Host-Guest Chemistry of a Tetracationic Cyclophane, Namely, Cyclobis (paraquat-*p*-phenylene)

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Hao Li, Tianyu Jiao, and Libo Shen

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3.1 Introduction

Since Pedersen's seminal report [1] of the synthesis and guest recognition behaviors of crown ether in the year of 1967, the research on host-guest recognition began to represent one of the major focuses in the field of supramolecular chemistry [2]. In the early stage, supramolecular chemistry was often referred to as host-guest chemistry [3], because of the following reasons. On the one hand, host molecules often exist in the form of macrocycles, which have many convergent binding sites that point into their cavities. The implication is that the host is able to accommodate a guest within its pocket where multiple noncovalent interactions could occur simultaneously in a cooperative manner. These supramolecular driving forces include labile coordination bond [4], π-electron interactions in the form of either donor-acceptor

H. Li (✉) · T. Jiao · L. Shen
Department of Chemistry, Zhejiang University, Hangzhou, China
e-mail: lihao2015@zju.edu.cn

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interactions [5] or aromatic radical-pairing interactions [6], solvophobic effect often in the form of hydrophobic forces [7] expressed in aqueous solutions, hydrogen bonding [8], electrostatic forces [9], anion binding [10], as well as a variety of van der Waals interactions [11]. On the other hand, host molecules often have pre-organized conformations. As a consequence, host-guest recognition could occur without too much entropy loss in the cases when the guests have complementary sizes and geometries to fit within the host cavities. Host-guest recognition enables many tasks to be accomplished, including labile guest stabilization [12], accelerating reaction rates [13], as well as developing mechanically interlocked molecules [14].

Besides crown ethers, a few other macrocyclic molecules including cyclodextrins [15], calixarenes [16], cucurbiturils [17], and pillararenes [18] have been playing important roles in supramolecular chemistry. In the year of 1988, Sir Fraser Stoddart, the chemistry Nobel Laureate [19] of 2016 for his contribution in the development of molecular machines, designed and developed a rectangle-shaped host molecule, namely, cyclobis(paraquat-*p*-phenylene) (**CBPQT**$^{4+}$) [20] (Fig. 1). This tetracationic cyclophane represents another milestone in the river of supramolecular chemistry, because (i) **CBPQT**$^{4+}$ is relatively synthetically accessible and (ii) **CBPQT**$^{4+}$ can recognize a variety of π-electron guests in both fully oxidized state and biscationic diradical state, driven by donor-acceptor and radical-pairing interactions, respectively.

In this chapter, we are going to make a rough discussion of the following issues of **CBPQT**$^{4+}$, including (i) the structural feature of **CBPQT**$^{4+}$; (ii) its preparation including the template-directed synthesis; (iii) its binding behavior in its oxidized and radical states, namely, **CBPQT**$^{4+}$ and **CBPQT**$^{2(\bullet+)}$, respectively; (iv) mechanically interlocked molecules including rotaxanes and catenanes containing **CBPQT**$^{4+}$ as a macrocyclic building block whose switchable features have been taken advantage of in the design of molecular switches and machines; and (v) the extended derivatives of **CBPQT**$^{4+}$. Even although a few other groups also employed **CBPQT**$^{4+}$ ring for self-assembly and molecular recognition, in this chapter, we mainly focus on the works of the group led by Stoddart, the inventor of this tetracationic cyclophane.

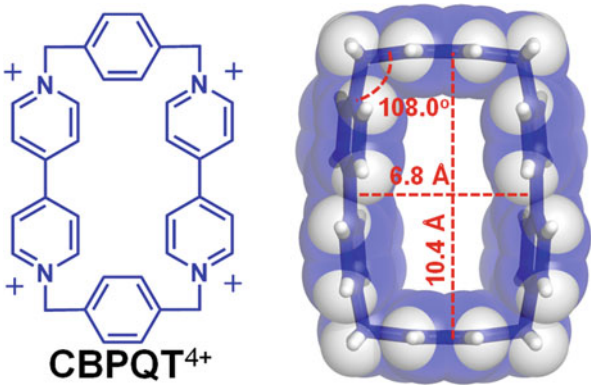


Fig. 1 Structural formula of the tetracationic cyclophane **CBPQT**$^{4+}$ and its single-crystal X-ray structure. Counterions are omitted for the sake of clarity

3.2 Structural Features

CBPQT^{4+} has been referred to as "**Blue Box**" in the community of supramolecular chemistry including the group of Sir Fraser Stoddart. Two major reasons might account for this "nickname." First, the two 4,4′-bipyridinium (**BIPY**$^{2+}$) units in **CBPQT**$^{4+}$ can easily undergo reduction, producing blue-colored solution of **CBPQT**$^{2(\bullet+)}$ containing two **BIPY**$^{\bullet+}$ moieties that absorb red wavelengths of light [21]. Second, the color of blue is often used to represent electron-deficient part in a molecule in the community of chemistry. The tetracationic **CBPQT**$^{4+}$ ring has a π-electron-deficient nature. We therefore often employ blue color to draw the rectangular molecular structural formula of **CBPQT**$^{4+}$, in order to indicate that this ring is electron-poor. This might be another origin of the name of "**Blue Box**."

In the solid-state framework of **CBPQT**$^{4+}$ [20] (Fig. 1), two **BIPY**$^{2+}$ units are bridged in a face-to-face manner by two *p*-xylyl linkers. The rigidity of the building blocks, including both the **BIPY**$^{2+}$ and the *p*-xylyl spacers, affords the cyclophane a preorganized and rigid cavity. The distance between the two **BIPY**$^{2+}$ in their middle parts is around 6.8 Å, which is twice of π-π interaction distance. The implication is that, when a π-electron guest inserts into the macrocycle cavity, the interplane distances between the guest and each of the two **BIPY**$^{2+}$ moieties would be around 3.4 Å, an optimized distance for the occurrence of π-π interactions. As a consequence, both of the two **BIPY**$^{2+}$ units are able to undergo π-π interactions with the guest in the host cavity in a cooperative manner. This feature explains the phenomena that **CBPQT**$^{4+}$ is highly promiscuous in binding a variety of π-electron-rich guests with complementary geometries.

It is also noteworthy that the **BIPY**$^{2+}$ contains a few acidic protons, including the pyridinium protons in four α-positions with respect to the two pyridinium nitrogen atoms, as well as the methylene protons in the *p*-xylyl linkers. Their acidity results from the electron-withdrawing nature of the nitrogen atoms, on account of either conjugation or inductive effects. The consequence is that these protons represent promising hydrogen bond donors in host-guest recognition. More specifically, **CBPQT**$^{4+}$ can provide larger binding affinities for those π-electron-rich guests that bear ethylene glycol side chains, whose oxygen atoms are considered hydrogen bond acceptors. This issue is discussed in more detail in the coming section.

The rectangle architecture of **CBPQT**$^{4+}$ introduces ring strain. It is well-known that a sp^3-hybridized carbon atom should have an optimized bond angle of around 109.5° in order to minimize the repulsion between the four bonding electron pairs. Considering each of the four methylene linkers in **CBPQT**$^{4+}$ framework contains two less steric bulky protons, the optimized C–C–C bond angle (i.e., the central carbon is the methylene one) is supposed to be even larger than 109.5°. This value significantly deviates from 90° in a regular rectangle framework. This deviation indicates that in a **CBPQT**$^{4+}$ framework, either the C–C–C bond angle is smaller than the optimized value, namely, 109.5°, or the **BIPY**$^{2+}$ moiety or *p*-xylyl linker undergo bend. Both of these two behaviors introduce ring strain. In fact, in a solid-state structure of **CBPQT**$^{4+}$, the C–C–C bond angle is observed to be around 108°. In addition, the two pyridinium moieties in a **BIPY**$^{2+}$ are not in the same plane,

which supports our aforementioned hypothesis that these aromatic building blocks in the **CBPQT**$^{4+}$ framework have bent conformation.

The **CBPQT**$^{4+}$ ring has an amphiphilic nature, i.e., its cationic **BIPY**$^{2+}$ and the neutral *p*-xylyl building blocks are hydrophilic and hydrophobic, respectively. Therefore, the solubility of this tetracationic cyclophane is often determined by its counterions. When the counterions are less polar and hydrophobic PF_6^- or BF_4^-, the salts, namely, **CBPQT**$^{4+}$•4PF_6^- or **CBPQT**$^{4+}$•4BF_4^-, are soluble in polar organic solvents, such as MeCN, DMF, and $MeNO_2$. When the counterions are changed to those that are highly solvated in water, including Cl^-, Br^-, or NO_3^-, the cyclophane becomes soluble in water.

3.3 Synthesis

The design of **CBPQT**$^{4+}$ was based on the discovery [22] (Fig. 2) of the group led by Stoddart that a **BIPY**$^{2+}$ derivative **1**$^{2+}$ could be recognized by a crown ether containing two π-electron-rich hydroquinone (**HQ**) units, namely, bis-para-phenylene[34]crown-10 (**BPP34C10**). The driving forces for the formation of the complex **1**$^{2+}$⊂**BPP34C10** include charge-transfer interactions between the **1**$^{2+}$ guest and the two **HQ** units in the host, which act as the π-electron acceptor and donor, respectively. The Stoddart research group thus envisioned that it might be possible to

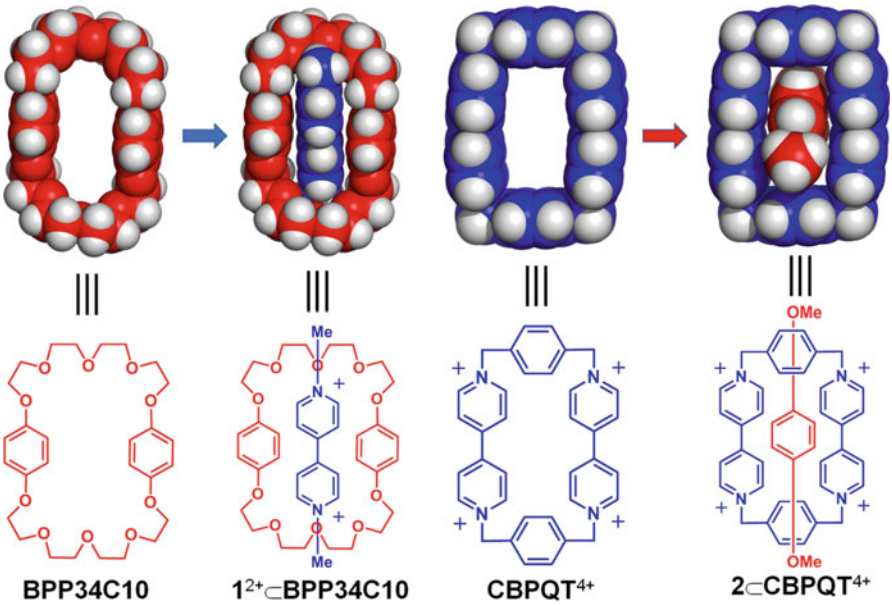


Fig. 2 Structural formulaes and the corresponding single-crystal X-ray structures of **BPP34C10** and **CBPQT**$^{4+}$, before and after they recognize π-electron-deficient and rich guests **1**$^{2+}$ and **2**, respectively. Counterions are omitted for the sake of clarity

reverse the constitutionally roles of the host and guest, by introducing two **BIPY**$^{2+}$ units into a macrocycle, namely, **CBPQT**$^{4+}$, which was supposed to bind a π-electron-rich guest including a **HQ** derivative **2**.

The synthesis (Fig. 3) of **CBPQT**$^{4+}$ relies on the S_N2 reaction in which pyridine and benzyl bromide act as nucleophile and electrophile, respectively. The Stoddart group firstly synthesized compound **3**•2PF_6^-, which has been referred to as "horseshoe" on account of its half-macrocyclic geometry. Combining **3**•2PF_6^- and stoichiometric amount of α,α′-dibromo-*p*-xylene in dry polar organic solvent such as MeCN produced a yellow solid-state product including **CBPQT**$^{4+}$ (counterion could be either Br^- or PF_6^-), as well as other polymeric and oligomeric byproducts. Water has to be avoided during the reaction, because water might result in hydrolysis of benzyl bromide. By using chromatographic purification followed by counterion exchange, the Stoddart group obtained **CBPQT**$^{4+}$•4PF_6^- in 12% yield, assuming that the salt was not solvated.

This 12% yield of **CBPQT**$^{4+}$ is relatively low, compared with other [1+1] cyclization reactions. This low yield results from two major reasons. First, S_N2 reaction is generally irreversible in most cases. The implication is that, if the reaction between **3**$^{2+}$•2PF_6^- and α,α′-dibromo-*p*-xylene yields oligomeric or polymeric byproducts, the "errors" could not be corrected. Second, the ring stain of **CBPQT**$^{4+}$ makes the cyclization less favored in the context of both thermodynamics and kinetics.

