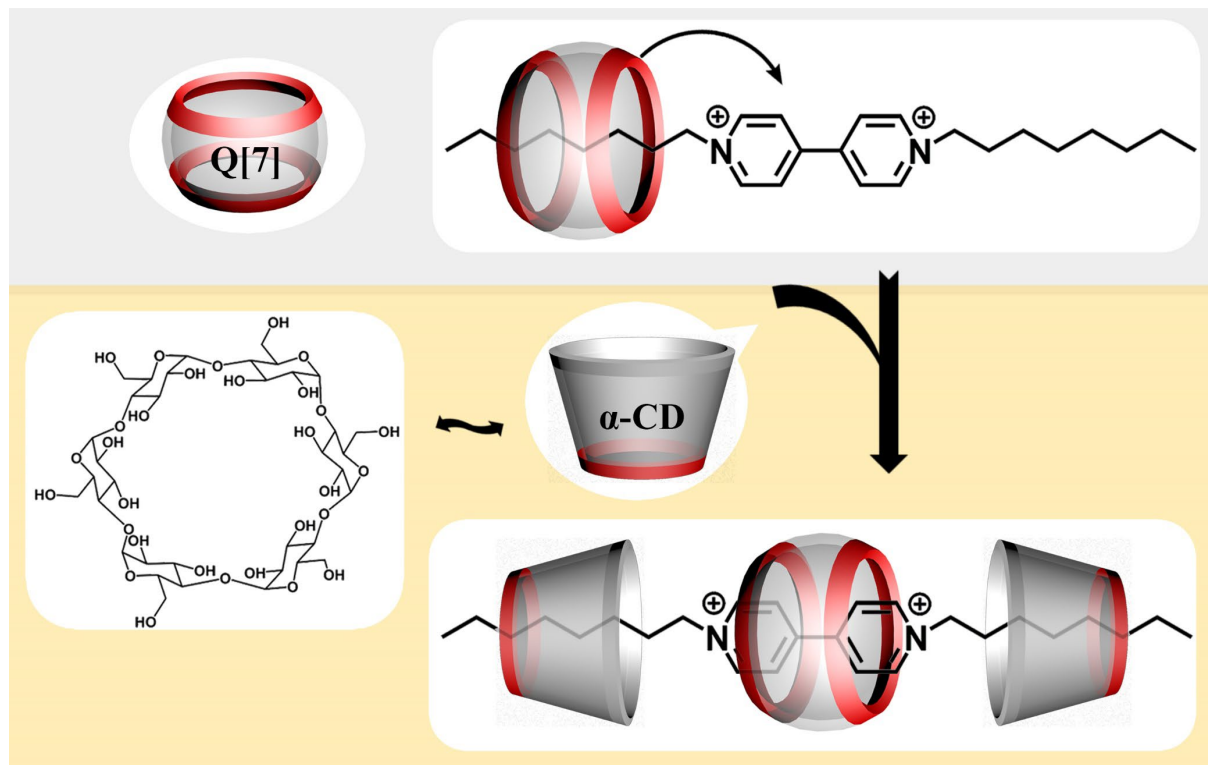


Figure 21. Schematic representation showing the construction of a heterowheel pseudorotaxanes by using Q[7] and α -CD.

