Supramolecular assemblies built with host-stabilized charge-transfer interactions

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Host-stabilized charge-transfer (CT) interactions and supramolecular assemblies built with these interactions are described. A variety of supramolecular assemblies including polyrotaxanes, molecular necklaces, and rotaxane dendrimers were synthesized through the intramolecular or intermolecular host-stabilized CT complex formation using cucurbit[8]uril (CB[8]) and D–A molecules having both electron-donor and electron-acceptor units connected by various types of linkers. Applications, including the design and synthesis of redox-driven molecular machines such as molecular loop locks, development of redox-controllable vesicles and detection of biologically important molecules, are also described.

1. Introduction

The charge-transfer (CT) interactions or donor–acceptor interactions[1] between π-systems are an important class of non-covalent interactions and have been greatly exploited in the design and synthesis of self-organizing systems. In particular, the CT interactions between electron-deficient 4,4′-bipyridinium derivatives and electron-rich aromatics have been extensively used to build mechanically interlocked molecules such as rotaxanes and catenanes,[2] which later led to elegant studies of molecular machines and switches.[3] Electron-rich tetrathiafulvalene derivatives have also been incorporated into elaborate molecular systems acting as sensors or molecular switches by virtue of their ability to form CT complexes with a variety of π-electron acceptors.[4] The organization of alternating electron-rich and electron-deficient units has also been employed to create novel macromolecules with folded structures[5a–5c] and discotic liquid crystalline materials.[5d]

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Although formation of stable CT complexes in the pores of zeolites had been reported,[6] there was no report on stable CT complex formation in a molecular host until 2001, when we reported the first example of selective inclusion of an electron-donor and -acceptor pair in cucurbit[8]uril, driven by the strong CT interaction between the guests.[7] The host-stabilized CT complex formation is an interesting phenomenon in its own right but, more importantly, it offers new opportunities to construct supramolecular assemblies. Indeed, for the last several years, we and others reported a wide variety of supramolecular assemblies such as molecular necklaces, molecular loop locks, and redox controllable vesicles, based on this chemistry. This *feature article* focuses on supramolecular assemblies built with the host-stabilized CT interactions primarily based on our own work.

2. Host-stabilized charge-transfer interactions

2.1. Cucurbit[*n*]uril

The host family cucurbit[*n*]uril (CB[*n*], $n = 5$–10), comprising n glycoluril units,[8–10] have a hydrophobic cavity and two

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identical carbonyl-laced portals, which allow them to form stable inclusion complexes with a wide variety of guest molecules.[11] Going from CB[5] to CB[10], the ring size increases progressively while the height remains constant. The cavity diameter increases from 4.4 Å to 11.7 Å and the portal diameter from 2.4 Å to 10.0 Å.[9] Although they share common structural features, their varying cavity and portal sizes lead to remarkable molecular recognition properties different from each other.[11] For example, CB[6] forms stable 1 : 1 host–guest complexes with protonated α,ω-diaminoalkanes.[10] On the other hand, CB[7] forms stable 1 : 1 complexes with larger guest molecules such as adamantylamine as well as methyl viologen dication, which are not included in CB[6]. CB[8] (Fig. 1), which has a cavity comparable to that of γ-cyclodextrin, exhibits remarkable host–guest properties different from those of the smaller homologues, including the encapsulation of two aromatic guest molecules such as naphthalene derivatives inside the cavity to form a stable 1 : 2 host–guest complex.[10a,12] The cavity of CB[8] is large enough to encapsulate a macrocycle such as cyclen and cyclam to form a macrocycle within a macrocycle.[12a] The cavity of CB[8] has been used as a reaction chamber to mediate chemical reactions such as stereospecific [2 + 2] cycloadditions.[12b,12c] Furthermore, by encapsulation, the molecular host can stabilize otherwise unstable species. For example, methyl viologen cation radicals or tetrathiafulvalene cation radicals form stable π-dimers in the cavity of CB[8].[12d,12e] Most remarkably, CB[8] encapsulates two different guest molecules, an electron-deficient molecule and an electron-rich molecule, inside the cavity to form a stable 1 : 1 : 1 complex, which is driven by the markedly enhanced charge-transfer (CT) interaction between the guest pair inside the hydrophobic cavity of CB[8], as described in detail in the following section.