The effort to increase the yield of **CBPQT**$^{4+}$ was performed [23] (Fig. 4) by using template-directed approach. The Stoddart group firstly prepared a guest **4** bearing a **HQ** moiety on which two ethylene glycol chains were grafted. The first S_N2 reaction of **1**$^{2+}$ and α,α′-dibromo-*p*-xylene yielded a triscationic reaction intermediate **5**$^{3+}$. This *π*-electron-deficient pseudo-macrocycle "warp around" the guest **4**, by which the terminal pyridine and benzyl bromide units orientated close to each other, favoring the occurrence of S_N2 reaction in an intramolecular manner. In MeCN, the yield of **CBPQT**$^{4+}$•4PF_6^- increased to 36% in the

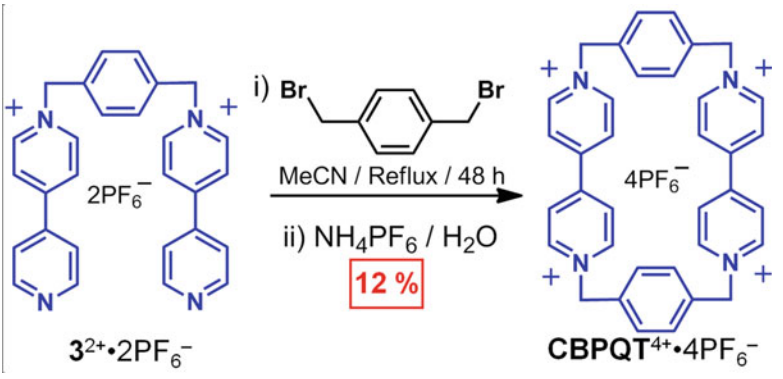


Fig. 3 The non-template protocol for the synthesis of **CBPQT**$^{4+}$•4PF_6^- by performing S_N2 reaction of **3**$^{2+}$•2PF_6^- and α,α′-dibromo-*p*-xylene in MeCN, followed by counterion exchange

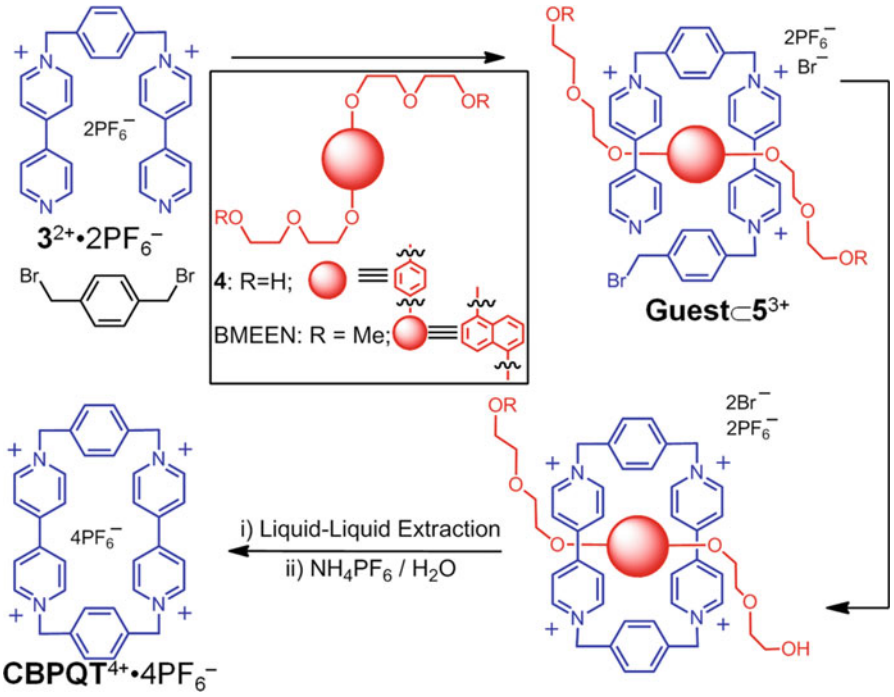


Fig. 4 The template-directed protocol for the synthesis of $\mathbf{CBPQT}^{4+}\bullet 4PF_6^-$ by performing S_N2 reaction of $\mathbf{3}^{2+}\bullet 2PF_6^-$ and α,α′-dibromo-*p*-xylene in the presence of a template **4** in MeCN, followed by guest removal and counterion exchange

presence of **4**, which is almost three times compared to that in the absence of template. It is noteworthy that when the solvent was switched from MeCN to DMF, the yield increased from 36% to 45%, which might be explained by the fact that the triscationic reaction intermediate $\mathbf{5}^{3+}\bullet 2PF_6^-\bullet Br^-$ has better solubility in DMF. The same group also discovered that the yield of $\mathbf{CBPQT}^{4+}$ was dependent on the electron-donating ability of the guest. For example, when the guest 1,5-bis-[2-(2-methoxyethoxy)-ethoxy]naphthalene (**BMEEN**), an analogue of **4**, was employed to template the formation of $\mathbf{CBPQT}^{4+}$ in DMF, the yield underwent further increase to 62%. This higher yield is attributed to the 1,5-dialkoxy-naphthalene (**DNP**) unit in **BMEEN**, which introduces stronger π-electron donor-acceptor interactions to the intermediate $\mathbf{5}^{3+}$, compared to the **HQ** unit in **4**.

One of the disadvantages of using templates for the synthesis of $\mathbf{CBPQT}^{4+}$ is that template removal is technically demanding and time-consuming, especially in the case of high binding constant of guest⊂$\mathbf{CBPQT}^{4+}$. In fact, when the guest 1,5-bis[2-(2-hydroxyethoxy)ethoxy]-naphthalene (**BHEEN**) was employed to template the ring formation, it took a few days or weeks to remove the template from the ring cavity by performing liquid-liquid extraction. This problem was resolved (Fig. 5) by Stoddart group in the year 2010, by using a guest exchange strategy [24]. After the

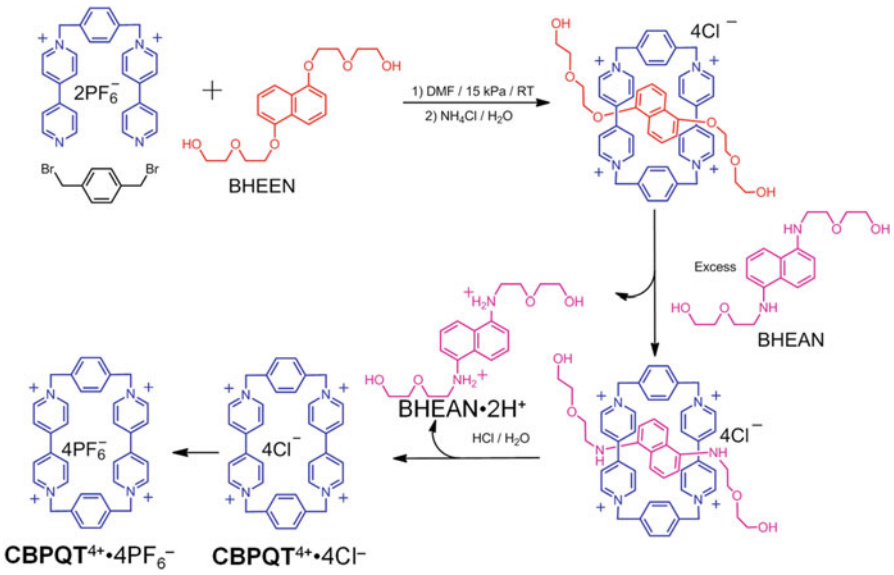


Fig. 5 The template-directed protocol for the synthesis of **CBPQT**$^{4+}$•4PF_6^- by using **BHEEN** as the template. The guest removal is accomplished by means of guest exchange strategy. **BHEAN** is used to replace **BHEEN** in the ring cavity. In acidic condition, **BHEAN** is protonated and driven out from the ring cavity

ring formation reaction, another guest 1,5-bis[2-(2-hydroxyethoxy)ethylamino] naphthalene (**BHEAN**), which contains a 1,5-diamino-naphthalene unit, was added into the aqueous solution of the reaction mixture to drive the template **BHEEN** out from the ring cavity, forming **BHEAN**⊂**CBPQT**$^{4+}$. In the presence of acid, **BHEAN** undergoes protonation and exists in a cationic form, namely, **BHEAN**•2H^+, thanks to the basicity of the amino functions in **BHEAN**. The cationic **BHEAN**•2H^+ is no longer π-electron-rich and exhibits no binding affinity within the cavity of **CBPQT**$^{4+}$. Adding NH_4^+•PF_6^- into the mixture in water could precipitate **CBPQT**$^{4+}$•4PF_6^-, leaving the water-soluble **BHEAN**•2H^+ in the aqueous solution.

More recently, the Stoddart group developed [25] (Fig. 6) a pseudo-dynamic approach in the synthesis of **CBPQT**$^{4+}$, as well as its extended derivative. Addition of tetrabutylammonium iodide into the ring closing reaction mixture of the 4,4′-bipyridine and a so-called reverse horseshoe compound **6**$^{2+}$•2PF_6^- in refluxed MeCN could accelerate the reaction, producing **CBPQT**$^{4+}$•4PF_6^- in 20% yield. The C–N bond formation is somewhat reversible, given that I^- anion is both a good nucleophile and a good leaving group. This dynamic nature allows the system to perform error checking to some extent, producing more **CBPQT**$^{4+}$, which is more thermodynamically favored in terms of entropy compared to those oligomeric byproducts.

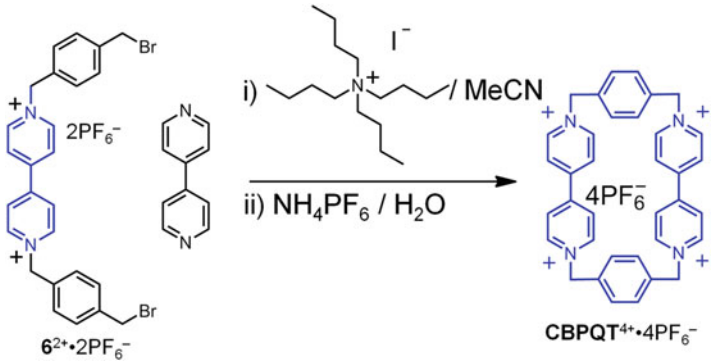


Fig. 6 The non-template protocol for the synthesis of **CBPQT**$^{4+}$•4PF_6^- by performing S_N2 reaction of **6**$^{2+}$•2PF_6^- and 4,4′-bipyridine in MeCN in the presence of tetrabutylammonium iodide catalyst, followed by counterion exchange

3.4 Guest Recognition Ability of CBPQT Ring

3.4.1 Guest Recognition Ability of CBPQT^{4+}

As we mentioned before, **CBPQT**$^{4+}$ is able to recognize a variety of π-electron-rich guests within its cavity. The driving forces for the host-guest recognition include:

(i) π–π donor-acceptor interactions. This noncovalent force is also referred to as charge-transfer interactions. It is noteworthy that the width of **CBPQT**$^{4+}$ ring, namely, 6.8 Å, allows the guest to be able to undergo π–π donor-acceptor interactions with both of the two **BIPY**$^{2+}$ units in the host. However, in a given instant, only one of the two electron acceptors is strongly engaged in the noncovalent interactions. This proposition is supported by the observation that upon recognition of a π-electron-rich guest, the two **BIPY**$^{2+}$ units in the **CBPQT**$^{4+}$ ring have different reduction potentials on the cyclic voltammetry (CV) timescale, i.e., one **BIPY**$^{2+}$ unit in the **CBPQT**$^{4+}$ ring is easier to be reduced than the other one, in the cases when the dissociation process of the complex is slow or prohibited.
Charge-transfer interactions lead to the optical absorption of the complexes in the visible light region, which brings about various colors of the complexes in solution. This is because when the complex absorbs a photon with a specific wavelength, electrons undergo transfer from the HOMO of the π-electron-rich guests to the LUMO of one of the two **BIPY**$^{2+}$ units in the **CBPQT**$^{4+}$ ring, leading a charge-separated excited state. For example, upon complexation with the **CBPQT**$^{4+}$ ring, guest-bearing dioxyarene functions are typically orange to red [26], while diaminoarenes and TTF derivatives have green colors [27]. The difluorobenzidine-contained guest produces a blue color in solution [28].

In addition, the difference in binding constants (K_a) for the guests bearing different π-electron moieties also reveals the occurrence and importance of π–π donor-acceptor interactions in guest recognition. For example, K_a of the guests containing a **DNP** unit are often a few order (two or three) of magnitude larger (Fig. 7) than that containing a **HQ**, on account of the fact that the former guest is generally more electron-rich than the latter. Tetrathiafulvalene (**TTF**), which is even more electron-donating than **DNP**, is used to synthesize guests with larger K_a. Introducing electron-withdrawing functional groups into the guest weakens the π–π donor-acceptor interactions and therefore reduces K_a. For example, the guest **4** bearing a **HQ** unit has a K_a of 2220 M^{-1} [26], which is nearly two order of magnitude larger than that of the analogue guest **7** bearing two fluorine atoms [29] (Fig. 8a). The guest **8** containing four fluorine atoms demonstrates no binding affinity.

TTF undergoes reversible redox process. The oxidation products, including the monocationic $\mathbf{TTF}^{\bullet+}$ and the dicationic $\mathbf{TTF}^{2+}$, are π-electron-deficient and therefore lose its ability to associate with the $\mathbf{CBPQT}^{4+}$ ring (Fig. 8b). This switching behavior was taken advantage of in the design of molecular switches and machines in the form of catenanes and rotaxanes. We will discuss it in more detail in the coming section.

(ii) As we mentioned previously, the $\mathbf{BIPY}^{2+}$ in the $\mathbf{CBPQT}^{4+}$ ring contains a number of acidic protons that are considered as hydrogen bond donors. The implication is that, when the guest bears hydrogen bond acceptors such as glycol oxygen atoms, the host-guest recognition could be enhanced by

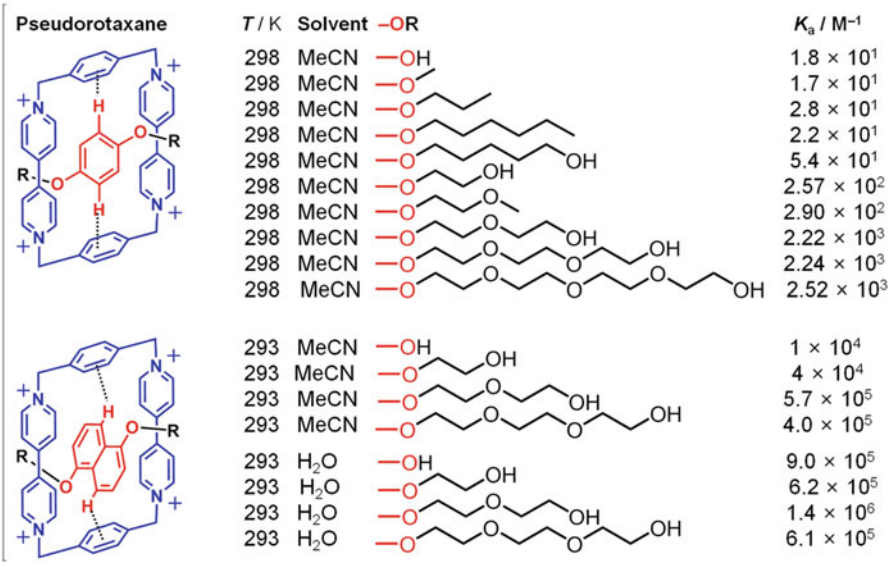
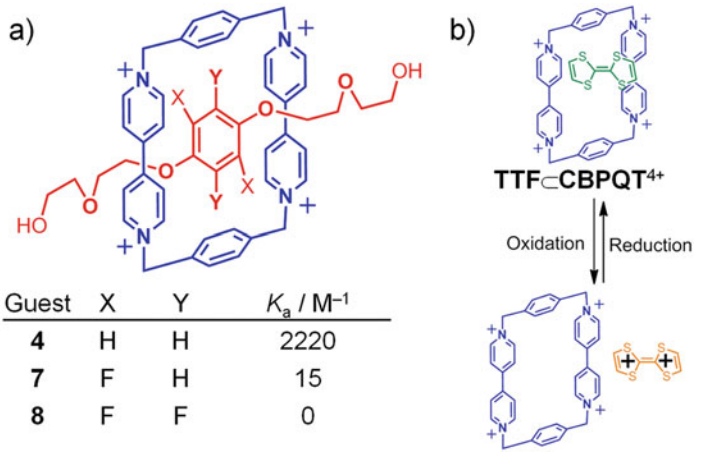


Fig. 7 Association constants, K_a, of two series of pseudorotaxanes, in either MeCN or H_2O. The guests contain either HQ or DNP units in the middle part



Guest	X	Y	K_a / M^{-1}
4	H	H	2220
7	F	H	15
8	F	F	0

Fig. 8 (**a**) Association constants, K_a, of a series of pseudorotaxanes in MeCN. When more fluorine atoms are grafted onto the **HQ** in the guest, K_a undergoes significant decrease. (**b**) A pseudorotaxane **TTF⊂CBPQT**$^{4+}$ undergoes dissociation after the **TTF** guest undergoes oxidation

hydrogen-bonding interactions in the form of [C–H•••O]. The occurrence of relatively strong hydrogen-bonding interactions for glycol chain relies on the gauche effect. That is, the two vicinal oxygen atoms in an ethylene glycol unit orientate in a manner that the O–C–C–O torsion angle is round 60°, instead of 180° that occurs in the case of C–C–C–C in a *n*-butane molecule. The gauche effect results from an orbital mixing between a C–H bond in a methylene and the empty anti-bonding orbital of the adjacent C–O bond. The gauche conformation of the glycol chain allows the glycol chain to wrap around a **BIPY**$^{2+}$ unit, as a consequence of which, the multiple oxygen atoms in the former could form hydrogen bonds with one or a few acidic protons in a **BIPY**$^{2+}$ unit simultaneously. This proposition is supported by the observation that when mono or di(ethylene glycol) chains are grated onto the guests bearing **HQ** or **DNP** moiety, K_a values of these guests to bind with **CBPQT**$^{4+}$ could raise up by one or two orders of magnitude [26, 30] (Fig. 7).