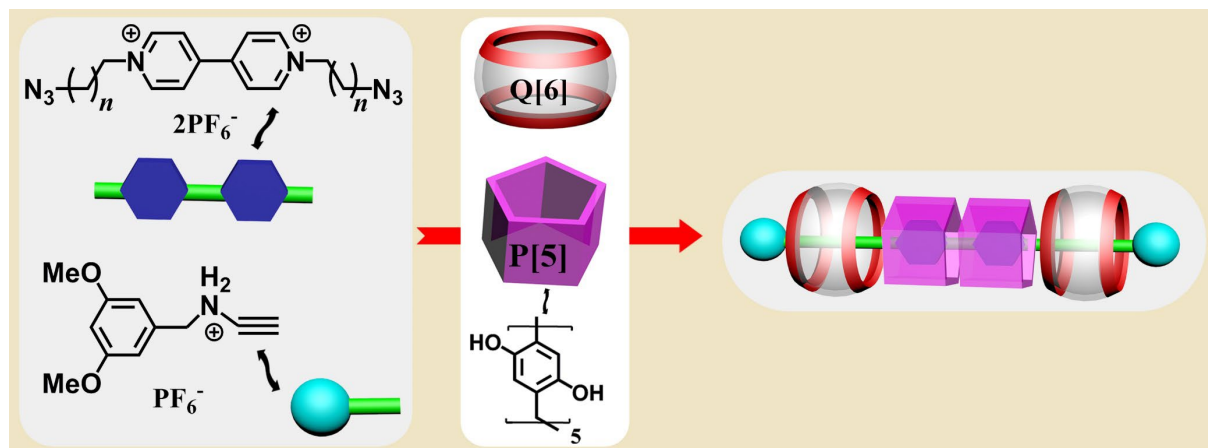


Figure 22. Schematic representation showing the fabrication of a heterowheel [5]rotaxane.

In 2009, Masson *et al.*¹⁴⁴ demonstrated a heterowheel [4]pseudorotaxane (Figure 23), of which three wheels Q[6], Q[7] and Q[6] are threaded on an axle of a spermine derivative in a well-defined, kinetically favoured sequence. Upon thermal activation at 90 °C and the

addition of Q[6], this heterowheel [4]pseudorotaxane undergoes a reorganization toward a homowheel [4]pseudorotaxane bearing three Q[6] wheels. In the same year, Tuncel and co-workers reported another kind of heterowheel [4]pseudorotaxane (Figure 24).¹⁴⁵ A linear

axle containing two distinct recognition regions was prepared via a Click reaction. The hosts Q[6] and Q[8] can bind with the linear axle to form a heterowheel

[4]pseudorotaxane through sequence-specific self-sorting.

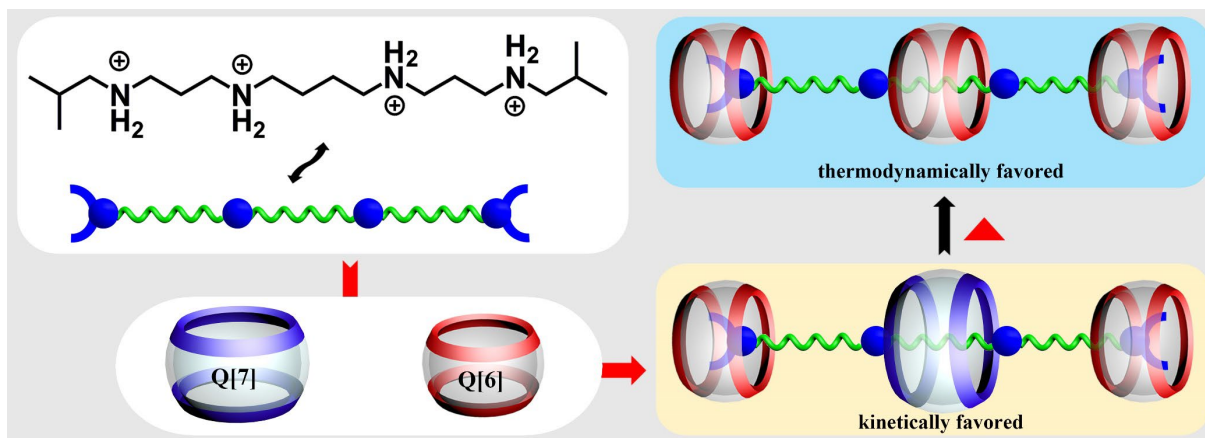


Figure 23. Schematic representation showing the reorganization from heterowheel [4]pseudorotaxane to homowheel [4]pseudorotaxane.