2.2. Cucurbit[8]uril-stabilized charge-transfer interactions

4,4′-Bipyridinium dications (also called viologens, $\mathbf{V}^{2+}$), well-known electron-deficient molecules, have been widely incorporated into many supramolecular systems.[2–4] The host–guest interaction between redox-active viologens and cyclodextrins has been extensively studied.[13] While methyl viologen ($\mathbf{MV}^{2+}$) shows little interaction with β- or γ-cyclodextrin,[13a] it readily

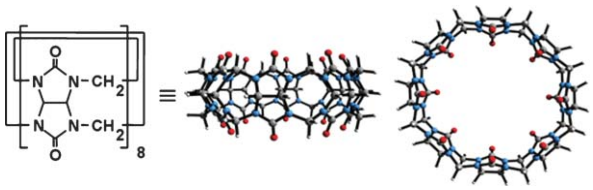
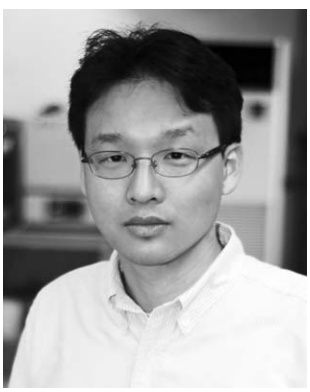


Fig. 1 Structural formula and X-ray crystal structure of CB[8]. Color codes: carbon: grey; nitrogen: blue; oxygen: red.

forms a 1 : 1 host–guest complex with CB[8] ($\mathbf{MV}^{2+}\subset$CB[8]) in water with a formation constant of 1.1×10^5 M^{-1}.[12d] Furthermore, addition of 1 equivalent of an electron-rich aromatic compound such as 2,6-dihydroxynaphthalene (**HN**) or 1,4-dihydroxybenzene (**HB**), to the 1 : 1 complex of $\mathbf{MV}^{2+}$ and CB[8] results in instantaneous and quantitative formation of an inclusion complex containing the electron-donor–acceptor pair ($\mathbf{MV}^{2+}\cdot\mathbf{HN}\subset$CB[8]).[7] Similarly, when added to the 1 : 1 complex of $\mathbf{MV}^{2+}$ and CB[8], a water-soluble tetrathiafulvalene (**TTF**) derivative[12e] forms a very stable CT complex with $\mathbf{MV}^{2+}$ inside the host.[14] *N*,*N*′-Dimethyldipyridyliumylethylene ($\mathbf{MPE}^{2+}$), which is a stronger electron-acceptor than $\mathbf{MV}^{2+}$, not only forms a 1 : 1 complex with CB[8] but also the resulting 1 : 1 complex has higher affinity toward electron-rich guest molecules ($K > \sim 10^4$ M^{-1}), resulting in a more stable ternary complex.[15]

Such ternary complexes are also formed exclusively when their components are mixed in a 1 : 1 : 1 ratio in aqueous solution (Scheme 1). It should be noted that electron-rich guest molecules themselves do not bind to CB[8] in the absence of an electron-acceptor. Therefore, the major driving force for the ternary complex formation appears to be strong CT interaction between an electron-donor and -acceptor pair inside the host cavity. The 1 : 1 : 1 ternary complexes exhibits a CT absorption band between 400 and 600 nm which is largely red-shifted ($\Delta\lambda \sim 100$ nm) with concomitant high increase in intensity compared to those of the corresponding CT complexes formed in the absence of CB[8]. Strong fluorescence quenching is also observed upon formation of the CT complexes inside CB[8]. The highly enhanced CT interaction between the two guests is probably due to their close contact within the cavity of CB[8], which has been confirmed by X-ray