(iii) When some aromatic guests bearing **HQ** and **DNP** insert into the cavity of the host, the aromatic protons in the guests point toward one of the phenyl moieties in the *p*-xylyl linker of the host (Fig. 9). This orientation allows the occurrence of C–H•••π interaction, which, in some cases, act as the secondary driving force to strengthen the host-guest recognition. The occurrence of C–H•••π interaction could be convinced by the remarkable upfield shifts of the guest resonances in the corresponding ^{1}H NMR spectra, given that the aromatic surfaces provide a shielded magnetic environment. Short contacts (e.g., 2.5 Å) between the protons in the guest and the phenyl moieties in the host also reveal its occurrence in solid state, as inferred from the single-crystal X-ray diffraction analysis.

(iv) When the **CBPQT**$^{4+}$ accommodates guest in water, in the case that the counterions were Cl^-, Br^-, or NO_3^-, hydrophobic effect might occur and enhance

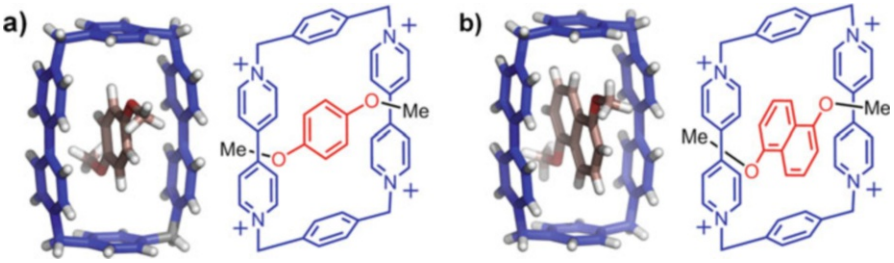


Fig. 9 Structural formulaes and the corresponding single-crystal X-ray structures of two pseudorotaxanes. The guests contain either **HQ** or **DNP** units in the middle. C–H•••π interactions are clearly observed

the host-guest recognition, even although hydrogen-bonding interactions are weakened in these cases. This hypothesis is supported by the stronger K_a for the macrocycle to accommodate the guest **BHEEN** in water than that in MeCN (see Fig. 7).

3.4.2 Guest Recognition Ability of $CBPQT^{2(\bullet+)}$

One of the reduced states of $CBPQT^{4+}$, namely, the bisradical dicationic $CBPQT^{2(\bullet+)}$, contains two $BIPY^{\bullet+}$ radical cations. Different from the $BIPY^{2+}$ contains an empty LUMO that affords $BIPY^{2+}$ the ability to function as a π-electron acceptor, the SOMO of a $BIPY^{\bullet+}$ already contains an electron. As a consequence, $BIPY^{\bullet+}$ is not capable of undergoing donor-acceptor interactions with π-electron donors. Instead, $BIPY^{\bullet+}$ undergoes a type of homo-loving interactions, namely, radical-pairing interactions [31]. That is, the two SOMOs of two $BIPY^{\bullet+}$ undergo efficient overlapping, forming a set of two larger delocalized molecular orbitals of a $(BIPY^{\bullet+})_2$ dimer. The two radical electrons thus occupy the newly formed HOMO of the $(BIPY^{\bullet+})_2$ dimer and therefore get spin paired. The formation of the diamagnetic $(BIPY^{\bullet+})_2$ dimer could be proven by the observation that a solution of $BIPY^{\bullet+}$ has clear EPR signal in the condition of low concentration and/or higher temperature, while in the condition of higher concentration and/or lower temperature, the EPR signal becomes weaker or even silent in some cases. The behavior that two identical aromatic radicals get spin paired by means of π-π stacking was also observed in a few of other aromatic radical systems, including $TTF^{\bullet+}$ radical cation [32] and naphthalene-1,8:4,5-bis(dicarboximide) ($NDI^{\bullet-}$) radical anion [33].

In the case of $CBPQT^{2(\bullet+)}$, spin pairing does not occur to its two $BIPY^{\bullet+}$ units, because their distance, namely, 7 Å, is too large to allow the occurrence of radical spin pairing by means of π-π interactions, given that the efficient π-π interaction distance is around 3.5 Å. Instead, when a $BIPY^{\bullet+}$ guest inserts within the cavity, the guest is able to undergo spin-pairing interactions with both of the two $BIPY^{\bullet+}$ units in the macrocycle simultaneously, forming a $BIPY^{\bullet+}\subset CBPQT^{2(\bullet+)}$ complex [21, 34] (Fig. 10). Because the formation of $BIPY^{\bullet+}\subset CBPQT^{2(\bullet+)}$ is driven

by the formation of "dual" $(\mathbf{BIPY}^{\bullet+})_2$ dimers or a $(\mathbf{BIPY}^{\bullet+})_3$ trimer, the binding constant K_a (i.e., 10^5 M^{-1}) is generally significantly larger than that of the $(\mathbf{BIPY}^{\bullet+})_2$ dimer.

The formation of $\mathbf{BIPY}^{\bullet+}\subset\mathbf{CBPQT}^{2(\bullet+)}$ has been convinced both experimentally and theoretically. The single-crystal X-ray diffraction analysis (Fig. 10) clearly demonstrates the formation of $\mathbf{BIPY}^{\bullet+}\subset\mathbf{CBPQT}^{2(\bullet+)}$ in the solid state. In solution, the formation of $\mathbf{BIPY}^{\bullet+}\subset\mathbf{CBPQT}^{2(\bullet+)}$ could be convinced by the following observations. First, the solution of $\mathbf{BIPY}^{\bullet+}\subset\mathbf{CBPQT}^{2(\bullet+)}$ exhibits an absorption band in the near-IR (NIR) region in the UV-Vis-NIR absorption spectra, a characteristic absorption band indicating the formation of a $(\mathbf{BIPY}^{\bullet+})_2$ dimer. This NIR absorption band is not observed in the solution of either $\mathbf{BIPY}^{\bullet+}$ or $\mathbf{CBPQT}^{2(\bullet+)}$, ruling out the possibility of the occurrence of side-on dimerization of either $(\mathbf{BIPY}^{\bullet+})_2$ or $(\mathbf{CBPQT}^{2(\bullet+)})_2$. Second, in the CV spectrum of a 1:1 mixture solution of $\mathbf{BIPY}^{\bullet+}$ and $\mathbf{CBPQT}^{2(\bullet+)}$, $\mathbf{BIPY}^{\bullet+}$ has a less negative reduction potential compared to that in its individual solution. This is because the formation of $\mathbf{BIPY}^{\bullet+}\subset\mathbf{CBPQT}^{2(\bullet+)}$ acts as a driving force, making the reduction of $\mathbf{BIPY}^{2+}$ to $\mathbf{BIPY}^{\bullet+}$ easier to occur.

The discovery of the complexation of $\mathbf{BIPY}^{\bullet+}\subset\mathbf{CBPQT}^{2(\bullet+)}$ represents a milestone in the field of host-guest chemistry. First, radical-involved interactions begin to be employed as a driving force in host-guest recognition, even although for years radicals have been considered as labile species and infeasible to use in supramolecular recognition. Second, when this driving force is employed in the synthesis of mechanically interlocked molecules followed by oxidation, each of the latter molecules could contain a $\mathbf{CBPQT}^{4+}$ interlocked by a dumbbell or a ring containing a $\mathbf{BIPY}^{2+}$ unit. These interlocked components thus are repulsive to each other on account of Coulombic repulsion between these cationic building blocks, defying the commonly received viewpoint that mechanically interlocked molecules should contain mutually attractive components.

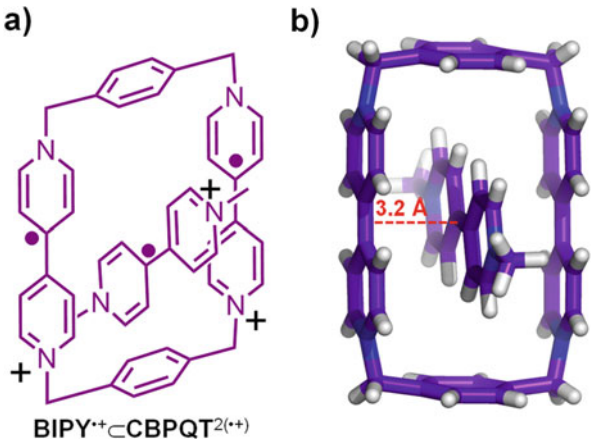


Fig. 10 Structural formulae and the corresponding single-crystal X-ray structures of $\mathbf{BIPY}^{\bullet+}\subset\mathbf{CBPQT}^{2(\bullet+)}$. Counterions are omitted for the sake of clarity

3.5 Mechanically Interlocked Molecules Containing $CBPQT^{4+}$ Ring

Mechanically interlocked molecules (MIMs) [14a] have been considered as a type of nonclassic molecules. On the one hand, different from those normal or "classic" molecules whose atoms are all connected covalently with the molecular moiety, MIMs contain multiple components, between which covalent bonds are absent. When some noncovalent interactions occur between the interlocked molecular components, these MIMs might exist in some specific co-conformations. The preference of these co-conformations could be switched by using some external stimuli to tune these intercomponent intramolecular noncovalent interactions including either weakening the primary one or strengthening the secondary one, which results in mechanical movement of these molecular components with respect to each other. This behavior affords MIMs the ability to develop smart materials whose physical properties could be reversibly controlled. On the other hand, these molecular components are mechanically interlocked with each other, in reminiscence of the many interlocked rings in a necklace or metal chain. Without destroying at least one covalent bond, the architecture of a MIM would remain intact. This feature distinguishes MIMs from those supramolecular complexes, whose molecular components can undergo reversible association/dissociation.

The often studied MIMs include rotaxanes and catenanes, both of which contain a macrocyclic component that encircles either a dumbbell-shaped or another ring component, respectively. When a linear molecule is encircled by a ring, this system is called a pseudorotaxane, which is a type of supramolecular complexes. Pseudorotaxanes are often used as the precursors in the synthesis of rotaxanes and catenanes, when the terminal groups of the former undergo reactions with larger and bulky molecules, or each other, respectively. We are going to discuss it in more detail in the coming section.

3.5.1 Catenanes Containing $CBPQT^{4+}$ Ring

The often used approach to obtain catenanes is the template-directed synthesis. Some noncovalent interactions are employed to drive a macrocycle to encircle a thread-shaped molecule, forming a so-called pseudorotaxane. The supramolecular driving forces are of importance, given that they lead to enthalpy release to compensate the entropy loss during the association of the supramolecular complex. When the two groups undergo reaction with each other or another molecule containing two reacting units simultaneously, which has been called "clipping," a catenane is generated.

The formation of the donor-acceptor catenanes containing **$CBPQT^{4+}$** ring relies on the supramolecular interactions between a π-electron-rich ring and a **$CBPQT^{4+}$** ring. The driving forces include donor-acceptor interactions, hydrogen bonding, C–H•••π, as well as hydrophobic effect in aqueous solutions, as we mentioned before. The π-electron-rich ring thus often contains π-electron-rich unit such as

DNP and **TTF** grafted with ethylene glycol chains. One approach to synthesize catenanes is by clipping a $\mathbf{CBPQT}^{4+}$ ring around a π-electron-rich unit in a crown ether template. That is, combining a π-electron-rich crown ether **BPP34C10**, α,α′-dibromo-*p*-xylene, and $\mathbf{3}^{2+}\bullet\mathbf{2PF_6}^-$ in polar solvent, the latter two compounds would produce a $\mathbf{CBPQT}^{4+}$ ring around the π-electron-rich templating unit (Fig. 11) [35]. The overall yield of the catenane $\mathbf{9}^{4+}\bullet\mathbf{4PF_6}^-$ was reported to be around 70%.

It is also possible to clip the π-electron-rich ring around a $\mathbf{BIPY}^{2+}$ in a $\mathbf{CBPQT}^{4+}$ template. That is, a thread containing a central π-electron-rich unit bearing two ethylene glycol chains is recognized within the cavity of a $\mathbf{CBPQT}^{4+}$ ring. The two terminal groups undergo some high-yielding reactions, including Eglinton-Glaser-Hay coupling [36] (Fig. 12), Cooper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) [37], as well as esterification [38].