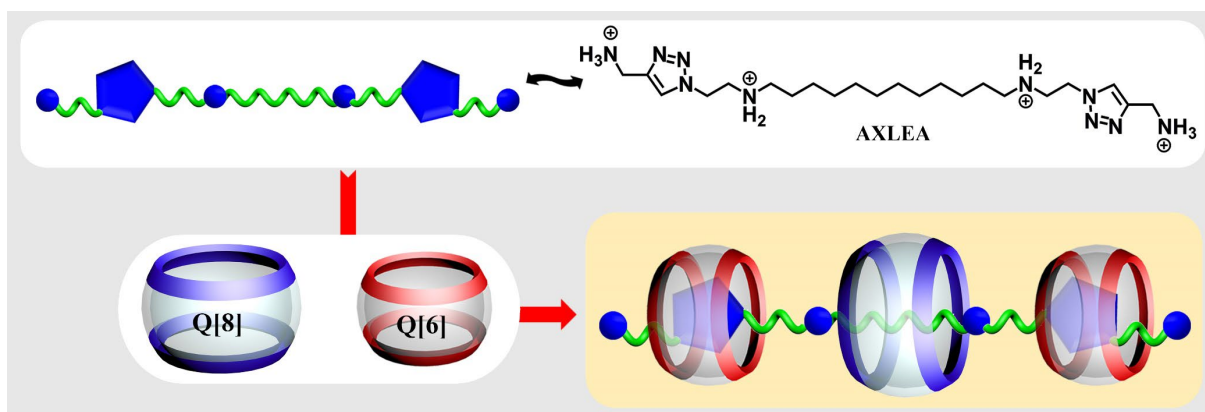


Figure 24. Heterowheel [4]pseudorotaxane of Q[6] and Q[8].

The Day group in 2017 constructed a heterowheel [4]pseudorotaxane consisting of Q[7], cyclopentanonocucurbit[6]uril (CyP₆Q[6]) and a tetraammonium chain. When bound within the host cavities, the tetraammonium chain performs the molecular machine function of ‘snuggle and stretch’ (Figure 25).¹⁴⁶

Recently, the Liu group constructed two novel heterowheel [4]pseudorotaxanes based on TMeQ[6] and Q[7].¹⁴⁷ As shown in Figure 26, the Q[7] can thread onto the alkyl chain of the axle to form a molecular shuttle.

Upon addition of TMeQ[6], the Q[7] moves to the central viologen unit, and two TMeQ[6] thread onto the terminal benzimidazolium units, generating a heterowheel [4]pseudorotaxane. Interestingly, the Q[7] wheel can rotate freely around the horizontal axis, while the TMeQ[6] cannot. Furthermore, the formation and dissociation of the [4]pseudorotaxanes is controlled by pH.

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7.2 Heterowheel poly(pseudo)rotaxanes

In 2006, Yui, Thompson, Kim and co-workers synthesized a polypseudorotaxane consisting of Q[7] and 2,6-*O*-dimethyl β -cyclodextrin (DM- β -CD) through the “Click” polymerization of two different [2]pseudorotaxane blocks (Figure 27).¹⁴⁸ The movement of the Q[7] on the guest polymer is controlled by the pH of the aqueous solution. After that, many other heterowheel polypseudorotaxanes involving cucurbiturils, cyclodextrins, and pillararenes were also successfully fabricated.^{149–151} A good example of such a heterowheel

polypseudorotaxane is a water-soluble pillar[6]arene based supramolecular pseudopolyrotaxane reported by Yang and co-workers, in which the pseudorotaxane-type monomers are connected through Q[8] host-enhanced π - π interaction.¹⁵¹

In a recent study, Xu and Ni *et al.* reported a linear supramolecular polymer (polypseudorotaxane) fabricated by *nor-seco-cucurbit[10]uril* (*ns-Q[10]*), Q[7] and a bifunctional guest monomer, which contains two naphthalene (Naph) moieties and a phenyl (Phen) moiety, through a self-sorting strategy (Figure 28).¹⁵²

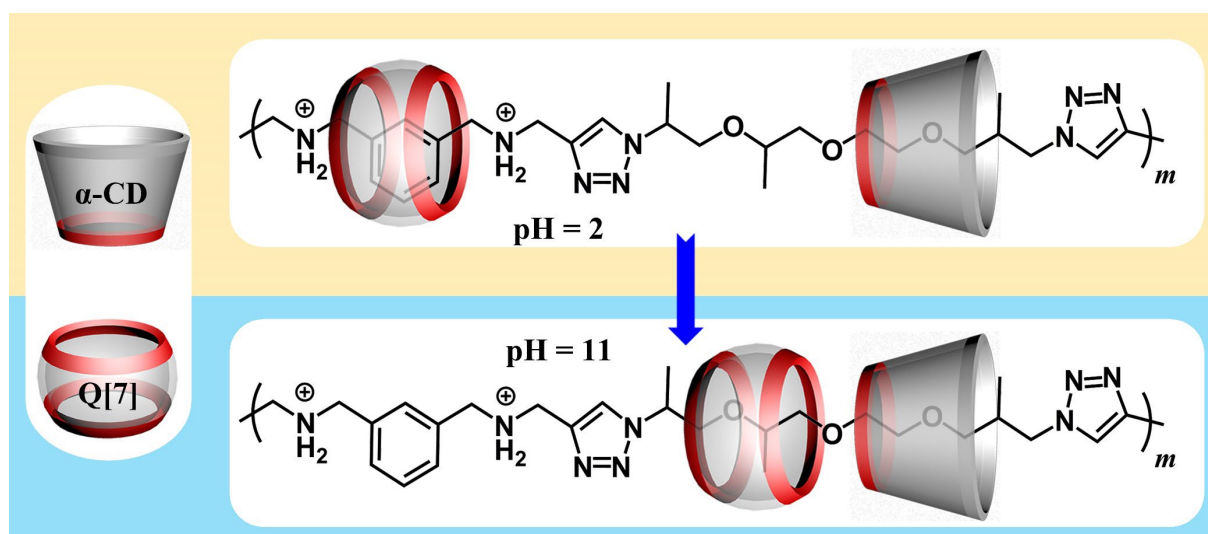


Figure 27. pH-controlled movement of the Q[7] wheels in a heterowheel polypseudorotaxanes.

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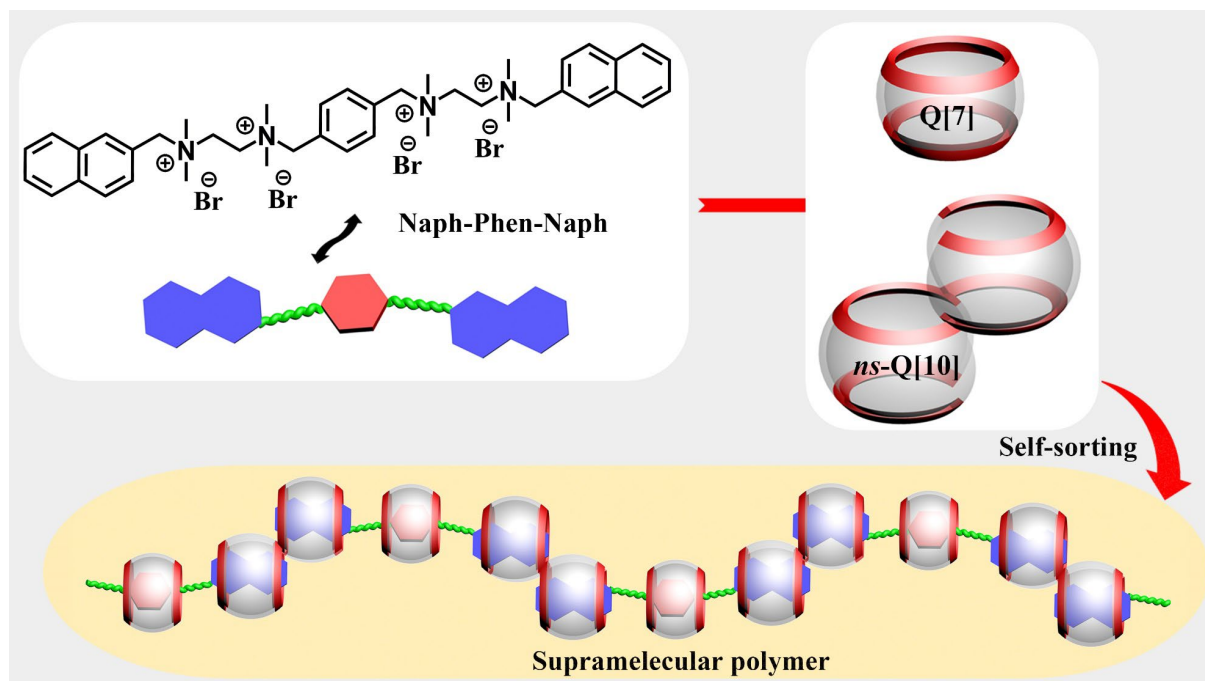