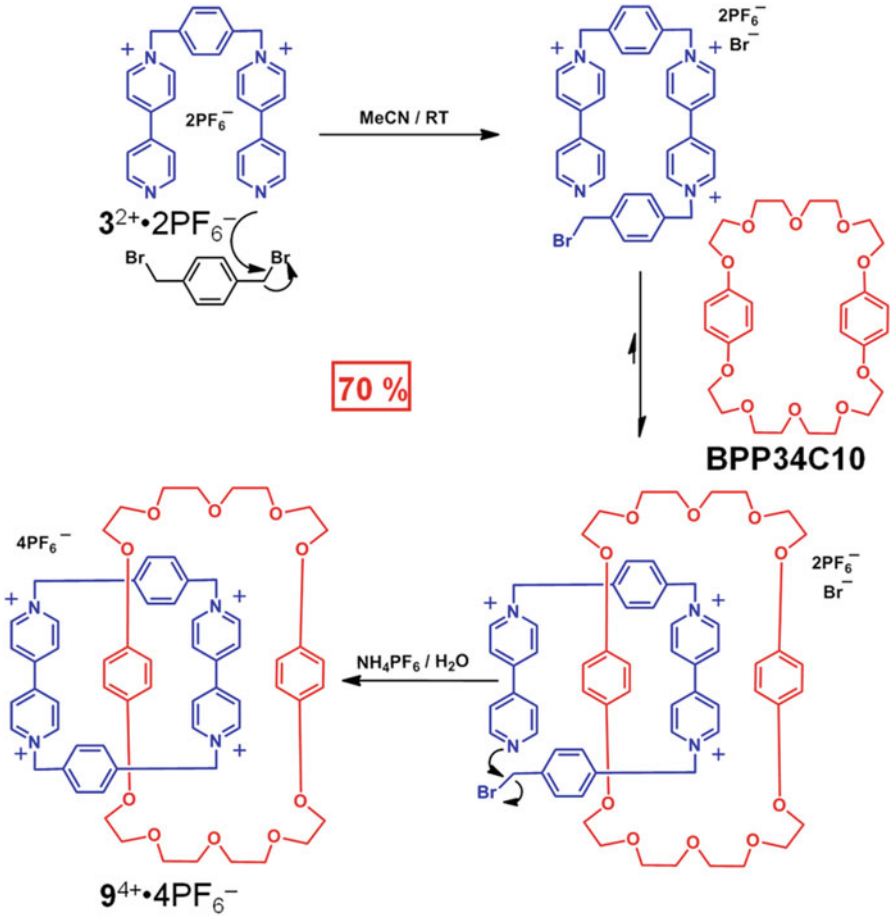


Fig. 11 The template-directed synthesis for the synthesis of a catenane $\mathbf{9}^{4+}\bullet 4PF_6^-$

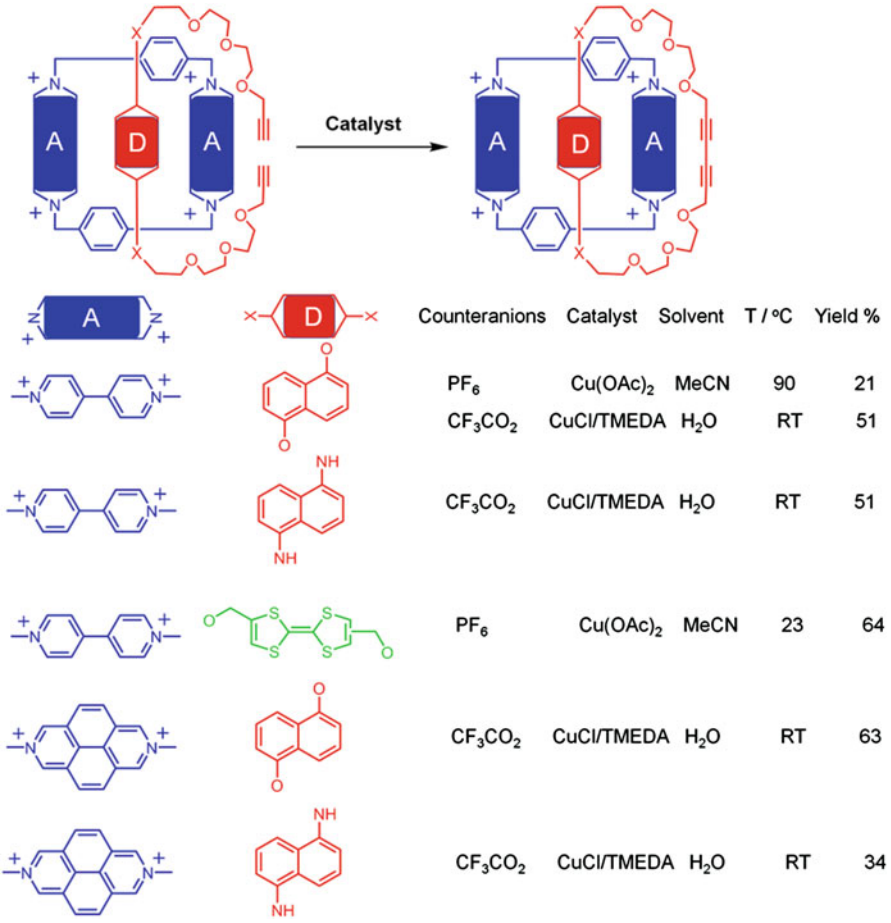


Fig. 12 Synthesis of a series donor-acceptor [2]catenanes, by clipping via Eglinton-Glaser-Hay coupling

A few reversible reactions were also employed in order to prepare the catenane in a reversible manner, such as imine bond formation [39], as well as metal-catalyzed olefin metathesis [40]. These dynamic approaches often resulted in higher yields, compared with those in the condition of irreversible ones. This is because (i) dynamic bond undergoes reversible forming/cleavage processes, which allows the systems to perform error checking, and therefore the MIMs are synthesized in a thermodynamic control and (ii) the guest recognition ability of **CBPQT**$^{4+}$ acts as the driving forces, making the MIMs more thermodynamically favored compared with other byproducts.

Even although **CBPQT**$^{4+}$ is considered as a macrocycle containing only irreversible covalent bonds, it has been discovered that one of the four C–N bonds between the pyridinium nitrogen and the methylene carbon could become reversible, by using

iodide anion as both the nucleophile and leaving group. One of the methylene units in **CBPQT**$^{4+}$ undergoes nucleophilic attack by an I^- anion, forming a linear-shaped intermediate whose two terminal groups are benzyl iodide and pyridine, respectively. The driving force is the release of ring strain of the **CBPQT**$^{4+}$ ring. In the presence of a π-electron-rich crown ether **BPP34C10**, the thread could be recognized within the cavity of the former, followed by an intramolecular S_N2 reaction between the benzyl iodide and pyridine. The latter process recovers the ring and yields a catenane. The leaving group, namely, the I^- anion, could undergo another attacking-followed-by-leaving cycle, catalyzing the transfer from **CBPQT**$^{4+}$ to catenane **9**$^{4+}$ [41] (Fig. 13).

After the discovery of **BIPY**$^{\bullet+}$⊂**CBPQT**$^{2(\bullet+)}$ complexation in reduction state, MIMs including catenanes containing **CBPQT** ring could be driven by radical-

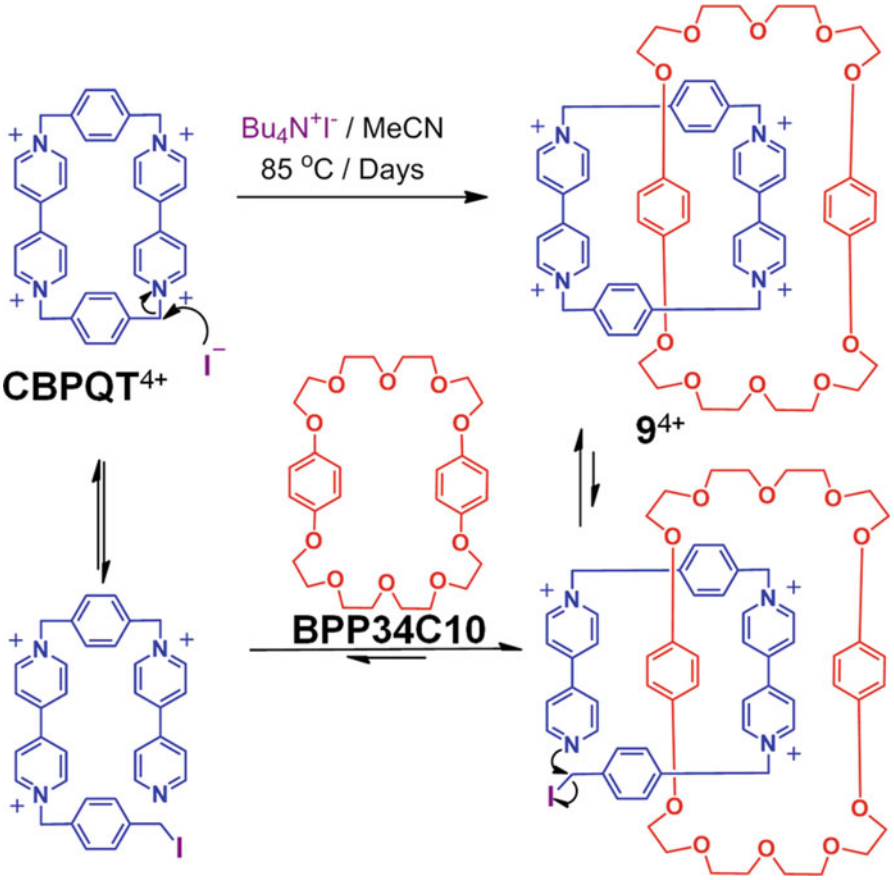


Fig. 13 Synthesis of a donor-acceptor [2]catenane **7**$^{4+}$, by using a dynamic approach in which an I^- anion acts as both the nucleophile that opens the **CBPQT**$^{4+}$ ring and the leaving group that yields the catenane

pairing interactions. In the year of 2013, Stoddart group reported (Fig. 14) the synthesis of a homo-catenane $\mathbf{10}^{8+}$, which is composed of two mechanically interlocked **CBPQT** ring [42]. A reverse horseshoe-shaped guest $\mathbf{6}^{2+}$ containing a central $\mathbf{BIPY}^{\bullet+}$ moiety was recognized by a $\mathbf{CBPQT}^{2(\bullet+)}$, by using Zn dust to reduce the corresponding $\mathbf{BIPY}^{2+}$ units to radical states. The two benzyl bromide terminal groups in the former undergo S_N2 reaction with the two pyridine functions in a 4,4′-bipyridine molecule simultaneously. After oxidation by using a strong oxidant, a catenane $\mathbf{10}^{8+}$ bearing eight positive charges could be obtained. Different from those donor-acceptor counterparts, this catenane contains two $\mathbf{CBPQT}^{4+}$ rings that are highly repulsively to each other, on account of

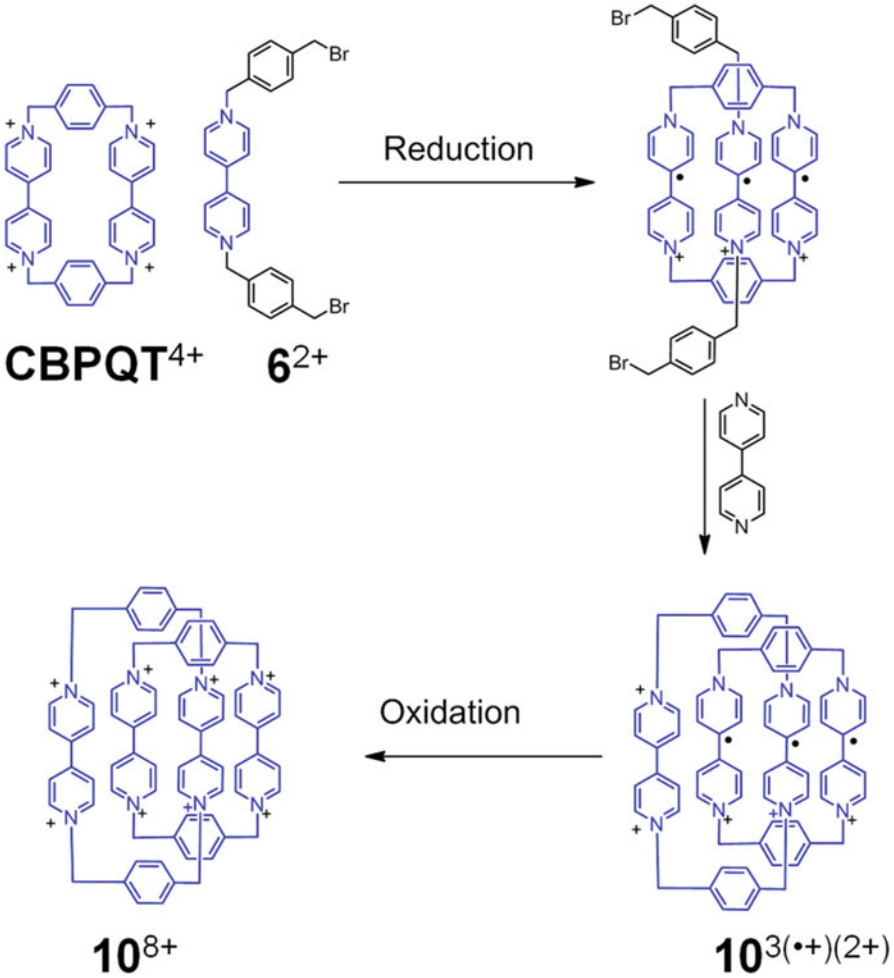


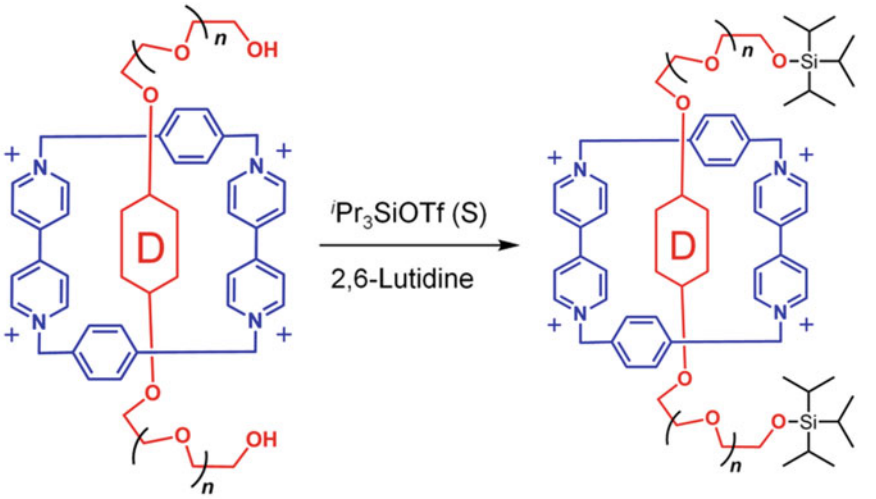
Fig. 14 Synthesis of a homo-[2]catenane $\mathbf{10}^{2+}$ composed of two mechanically interlocked $\mathbf{CBPQT}^{4+}$ ring by radical-pairing interactions. Counterions are omitted for the sake of clarity

the Coulombic repulsion between the cationic building blocks. This feature also brings about a unique property of this catenane. That is, in order to decrease the Coulombic repulsion, one or two of the **BIPY**$^{2+}$ units in the catenane prefer to stay in the radical state, namely, **BIPY**$^{\bullet+}$. As a consequence, the radical is highly stabilized, opening up opportunities to develop purely organic paramagnetic materials.