Figure 28. A polypseudorotaxane based on *ns*-Q[10] and Q[7].

8 Summary and Outlook

About two decades have passed since Kim, Day, Isaacs and others separated Q[*n*] homologues in pure form.^{78, 79, 131} Numerous MIMs based on Q[*n*] homologues and derivatives have been designed and successfully synthesized. According to the size characteristics of the Q[*n*] cavity and the types of stimuli applied, this review summarizes the important advances in the field of MIMs based on Q[*n*]s over the past two decades.

For the smallest cucurbituril homologue Q[5], its small cavity cannot be threaded through any axles, and only a few MIMs based on Q[5] have been reported, which are formed by the coordination of Q[5] with metal ions. In the case of Q[6], Q[7] and Q[8], their cavities are suitable for the inclusion of axles of requisite sizes. Their binding abilities toward different binding sites on an axle are controlled by external stimulus, leading to the formation

of various stimuli-responsive MIMs. In particular, the Q[8] cavity is capable of accommodating two hetero/homo guests to form a Q[8]-stabilized inclusion complex, which facilitates the construction of redox responsive MIMs and various supramolecular polymers. As for Q[10] with its large cavity, it can form MIMs by wrapping cylindrical nanosized metallo-supramolecular helicates as the axle. Furthermore, this review also highlights advances in the area of heterowheel (pseudo)rotaxanes involving Q[*n*]s. The supramolecular chemistry of MIMs is evolving rapidly and the future outlook for Q[*n*] chemistry is encouraging. Using carefully designed molecular axles with multiple binding sites one may be able to fabricate multiple stimuli-responsive MIMs based on Q[*n*]s.¹⁵³ The heterowheel (pseudo)rotaxanes described here are two types of wheels threading onto an axle, which can be extended further using three or more types of wheels to

form more sophisticated molecular machines. In fact, Stoddart *et al.* recently reported a systematic approach to threading up to 10 adjacent rings consecutively.¹⁵⁴ Importantly, Huang, Yang and others have reported that the MIMs and supramolecular polymers based on Q[n]s can be envisioned in practical applications such as pharmaceutical science¹⁵⁵⁻¹⁵⁷ and functional material science.¹⁵⁸⁻¹⁶⁹

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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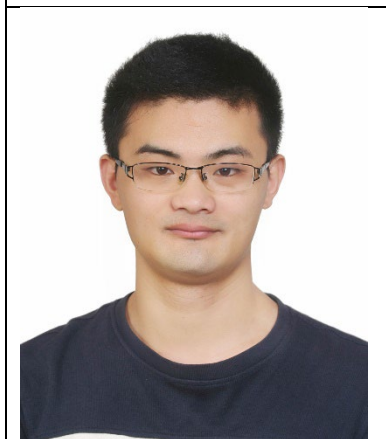
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REVIEW ARTICLE



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