3.5.2 Rotaxanes Containing CBPQT^{4+} Ring

The donor-acceptor rotaxanes are obtained in a similar approach as their catenanes counterparts, relying on the ability of a **CBPQT**$^{4+}$ ring or its precursors to recognize the π-electron-rich guests. Clipping reaction of α,α′-dibromo-*p*-xylene and **1**$^{2+}$ occurs in the presence of a dumbbell, yielding the corresponding rotaxanes [43]. Because the C–H•••O hydrogen bonds play an even more important role than that of donor-acceptor interactions, it was observed that the dumbbells containing more ethylene glycol units often produced rotaxanes in higher yields. The threading-followed-by-stoppering strategy is also often used in the synthesis of rotaxanes containing a **CBPQT**$^{4+}$ ring. Here the **CBPQT**$^{4+}$ ring encircles a thread on its π-electron-rich binding station. The two terminal OH groups of the thread react with two larger bulky silicon derivatives whose volume should be larger than the cavity of **CBPQT**$^{4+}$ ring to trap the corresponding rotaxane architectures [26] (Fig. 15). CuAAC [44], which has been referred to as click reaction, is an ideal reaction for rotaxanes synthesis [45], because of (i) high yield and (ii) room temperature condition that favors complexation.

The capability of **CBPQT**$^{2(\bullet+)}$ to recognize a guest containing **BIPY**$^{\bullet+}$ was also taken advantage (Fig. 16) of by the Stoddart group in the synthesis of rotaxanes [46]. A complex **11**$^{\bullet+}$⊂**CBPQT**$^{2(\bullet+)}$ was self-assembled. Tris(2,2′-bipyridine) dichlororuthenium(II) was used as a sensitizer, which reduces the **BIPY**$^{2+}$ units in both **CBPQT**$^{4+}$ and **11**$^{2+}$ to their radical states, in the presence of amino sacrificial reductant under visible light. The two azide terminal groups in **11**$^{\bullet+}$ were introduced to undergo a type of click reaction, namely, azide-alkyne cycloaddition. An electron-deficient alkyne **12** was chosen, because it has a low-lying LUMO and therefore can undergo azide-alkyne cycloaddition without Cu(I) catalyst. Avoiding Cu(I) catalyst is of importance, due to its oxidative nature that might quench the **BIPY**$^{\bullet+}$ radicals. After the click reaction was accomplished, a rotaxane **13**$^{6+}$ was obtained, whose dumbbell and ring components are repulsive to each other. A few years later, the Stoddart group also discovered [47] that the length of rotaxane could determine the stability of **BIPY**$^{\bullet+}$ radicals in the rotaxane against oxidation. In a shorter rotaxane, the distance between the **CBPQT**$^{4+}$ ring and the central **BIPY**$^{2+}$ unit in the dumbbell is smaller, which introduces larger Coulombic repulsion. The unfavorable repulsive interaction increases the tendency of the **BIPY**$^{2+}$ unit to be reduced, as a consequence of which, the radical state of the short rotaxane is remarkably stabilized.



D	n	Solvent	Box equiv	D equiv	S equiv	Lutidine equiv	T / °C	t / h	Yield %
	1	MeCN	1	3	7.5	7.5	RT	1	22
	2	MeCN	1	3	7.5	7.5	RT	1	22
	2	MeCN	1	3	7	7	RT	48	43
	2	MeCN	1	3	8	8	RT	12	39
	3	DMF	1	2.8	25	56	RT	36	39
	2	DMF	1	3	8	8	RT	12	5
	1	MeCN	1	2	10	24	RT	1.5	12
	1	MeCN	1	2	10	24	RT	1.5	15
	1	MeCN	1	2	10	24	RT	1.5	17
	1	MeCN	1	1.1	3.7	4.3	RT	1	26
	1	MeCN	1.1	1	4.0	4.6	RT	1.5	11

Fig. 15 Synthesis of rotaxanes by using a threading-followed-by-stoppering strategy. A 2,6-lutidine catalyzed Si–O bond formation is used for the stoppering reaction to capture the rotaxane structures

3.6 Molecular Machines and Molecular Switches

As mentioned before, MIMs could be switched between different *co*-conformations by tuning the noncovalent interactions between the interlocked molecular components. First, these different *co*-conformers, whose covalent structures are essentially the same, might have dramatically different physical properties, such as color, luminescence, electric conductivity, hydrophilicity, as well as viscosity. This

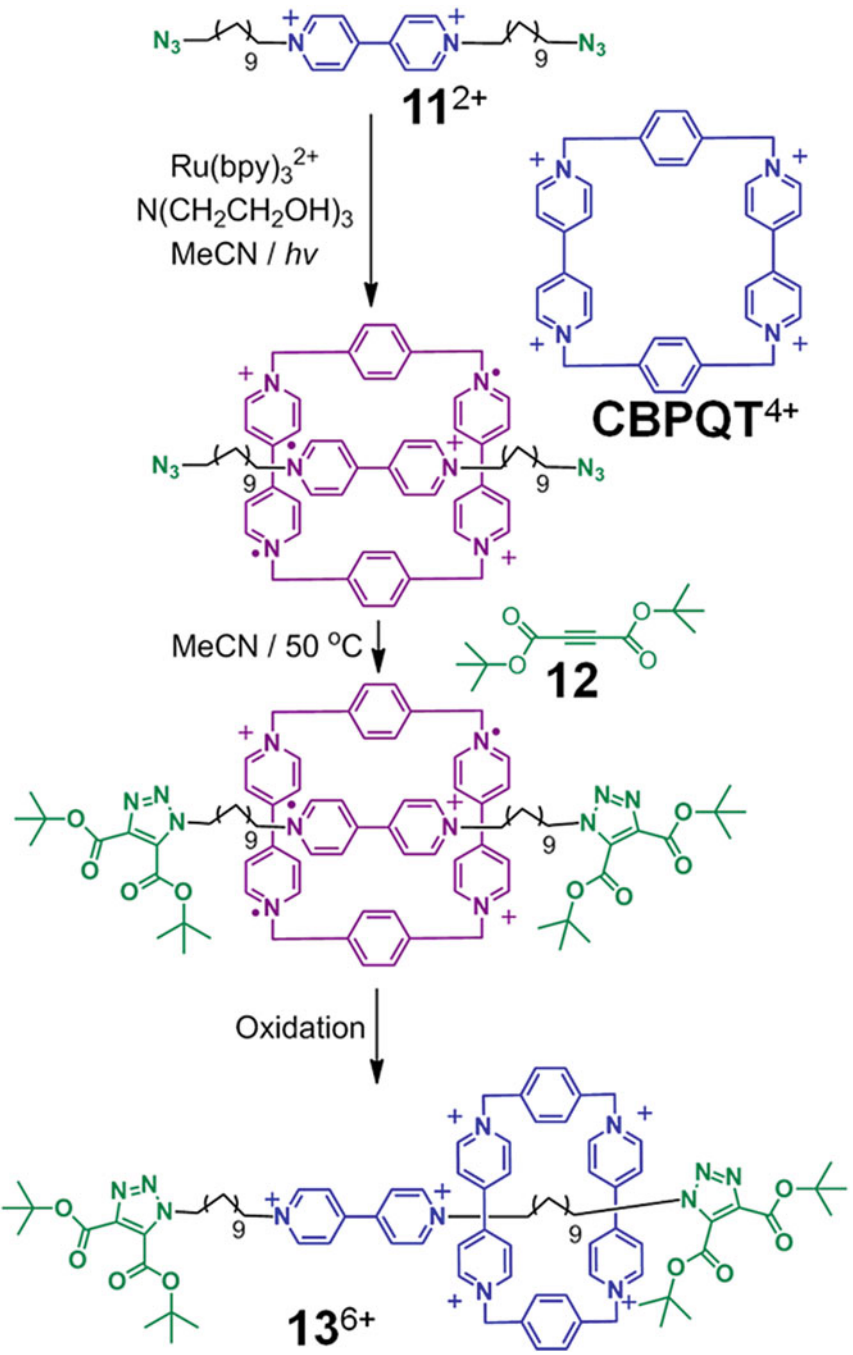


Fig. 16 Synthesis of a rotaxane $\mathbf{13}^{6+}$ by using radical templation. The counterions are omitted for the sake of clarity

switching behavior could be used to design smart materials, whose properties could be controlled by employing external stimuli. For example, when a bistable rotaxane whose two *co*-conformers have remarkable difference in electric conductivity, it has the potential application in the design of molecular computer [48], i.e., the two *co*-conformers could represent "0" and "1," respectively, for information storage. Second, switching between different *co*-conformers allows the components of a MIM to undergo intramolecular machinery mechanical movement, which could perform work on the surroundings and influence their properties. This potential ability opens up the opportunities for human to precisely control the microscopic world. The early trials include the nanoelectromechanical systems [49], in which the switching behavior of a MIM is employed to control the shapes and properties of an inorganic component. Using molecular switches to develop mechanized silica nanoscopic particles [50] for precisely targeted drug delivery represents another example of their potential applications.

In the year of 2016, the Nobel Prize in Chemistry was awarded to three chemists, including Jean-Pierre Sauvage [19a], Sir Fraser Stoddart [19b], as well as Bernard Feringa, on account of their contributions in the field of molecular machines. The former two chemists, namely, Jean-Pierre Sauvage and Sir Fraser Stoddart, employed MIMs in the design of molecular machines.

In order to shed light on the underneath mechanism how a molecular switch or machine works, we use a bistable rotaxane as a model compound. In the dumbbell component, two binding stations are introduced. This bistable rotaxane thus has two *co*-conformations, determined by which station the ring encircles. The ring is doing random Brownian movement along the dumbbell between the two stations, even although the energy barrier could be controllable by introducing a steric or electronic "speed bump" in the dumbbell between the two stations. When the macrocycle encircles the stronger or primary binding station, the rotaxane adopts a *co*-conformation that has been called ground state co-conformation (GSCC). In contrast, the co-conformation in which the ring sits on the weaker or secondary binding station has been called metastable-state co-conformation (MSCC). The ratio of the two *co*-conformations could be determined by the energy gap (ΔG) between the two *co*-conformations, as claimed by Boltzmann distribution, i.e., $-\Delta G = \mathrm{RT}\ln K$ (K is ratio of GSCC to MSCC). A molecular switch and machine based on a bistable catenane has a similar working mechanism, except that the dumbbell in a rotaxane is replaced by a macrocycle containing two binding stations in a catenane. When an external stimulus is introduced, which either weakens the binding between the primary binding station (i.e., station A) and the ring or strengthens the binding provided by the secondary binding station (i.e., station B), the preference of the macrocyclic component to encircle the two stations would change. That is, more macrocycles would prefer to encircle the station B, after addition of the external stimuli, which implies that it is a net effect that the ring is "moving" from station A to station B. This mechanism is different from its macroscopic counterparts, in which a macroscopic object undergoes direct change of its physical position. Removing the stimuli might recover the noncovalent bonding, and therefore the ring might move back to station A as a net effect.

In the year of 1994, the first molecular switch in the form of bistable [2]rotaxane $\mathbf{14}^{4+}$ containing $\mathbf{CBPQT}^{4+}$ as the macrocyclic component was synthesized [51] (Fig. 17) in the group led by Stoddart. The dumbbell component bears a benzidine as the primary station and a biphenol unit as the secondary one. The stronger binding affinity of benzidine compared to biphenol results from the fact that the two amino nitrogen atoms on benzidine represent better electron donors than the oxygen atoms on biphenol function. Either oxidation or protonation of the benzidine introduces a positive charge, which diminishes its binding affinity with the ring. As a consequence, the $\mathbf{CBPQT}^{4+}$ moves and encircles the biphenol station. Performing reduction or deprotonation of benzidine recovers its binding affinity, and therefore the ring moves back to this station.

TTF, whose switching behavior under redox stimuli is more reversible than benzidine, was also employed in the design of molecular switches in the form of both multi-stable rotaxanes [52] and catenanes. For example, in the catenane $\mathbf{15}^{4+}$ (Fig. 18), **TTF** and **DNP** act as the primary and secondary binding station for the ring, respectively. The ratio of GSCC to MSCC is around 150:1 determined by using slow scan rate cyclic voltammetry [53], in which the ring encircles the **TTF** and **DNP** unit, respectively. Oxidation of **TTF** would drive the ring to reside on the **DNP** station [54]. When the secondary binding station is a di-alkyne linker that has no binding affinity with the $\mathbf{CBPQT}^{4+}$ ring, a so-called push-button molecular switch

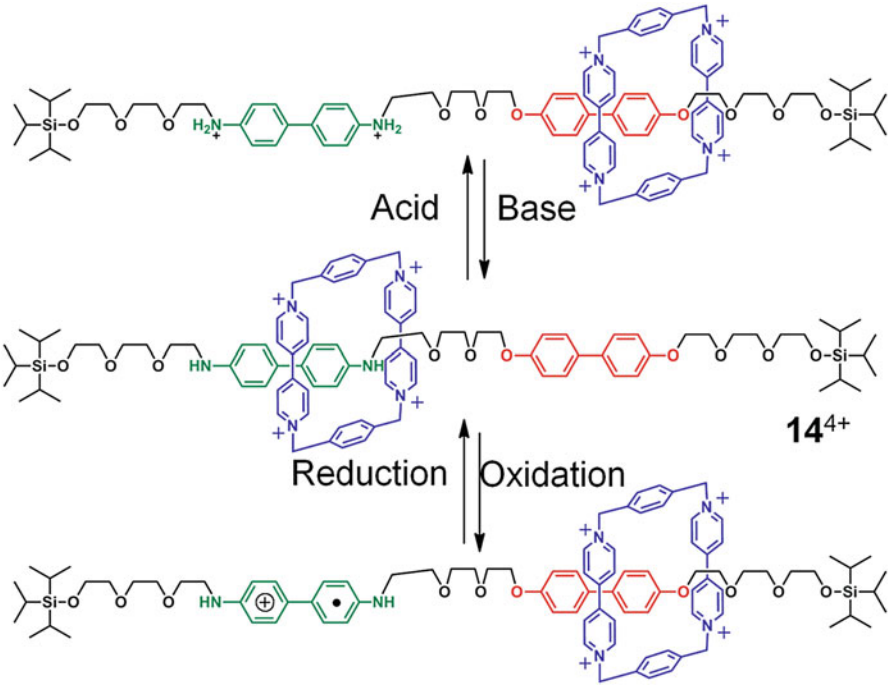


Fig. 17 The bistable [2]rotaxane $\mathbf{14}^{4+}$, which could be switched between two *co*-conformers by using redox or acid/base stimuli

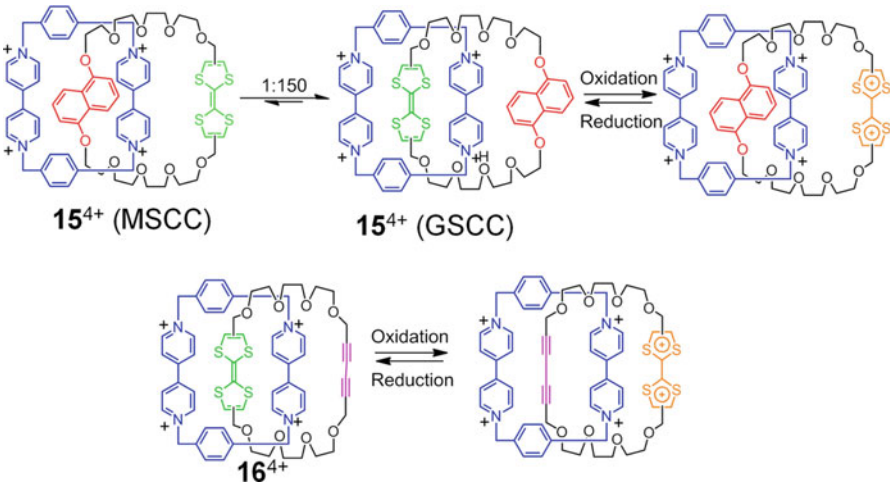


Fig. 18 The bistable [2]catenanes $\mathbf{15}^{4+}$ and $\mathbf{16}^{4+}$, in both of which, **TTF** acts as the primary binding station. In $\mathbf{15}^{4+}$, **DNP** acts as a secondary binding station. The ratio of GSCC to MSCC is around 150:1. Counterions are omitted for the sake of clarity

[36a] in the form of a catenane $\mathbf{16}^{4+}$ was obtained. That is, in the neutral state, the catenane $\mathbf{16}^{4+}$ adopts (Fig. 18) a *co*-conformation that the $\mathbf{CBPQT}^{4+}$ ring encircles the **TTF** unit almost exclusively, on account of the absence of any binding affinity between the di-alkyne linker and the $\mathbf{CBPQT}^{4+}$ ring. Upon oxidation of the **TTF** unit to its cationic forms, either $\mathbf{TTF}^{\bullet+}$ or $\mathbf{TTF}^{2+}$, $\mathbf{CBPQT}^{4+}$ ring chooses to reside on the di-alkyne exclusively, in order to avoid Coulombic repulsion introduced by the cationic $\mathbf{TTF}^{\bullet+}$ or $\mathbf{TTF}^{2+}$ unit.

This all-or-nothing switching behavior is even more obvious in the molecular switch whose switching behavior is driven by using the radical-pairing interactions. A bistable rotaxane $\mathbf{17}^{8+}$ was designed [21] (Fig. 19), containing a $\mathbf{CBPQT}^{4+}$ ring threaded onto a dumbbell that bears a **DNP** and a $\mathbf{BIPY}^{2+}$ unit. In the fully oxidized state, the tetracationic ring resides on the former station, driven by donor-acceptor interactions. The preference of the ring to encircle **DNP** is close to exclusive, given that **DNP** is the only π-electron-rich unit that has binding affinity with the ring. In the reduced state, the $\mathbf{CBPQT}^{2(\bullet+)}$ resides on the $\mathbf{BIPY}^{\bullet+}$ station exclusively, driven by radical-pairing interactions. Introducing oxygen into the system could oxidize the radicals to the dicationic state, resetting the rotaxane. A few years later, the same group developed a light-stimulated "version," namely, a bistable rotaxane $\mathbf{17}^{8+}$ [55] by introducing a photosensitizer as one of the two stoppers onto the rotaxane $\mathbf{17}^{8+}$. The light-stimulated excited state of a photosensitizer, namely, a tris(2,2′-bipyridine) dichlororuthenium(II) stopper, is able to reduce $\mathbf{BIPY}^{2+}$ units in the rotaxane into $\mathbf{BIPY}^{\bullet+}$ in the presence of amino sacrificial reagent, namely, tri(ethanol)amine.

It is noteworthy that the aforementioned molecular switches produce the ring movement in a reciprocating manner. That is, when a stimulus is used to drive the movement of the $\mathbf{CBPQT}^{4+}$ ring, the work produced by the macrocycle would be

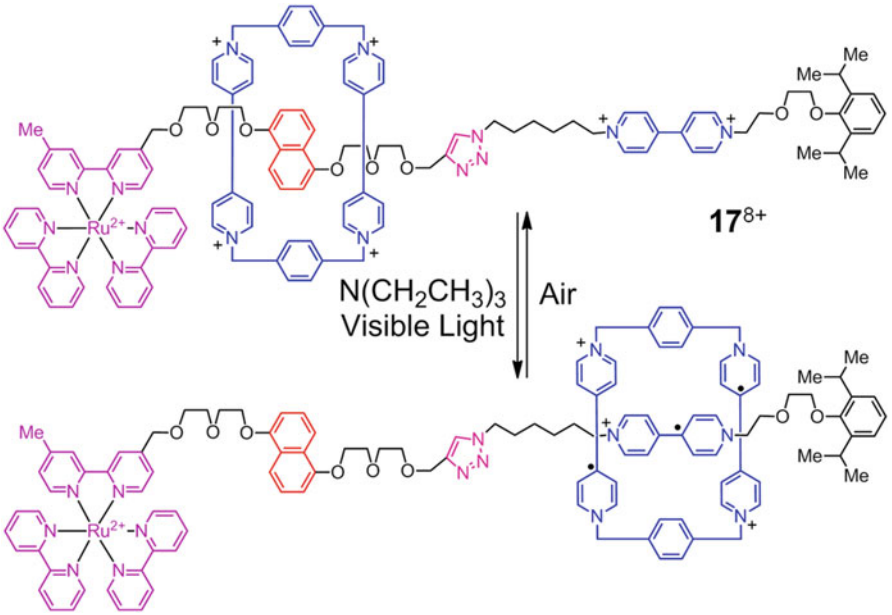


Fig. 19 The light-stimulated bistable [2]catenanes $\mathbf{17}^{8+}$. In oxidative conditions, the ring encircles the **DNP** station. Under visible light, the tris(2,2′-bipyridine)dichlororuthenium(II) stopper can reduce the $\mathbf{BIPY}^{2+}$ units in both the ring and the dumbbell components with the assistance of N $(CH_2CH_3)_3$ as a sacrificial reagent. After reduction, the ring shuttles and encircles the $\mathbf{BIPY}^{\bullet+}$ station

cancelled or neutralized when we reset the molecular switch, because the ring returns to its original position by using a reversed pathway. Or expressed in another way, the net energy produced by the molecular switch is nothing after a full switching cycle. In order to produce a real artificial molecular machine that is able to produce useful work to the surroundings, a pseudorotaxane $\mathbf{18}^{+}\subset\mathbf{CBPQT}^{4+}$ that produces unidirectional motion was designed [56] (Fig. 20). A $\mathbf{CBPQT}^{4+}$ ring encircles a **DNP** unit in a dumbbell-shaped molecule $\mathbf{18}^{+}$ bearing two terminal units, namely, a neutral 2-isopropylphenyl group and a positively charged 3,5-dimethylpyridinium unit. The formation of the pseudorotaxane $\mathbf{18}^{+}\subset\mathbf{CBPQT}^{4+}$ is again driven by donor-acceptor interactions. However, due to the Coulombic repulsion introduced by the 3,5-dimethylpyridinium, the association of the pseudorotaxane occurs in the manner that the ring passes the 2-isopropylphenyl unit. Reduction of the ring diminishes its binding affinity for the **DNP** station and therefore results in the dissociation of the pseudorotaxane. At the same time, the Coulombic repulsion between the reduced ring and the 3,5-dimethylpyridinium unit undergoes significant decrease. In order to avoid the steric hindrance introduced by the 2-isopropylphenyl group, the $\mathbf{CBPQT}^{2(\bullet+)}$ ring chooses to pass the 3,5-dimethylpyridinium unit to finish dissociation. These switching behaviors enable the ring to perform unidirectional movement from one end of the dumbbell to another, generating useful work.

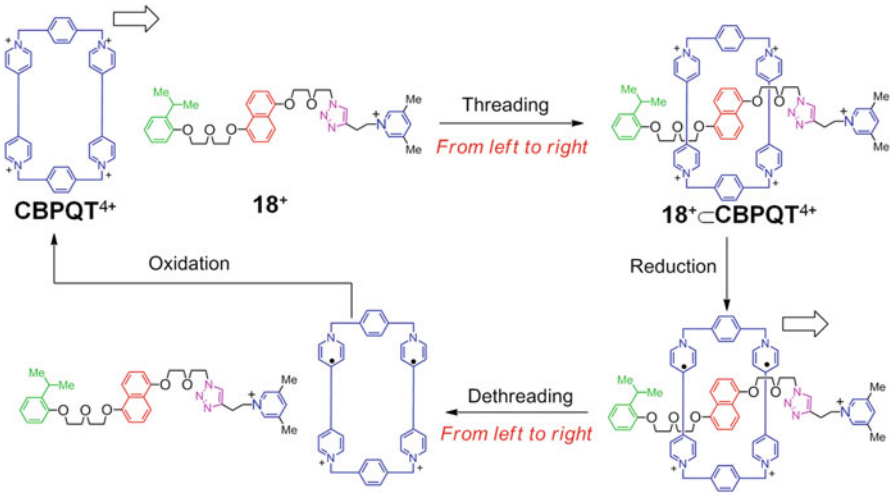


Fig. 20 A pseudorotaxane $\mathbf{18}^{+}\subset\mathbf{CBPQT}^{4+}$ which can perform unidirectional association and dissociation motion under redox stimuli

3.7 Extended Derivatives of CBPQT^{4+} Ring

A number of extended "versions" of $\mathbf{CBPQT}^{4+}$ rings were also designed and synthesized, which acts as larger counterparts of the small **Blue Box**. These extended derivatives are able to host either larger guests or in some cases, multiple guests simultaneously.

In the year of 1996, a wider counterpart of $\mathbf{CBPQT}^{4+}$ ring, namely, cyclobis (paraquat-4,4′-biphenylene) ($\mathbf{CBPQB}^{4+}$) [57], was obtained (Fig. 21), by using ferrocene, a relatively "thicker" guest to template its formation. The two $\mathbf{BIPY}^{2+}$ units are bridged by two 4,4′-bitolyl spacers, instead of the *p*-xylyl linkers in the synthesis of $\mathbf{CBPQT}^{4+}$. The distance between the two $\mathbf{BIPY}^{2+}$ units in $\mathbf{CBPQB}^{4+}$ is around 11 Å, enabling the ring to recognize two π-electron guests within the cavity, where both of the two guests undergo donor-acceptor interactions with the two $\mathbf{BIPY}^{2+}$ units in $\mathbf{CBPQB}^{4+}$ ring in an A-D-D-A manner (A, acceptor; D, donor). This recognition behavior opens up opportunities to use $\mathbf{CBPQB}^{4+}$ to synthesize [3] catenanes. In fact, the [3]catenane $\mathbf{20}^{4+}$ (Fig. 22) containing $\mathbf{CBPQB}^{4+}$ was even synthesized [58] before $\mathbf{CBPQB}^{4+}$ itself. The two crown ether rings in the $\mathbf{20}^{4+}$ act as the intrinsic templates for the ring closing reaction. A few years later, [3]catenane $\mathbf{21}^{4+}$ (Fig. 23) containing two **TTF** recognition sites was obtained [59]. Both the two **TTF** units in the two crown ether rings locate within the cavity of $\mathbf{CBPQB}^{4+}$. Interestingly, upon oxidation of **TTF** units into cationic $\mathbf{TTF}^{\bullet+}$ radicals, the two $\mathbf{TTF}^{\bullet+}$ units continue to reside within the macrocycle cavity, undergoing radical-pairing interactions. This behavior indicates that radical-pairing interactions within a $(\mathbf{TTF}^{\bullet+})_2$ dimer are strong enough to overcome the Coulombic repulsion between

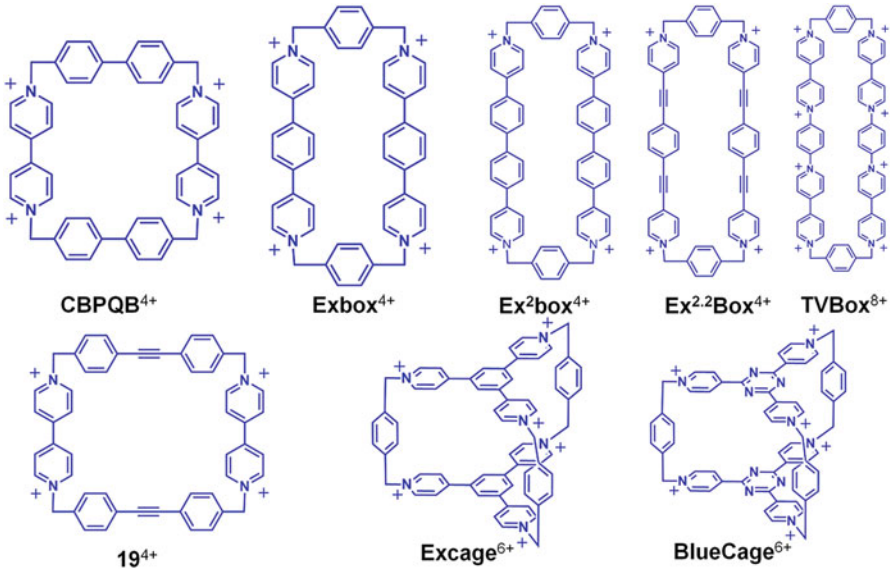


Fig. 21 Structural formulaes of the extended derivatives of **CBPQT**$^{4+}$

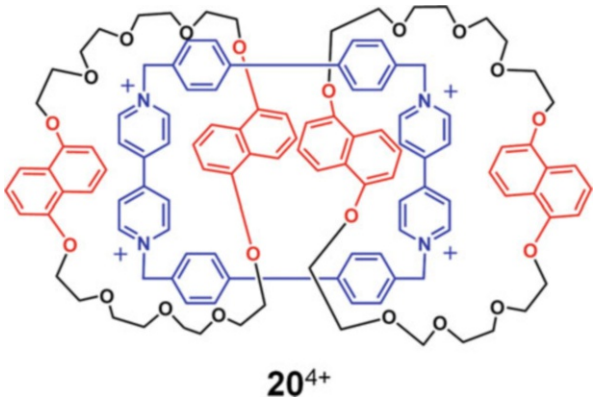


Fig. 22 Structural formula of a [3]catenane **20**$^{4+}$

the **TTF**$^{\bullet+}$ units and the tetracationic cyclophane. It is also strong enough to compensate the potential enthalpy release that results from the donor-acceptor interactions between the **DNP** unit and the **CBPQB**$^{4+}$ ring. Further oxidizing **TTF**$^{\bullet+}$ to **TTF**$^{2+}$ diminished the (**TTF**$^{\bullet+}$)$_2$ radical-pairing interactions, leading to a *co*-conformation that the ring encircled the two **DNP** stations.

Different from **CBPQT**$^{2(\bullet+)}$ that can recognize a **BIPY**$^{\bullet+}$ guest, the ability of **CBPQB**$^{2(\bullet+)}$ to accommodate two **BIPY**$^{\bullet+}$ guests in the cavity is relatively weak. This is probably because encapsulation of two **BIPY**$^{\bullet+}$ guests within the cavity of **CBPQB**$^{2(\bullet+)}$ simultaneously leads to too much entropy loss. However, when the two **BIPY**$^{\bullet+}$ units are connected by two *m*-xylyl linkers, the macrocyclic **22**$^{2(\bullet+)}$ could be

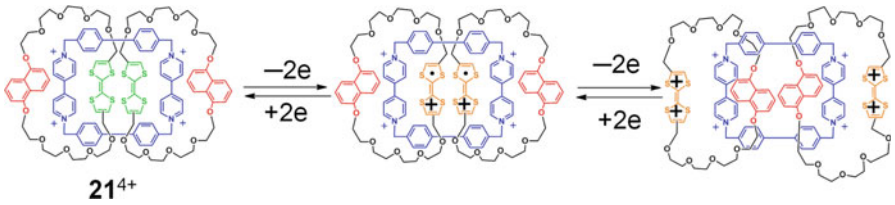


Fig. 23 Structural formula of a [3]catenane $\mathbf{21}^{4+}$ and its redox-switching behavior

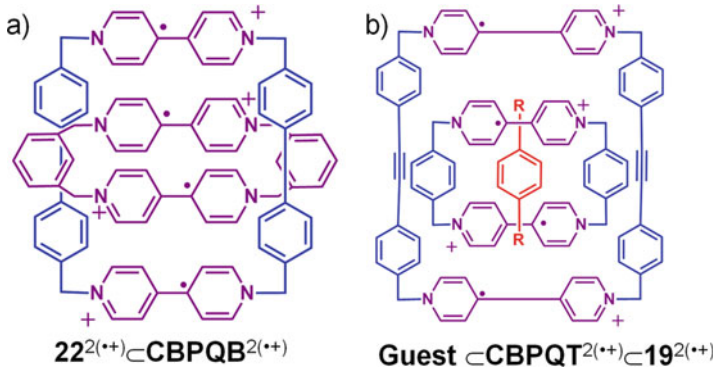


Fig. 24 Structural formulas of the ring-in-ring complexes, including (**a**) $\mathbf{22}^{2(\bullet+)}\subset\mathbf{CBPQB}^{2(\bullet+)}$ and (**b**) $\mathbf{Guest}\subset\mathbf{CBPQT}^{2(\bullet+)}\subset\mathbf{19}^{2(\bullet+)}$

recognized within the $\mathbf{CBPQB}^{2(\bullet+)}$ ring (Fig. 24a). The complex $\mathbf{22}^{2(\bullet+)}\subset\mathbf{CBPQB}^{2(\bullet+)}$ [60] contains two $(\mathbf{BIPY}^{\bullet+})_2$ dimers, as a consequence of which, it is diamagnetic and can be characterized by NMR spectroscopy. This ring-in-ring recognition is taken advantage of in synthesizing a rotaxane [61], whose dumbbell component contains a macrocyclic binding station.

In a recent report, by introducing an ethyne unit between the two phenyl rings in the 4,4′-bitolyl spacer, the Stoddart group obtained a wider cyclophane $\mathbf{19}^{4+}$. This ring in its radical state is able to accommodate a $\mathbf{CBPQT}^{2(\bullet+)}$, which, again, is driven by radical-pairing interactions. Within the cavity of $\mathbf{19}^{2(\bullet+)}$, the $\mathbf{CBPQT}^{2(\bullet+)}$ ring can still act as a host to recognize a variety of guests forming a series of supramolecular architectures that are reminiscence of the Russian dolls [62] (Fig. 24b).

The extension of $\mathbf{CBPQT}^{4+}$ could also be performed in the $\mathbf{BIPY}^{2+}$ part. By introducing a phenyl unit between the two pyridinium moieties in the $\mathbf{BIPY}^{\bullet+}$ functions, a so-called $\mathbf{Exbox}^{4+}$ [63] was obtained. The central phenyl moiety is rather electron-deficient, due to the electron-withdrawing effect from the two pyridinium either by means of inductive effect or conjugation. $\mathbf{Exbox}^{4+}$ is thus able to recognize a few π-electron-rich aromatic hydrocarbon compounds, such as anthracene, phenanthrene, pyrene, etc.

Introducing two phenyl units in each of the two $\mathbf{BIPY}^{\bullet+}$ functions in $\mathbf{CBPQT}^{4+}$ could produce an $\mathbf{Ex^2box}^{4+}$ [64]. In the $\mathbf{Ex^2box}^{4+}$, each of the central phenyl units is

connected with only one of the two pyridinium units. The consequence is that the central biphenyl units do not have good π-electron-accepting ability. Instead, the cavity of **Ex^{2}box**$^{4+}$ has a dual feature. In the terminal part, the cavity is rather electron-poor and can recognize electron-rich guest, which is reminiscent of **CBPQT**$^{4+}$ ring. In the middle part, the cavity of **Ex^{2}box**$^{4+}$ is able to recognize electron-deficient guest. **Ex^{2}box**$^{4+}$ is even able to accommodate two trichlorobenzene guests.

A few other extended boxes, including **TVBox**$^{8+}$ [65], **Ex$^{2.2}$Box**$^{4+}$ [66], as well as **ExBox2**$^{4+}$ [67], were also synthesized, whose structures are illustrated in Fig. 21. In addition, now cage-shaped versions of **CBPQT**$^{4+}$, namely, **Excage**$^{6+}$ [68] and **BlueCage**$^{6+}$ [69], were also obtained. These prism-shaped cages are composed of two triangular π-electron acceptors that are bridged by three spacers. Given that the triangular π-electron acceptors are triscationic and have better π-electron-accepting ability, these two cages often have larger binding affinity for π-electron-rich guests, compared to the ring counterparts (Figs. 23 and 24).

3.8 Conclusions and Outlook

In sum, the **CBPQT**$^{4+}$ ring represents one of the most important macrocyclic hosts in the field of supramolecular chemistry and host-guest chemistry. It can recognize a variety of aromatic guests, most of which are π-electron-rich. These capabilities are based on (i) the rigid macrocycle framework of **CBPQT**$^{4+}$, resulting in little to no entropy loss during guest accommodating, (ii) the distances between the two pyridinium moieties are optimal to allow the guests to undergo donor-acceptor interactions with both of them in either A-D-A or A-D-D-A manner. This host-guest recognition ability allows **CBPQT**$^{4+}$ ring to be used as the building block to synthesize a variety of supramolecular or mechanically interlocked architectures.

The driving forces for **CBPQT**$^{4+}$ to recognize guests including donor-acceptor interactions, hydrogen bonding, electrostatic forces, C–H•••π interaction, as well as hydrophobic effect are expressed in water. In the condition of reduction, the **CBPQT**$^{2(\bullet+)}$ ring becomes attractive to **BIPY**$^{\bullet+}$ guests, driven by radical-pairing interactions. By tuning these driving forces, the host-guest complexation could be controlled, in the form of either dissociation of pseudorotaxanes or co-conformation switching in the case of bistable rotaxanes or catenanes. These switching behaviors of the **CBPQT**$^{4+}$ ring based on supramolecular or mechanically interlocked architecture are taken advantage of in the design of molecular switches and machines, which could potentially be used in developing smart materials. The dream of human beings to precisely control the microscopic world might come true.

In order to allow the recognition of some larger guests, or realize multiple guest recognition, extended versions of **CBPQT**$^{4+}$ ring were developed. These macrocycles demonstrate different guest recognition behavior from that of **CBPQT**$^{4+}$ ring. Their recognition abilities enable more complex architectures to be synthesized.

References

1. (a) Pedersen CJ. Cyclic polyethers and their complexes with metal salts. (1967) J Am Chem Soc 89:7017; (b) Pedersen CJ. Cyclic polyethers and their complexes with metal salts. (1967) J. Am Chem Soc 89:2495
2. (a) Lehn JM. Supramolecular chemistry. (1993) Science 260:1762–1763; (b) Lehn JM. Perspectives in supramolecular chemistry—from molecular recognition towards molecular information processing and self-organization. (1990) Angew Chem Int Ed 29:1304–1319
3. (a) Cram DJ, Cram JM. Host-guest chemistry. (1974) Science 183:803–809; (b) Cram DJ. The design of molecular hosts, guests, and their complexes (Nobel Lecture). (1988) Angew Chem Int Ed 27:1009–1020
4. Dietrichbuchecker CO, Sauvage JP, Kintzinger JP. Une nouvelle famille de molecules : les metallo-catenanes. (1983) Tetrahedron Lett 24:5095–5098
5. Hunter CA, Sanders JKM. The nature of .pi.-.pi. interactions. (1990) J Am Chem Soc 112:5525–5534
6. Monk PMS (1998) The viologens: physicochemical properties, synthesis and applications of the salts of 4,4′-bipyridine. Wiley, New York
7. (a) Harada A, Li J, Kamachi M. The molecular necklace: a rotaxane containing many threaded α-cyclodextrins. (1992) Nature 356:325–327; (b) Fujita M, Ibukuro F, Hagihara H, Ogura K. Quantitative self-assembly of a [2]catenane from two preformed molecular rings. (1994) Nature 367:720–723
8. (a) Hunter CA. Synthesis and structure elucidation of a new [2]-catenane. (1992) J Am Chem Soc 114:5303–5311; (b) Kolchinski AG, Busch DH, Alcock NW. Gaining control over molecular threading: benefits of second coordination sites and aqueous–organic interfaces in rotaxane synthesis. (1995) J Chem Soc Chem Commun 1289–1291
9. (a) Hoffart DJ, Tiburcio J, de la Torre A, Knight LK, Loeb SJ. Cooperative ion–ion interactions in the formation of interpenetrated molecules. (2008) Angew Chem Int Ed 47:97–101; (2008) Angew Chem 120:103–107; (b) Lestini E, Nikitin K, Muller-Bunz H, Fitzmaurice D. Introducing negative charges into bis-p-phenylene crown ethers: a study of bipyridinium-based [2] pseudorotaxanes and [2]rotaxanes. (2008) Chem Eur J 14:1095–1106
10. (a) Beer PD, Sambrook MR, Curiel D. Anion-templated assembly of interpenetrated and interlocked structures. (2006) Chem Commun 2105–2117; (b) Vickers MS, Beer PD. Anion templated assembly of mechanically interlocked structures. (2007) Chem Soc Rev 36:211–225; (c) Mullen KM, Beer PD. Sulfate anion templation of macrocycles, capsules, interpenetrated and interlocked structures. (2009) Chem Soc Rev 38:1701–1713
11. Waals VD (1873) J. D. Ph. D Dissertation. Leiden
12. (a) Cram DJ, Tanner ME, Thomas R. The taming of cyclobutadiene. (1991) Angew Chem Int Ed 30:1024–1027; (b) Mal P, Breiner B, Rissanen K, Nitschke JR. White phosphorus is air-stable within a self-assembled tetrahedral capsule. (2009) Science 324:1697–1699
13. (a) Mock WL, Irra TA, Wepsiec JP, Manimaran TL. Cycloaddition induced by cucurbituril. a case of Pauling principle catalysis. (1983) J Org Chem 48:3619–3620; (b) Yoshizawa M, Tamura M, Fujita M. Diels-alder in aqueous molecular hosts: unusual regioselectivity and efficient catalysis. (2006) Science 312:251–254
14. (a) Schill G (1971) Catenanes, rotaxanes and knots. Academic, New York; (b) Amabilino DB, Stoddart JF. Interlocked and intertwined structures and superstructures. (1995) Chem Rev 95:2725–2828; (c) Dietrich-Buchecker JPSCO (1999) Molecular catenanes, rotaxanes and knots: a journey through the world of molecular topology. Wiley, New York
15. (a) French D. The schardinger dextrins. (1957) Adv Carbohydr Chem 12:189–280; (b) Szejtli J. Introduction and general overview of cyclodextrin chemistry. (1998) Chem Rev 98:1743–1753; (c) Freudenberg K, Cramer F, Die Konstitution der Schardinger-Dextrine α, β, und γ. Naturforsch Z (1948) B: Chem Sci 3:464–464
16. Sliwa W, Kozlowski C (1999) Calixarenes and resorcinarenes. Wiley-VCH, Weinheim

17. (a) Lagona J, Mukhopadhyay P, Chakrabarti S, Isaacs L. The cucurbit[*n*]uril family. (2005) Angew Chem Int Ed 44:4844–4870; (b) Behrend R, Meyer E, Rusche F. I. Ueber condensationsproducte aus glycoluril und formaldehyd. (1905) Liebigs Ann Chem 339:1–37
18. Ogoshi T, Kanai S, Fujinami S, Yamagishi TA, Nakamoto Y. *para*-Bridged symmetrical pillar [5]arenes: their lewis acid catalyzed synthesis and host–guest property. (2008) J Am Chem Soc 130:5022–5023
19. (a) Sauvage JP. From chemical topology to molecular machines (Nobel Lecture). (2017) Angew Chem Int Ed 56:11080–11093; (b) Stoddart JF. Mechanically interlocked molecules (MIMs)—molecular shuttles, switches, and machines (Nobel Lecture). (2017) Angew Chem Int Ed 56:11094–11125
20. Odell B, Reddington MV, Slawin AMZ, Spencer N, Stoddart JF, Williams DJ. Cyclobis(paraquat-*p*-phenylene). A tetracationic multipurpose receptor. (1988) Angew Chem Int Ed 27:1547–1550
21. Trabolsi A, Khashab N, Fahrenbach AC, Friedman DC, Colvin MT, Coti KK, Benitez D, Tkatchouk E, Olsen JC, Belowich ME, Carmielli R, Khatib HA, Goddard WA, Wasielewski MR, Stoddart JF. Radically enhanced molecular recognition. (2010) Nat Chem 2:42–49
22. Allwood BL, Spencer N, Shahriarizavareh H, Stoddart JF, Williams DJ. Complexation of paraquat by a bisparaphenylene-34-crown-10 derivative. (1987) J Chem Soc Chem Comm 1064–1066
23. Asakawa M, Dehaen W, Labbe G, Menzer S, Nouwen J, Raymo FM, Stoddart JF, Williams DJ. Improved template-directed synthesis of Cyclobis(paraquat-*p*-phenylene). (1996) J Org Chem 61:9591–9595
24. Sue CH, Basu S, Fahrenbach AC, Shveyd AK, Dey SK, Botros YY, Stoddart JF. Enabling tetracationic cyclophane production by trading templates. (2010) Chem Sci 1:119–125
25. Barnes JC, Juricek M, Vermeulen NA, Dale EJ, Stoddart JF. Synthesis of Ex^{n}Box cyclophanes. (2013) J Org Chem 78:11962–11969
26. Anelli PL, Ashton PR, Ballardini R, Balzani V, Delgado M, Gandolfi MT, Goodnow TT, Kaifer AE, Philp D, Pietraszkiewicz M, Prodi L, Reddington MV, Slawin AMZ, Spencer N, Stoddart JF, Vicent C, Williams DJ. Molecular meccano. 1. [2]rotaxanes and a [2]catenane made to order. (1992) J Am Chem Soc 114:193–218
27. (a) Cordova E, Bissell RA, Spencer N, Ashton PR, Stoddart JF, Kaifer AE. Novel rotaxanes based on the inclusion complexation of biphenyl guests by cyclobis(paraquat-*p*-phenylene). (1993) J Org Chem 58:6550–6552; (b) Cordova E, Bissell RA, Kaifer AE. Synthesis and electrochemical properties of redox-active [2]rotaxanes based on the inclusion complexation of 1,4-phenylenediamine and benzidine by cyclobis(paraquat-*p*-phenylene) (1995) J Org Chem 60:1033–1038
28. Ikeda T, Aprahamian I, Stoddart JF. Blue-colored donor−acceptor [2]rotaxane. (2007) Org Lett 9:1481–1484
29. Ballardini R, Balzani V, Credi A, Brown CL, Gillard RE, Montalti M, Philp D, Stoddart JF, Venturi M, White AJP, Williams BJ, Williams DJ. Controlling Ccatenations, properties and relative ring-component movements in catenanes with aromatic fluorine substituents. (1997) J Am Chem Soc 119:12503–12513
30. Castro R, Nixon KR, Evanseck JD, Kaifer AE. Effects of side arm length and structure of *para*-substituted phenyl derivatives on their binding to the host cyclobis(paraquat-*p*-phenylene). (1996) J Org Chem 61:7298–7303
31. Kosower EM, Cotter JL. Stable Free Radicals. II. The reduction of 1-methyl-4-cyanopyridinium ion to methylviologen cation radical. (1964) J Am Chem Soc 86:5524
32. Yoshizawa M, Kumazawa K, Fujita M. Room-temperature and solution-state observation of the mixed-valence cation radical dimer of tetrathiafulvalene, $[(TTF)_2]^{+\bullet}$, within a self-assembled cage. (2005) J Am Chem Soc 127:13456–13457
33. Wu YL, Frasconi M, Gardner DM, McGonigal PR, Schneebeli ST, Wasielewski MR, Stoddart JF. Electron delocalization in a rigid cofacial naphthalene-1,8:4,5-bis(dicarboximide) dimer. (2014) Angew Chem Int Ed 53:9476–9481; Angew Chem 2014, 126:9630–9635

34. Fahrenbach AC, Zhu ZX, Cao D, Liu WG, Li H, Dey SK, Basu S, Trabolsi A, Botros YY, Goddard WA, Stoddart JF. Radically enhanced molecular switches. (2012) J Am Chem Soc 134:16275–16288
35. Ashton PR, Goodnow TT, Kaifer AE, Reddington MV, Slawin AMZ, Spencer N, Stoddart JF, Vicent C, Williams DJ. A [2]catenane made to order. (1989) Angew Chem Int Ed 28:1396–1399
36. (a) Spruell JM, Paxton WF, Olsen JC, Benitez D, Tkatchouk E, Stern CL, Trabolsi A, Friedman DC, Goddard WA, Stoddart JF. A push-button molecular switch. (2009) J Am Chem Soc 131:11571–11580; (b) Fang L, Basu S, Sue CH, Fahrenbach AC, Stoddart JF. Syntheses and dynamics of donor−acceptor [2]catenanes in water. (2011) J Am Chem Soc 133:396–399
37. Miljanic OS, Dichtel WR, Mortezaei S, Stoddart JF. Cyclobis(paraquat-*p*-phenylene)-based [2]catenanes prepared by kinetically controlled reactions involving alkynes. (2006) Org Lett 8:4835–4838
38. Asakawa M, Brown CL, Menzer S, Raymo FM, Stoddart JF, Williams DJ. Structure−reactivity relationship in interlocked molecular compounds and in their supramolecular model complexes. (1997) J Am Chem Soc 119:2614–2627
39. Koshkakaryan G, Cao D, Klivansky LM, Teat SJ, Tran JL, Liu Y. Dual selectivity expressed in [2 + 2 + 1] dynamic clipping of unsymmetrical [2]catenanes. (2010) Org Lett 12:1528–1531
40. Li SJ, Liu M, Zheng B, Zhu KL, Wang F, Li N, Zhao XL, Huang FH. Taco complex templated syntheses of a cryptand/paraquat [2]rotaxane and a [2]catenane by olefin metathesis. (2009) Org Lett 11:3350–3353
41. Miljanic OS, Stoddart JF. Dynamic donor–acceptor [2]catenanes. (2007) Proc Natl Acad Sci U S A 104:12966–12970
42. Barnes JC, Fahrenbach AC, Cao D, Dyar SM, Frasconi M, Giesener MA, Benitez D, Tkatchouk E, Chernyashevskyy O, Shin WH, Li H, Sampath S, Stern CL, Sarjeant AA, Hartlieb KJ, Liu ZC, Carmieli R, Botros YY, Choi JW, Slawin AMZ, Ketterson JB, Wasielewski MR, Goddard WA, Stoddart JF. A radically configurable six-state compound. (2013) Science 339:429–433
43. (a) Zhao YL, Shveyd AK, Stoddart JF. Solid-state structures and superstructures of two charged donor–acceptor rotaxanes. (2011) Tetrahedron Lett 52:2044–2047; (b) Nygaard S, Laursen BW, Hansen TS, Bond AD, Flood AH, Jeppesen JO. Preparation of cyclobis(paraquat-*p*-phenylene)-based [2]rotaxanes without flexible glycol chains (2007) Angew Chem Int Ed 46:6093–6097; (2007) Angew Chem 119:6205–6209; (c) Anelli PL, Spencer N, Stoddart JF. A molecular shuttle. (1991) J Am Chem Soc 113:5131–5133; (d) Benniston AC, Harriman A, Lynch VM. Photoactive [2]rotaxanes: structure and photophysical properties of anthracene- and ferrocene-stoppered [2]rotaxanes. (1995) J Am Chem Soc 117:5275–5291; (e) Nygaard S, Leung KCF, Aprahamian I, Ikeda T, Saha S, Laursen BW, Kim SY, Hansen SW, Stein PC, Flood AH, Stoddart JF, Jeppesen JO. Functionally rigid bistable [2]rotaxanes. (2007) J Am Chem Soc 129:960–970; (f) Yoon I, Benitez D, Zhao YL, Miljanic OS, Kim SY, Tkatchouk E, Leung KCF, Khan SI, Goddard WA, Stoddart JF. Functionally rigid and degenerate molecular shuttles. (2009) Chem Eur J 15:1115–1122
44. Huisgen R, Szeimies G, Mobius L. 1.3-Dipolare cycloadditionen, XXXII. kinetik der additionen organischer azide an CC-mehrfachbindungen. (1967) Chem Ber-Recl 100:2494
45. Dichtel WR, Miljanic OS, Spruell JM, Heath JR, Stoddart JF. Efficient templated synthesis of donor−acceptor rotaxanes using click chemistry. (2006) J Am Chem Soc 128:10388–10390
46. Li H, Fahrenbach AC, Dey SK, Basu S, Trabolsi A, Zhu ZX, Botros YY, Stoddart JF. Mechanical bond formation by radical templation. (2010) Angew Chem Int Ed 49:8260–8265; Angew Chem 2010, 122:8436–8441
47. Li H, Zhu ZX, Fahrenbach AC, Savoie BM, Ke CF, Barnes JC, Lei JY, Zhao YL, Lilley LM, Marks TJ, Ratner MA, Stoddart JF. Mechanical bond-induced radical stabilization. (2013) J Am Chem Soc 135:456–467
48. Green JE, Choi JW, Boukai A, Bunimovich Y, Johnston-Halperin E, DeIonno E, Luo Y, Sheriff BA, Xu K, Shin YS, Tseng HR, Stoddart JF, Heath JR. A 160-kilobit molecular electronic memory patterned at 10^{11} bits per square centimetre. (2007) Nature 445:414–417

49. Huang TJ, Brough B, Ho CM, Liu Y, Flood AH, Bonvallet PA, Tseng HR, Stoddart JF, Baller M, Magonov S. A nanomechanical device based on linear molecular motors. (2004) Appl Phys Lett 85:5391–5393
50. Patel K, Angelos S, Dichtel WR, Coskun A, Yang YW, Zink JI, Stoddart JF. Enzyme-responsive snap-top covered silica nanocontainers. (2008) J Am Chem Soc 130:2382–2383
51. Bissell RA, Cordova E, Kaifer AE, Stoddart JF. A chemically and electrochemically switchable molecular shuttle. (1994) Nature 369:133–137
52. Andersen SS, Share AI, Poulsen BL, Korner M, Duedal T, Benson CR, Hansen SW, Jeppesen JO, Flood AH. Mechanistic evaluation of motion in redox-driven rotaxanes reveals longer linkers hasten forward escapes and hinder backward translations. (2014) J Am Chem Soc 136:6373–6384
53. Fahrenbach AC, Barnes JC, Li H, Benitez D, Basuray AN, Fang L, Sue CH, Barin G, Dey SK, Goddard WA, Stoddart JF. Measurement of the ground-state distributions in bistable mechanically interlocked molecules using slow scan rate cyclic voltammetry. (2011) Proc Natl Acad Sci U S A 108:20416–20421
54. Asakawa M, Ashton PR, Balzani V, Credi A, Hamers C, Mattersteig G, Montalti M, Shipway AN, Spencer N, Stoddart JF, Tolley MS, Venturi M, White AJP, Williams DJ. A chemically and electrochemically switchable [2]catenane incorporating a tetrathiafulvalene unit. (1998) Angew Chem Int Ed 37:333–337
55. Li H, Fahrenbach AC, Coskun A, Zhu ZX, Barin G, Zhao YL, Botros YY, Sauvage JP, Stoddart JF. A light-stimulated molecular switch driven by radical–radical interactions in water. (2011) Angew Chem Int Ed 50:6782–6788; Angew Chem 2011, 123:6914–6920
56. Li H, Cheng CY, McGonigal PR, Fahrenbach AC, Frasconi M, Liu WG, Zhu ZX, Zhao YL, Ke CF, Lei JY, Young RM, Dyar SM, Co DT, Yang YW, Botros YY, Goddard WA, Wasielewski MR, Astumian RD, Stoddart JF. Relative unidirectional translation in an artificial molecular assembly fueled by light. (2013) J Am Chem Soc 135:18609–18620
57. Asakawa M, Ashton PR, Menzer S, Raymo FM, Stoddart JF, White AJP, Williams DJ. Cyclobis (paraquat-4,4′-biphenylene)–an organic molecular square. (1996) Chem Eur J 2:877–893
58. Amabilino DB, Ashton PR, Brown CL, Cordova E, Godinez LA, Goodnow TT, Kaifer AE, Newton SP, Pietraszkiewicz M, Philp D, Raymo FM, Reder AS, Rutland MT, Slawin AMZ, Spencer N, Stoddart JF, Williams DJ. Molecular meccano. 2. self-assembly of [n]catenanes. (1995) J Am Chem Soc 117:1271–1293
59. Spruell JM, Coskun A, Friedman DC, Forgan RS, Sarjeant AA, Trabolsi A, Fahrenbach AC, Barin G, Paxton WF, Dey SK, Olson MA, Benitez D, Tkatchouk E, Colvin MT, Carmielli R, Caldwell ST, Rosair GM, Hewage SG, Duclairoir F, Seymour JL, Slawin AMZ, Goddard WA, Wasielewski MR, Cooke G, Stoddart JF. Highly stable tetrathiafulvalene radical dimers in [3]catenanes. (2010) Nat Chem 2:870–879
60. Lipke MC, Cheng T, Wu YL, Arslan H, Xiao H, Wasielewski MR, Goddard WA, Stoddart JF. Size-matched radical multivalency. (2017) J Am Chem Soc 139:3986–3998
61. Lipke MC, Wu YL, Roy I, Wang YP, Wasielewski MR, Stoddart JF. Shuttling Rates, Electronic states, and hysteresis in a ring-in-ring rotaxane. (2018) ACS Cent Sci 4:362–371
62. Cai K, Lipke MC, Liu ZC, Nelson J, Cheng T, Shi Y, Cheng CY, Shen DK, Han JM, Vemuri S, Feng YN, Stern CL, Goddard WA, Wasielewski MR, Stoddart JF. Molecular Russian dolls. (2018) Nat Commun 9:5275
63. Barnes JC, Juricek M, Strutt NL, Frasconi M, Sampath S, Giesener MA, McGrier PL, Bruns CJ, Stern CL, Sarjeant AA, Stoddart JF. ExBox: a polycyclic aromatic hydrocarbon scavenger. (2013) J Am Chem Soc 135:183–192
64. Juricek M, Barnes JC, Dale EJ, Liu WG, Strutt NL, Bruns CJ, Vermeulen NA, Ghooray KC, Sarjeant AA, Stern CL, Botros YY, Goddard WA, Stoddart JF. Ex^2Box: interdependent modes of binding in a two-nanometer-long synthetic receptor. (2013) J Am Chem Soc 135:12736–12746

65. Sun JL, Frasconi M, Liu ZC, Barnes JC, Wang YP, Chen DY, Stern CL, Stoddart JF. Formation of ring-in-ring complexes between crown ethers and rigid $TVBox^{8+}$. (2015) Chem Commun 51:1432–1435
66. Dale EJ, Vermeulen NA, Juricek M, Barnes JC, Young RM, Wasielewski MR, Stoddart JF. Supramolecular explorations: exhibiting the extent of extended cationic cyclophanes. (2016) Acc Chem Res 49:262–273
67. Barnes JC, Dale EJ, Prokofjevs A, Narayanan A, Gibbs-Hall IC, Juricek M, Stern CL, Sarjeant AA, Botros YY, Stupp SI, Stoddart JF. Semiconducting single crystals comprising segregated arrays of complexes of C_{60}. (2015) J Am Chem Soc 137:2392–2399
68. Dale EJ, Vermeulen NA, Thomas AA, Barnes JC, Juricek M, Blackburn AK, Strutt NL, Sarjeant AA, Stern CL, Denmark SE, Stoddart JF. ExCage. (2014) J Am Chem Soc 136:10669–10682
69. Hafezi N, Holcroft JM, Hartlieb KJ, Dale EJ, Vermeulen NA, Stern CL, Sarjeant AA, Stoddart JF. Modulating the binding of polycyclic aromatic hydrocarbons inside a hexacationic cage by anion–π interactions. (2015) Angew Chem Int Ed 54:456–461