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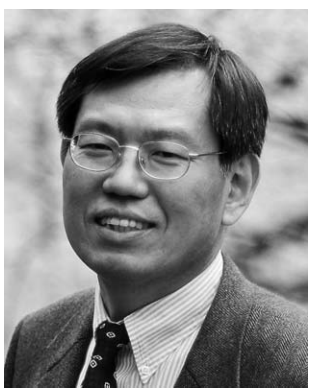

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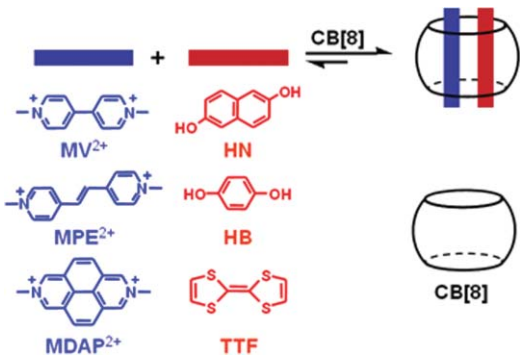


Scheme 1 Formation of a CT complex in CB[8].

crystallography (Fig. 2). The discovery of the host-stabilized CT complex formation prompted us to explore creation of elaborate supramolecular assemblies as well as recognition of biomolecules with aromatic residues based on this chemistry, as described below.

3. Supramolecular assemblies built with cucurbit[8]uril and a molecule containing both electron-donor and -acceptor units

In building novel supramolecular assemblies by exploiting the host-stabilized CT complex formation we decided to study the host–guest complex formation between CB[8] and a guest molecule (D–A molecule) having both electron-donor and electron-acceptor units connected by a suitable linker. We envisioned that several different types of supramolecular assemblies can be obtained by this process depending on the length and flexibility of the linker between the donor and acceptor units. A long and flexible linker would favor a 1 : 1 complex by the host-stabilized intramolecular CT interaction,[15] whereas a rigid and/or short linker would lead to a 2 : 2 complex or polymer (or poly(pseudorotaxane))[16] by host-stabilized intermolecular CT interactions. Finally, a rigid linker with a proper angle may lead to a cyclic oligomer, which is a molecular necklace in which a number of CB[8] beads are threaded on a large "ring" formed by intermolecular CT interactions (Scheme 2). Indeed, we observed all the above supramolecular assemblies as described below in detail.

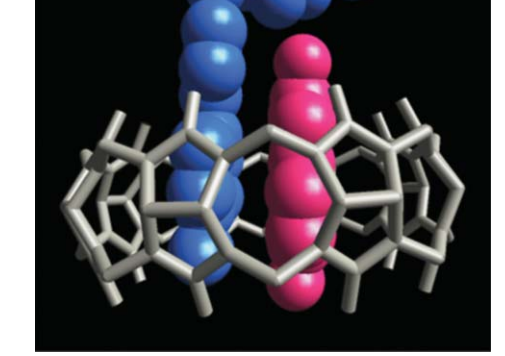
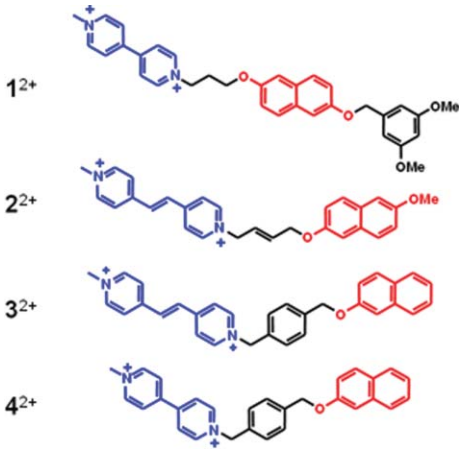


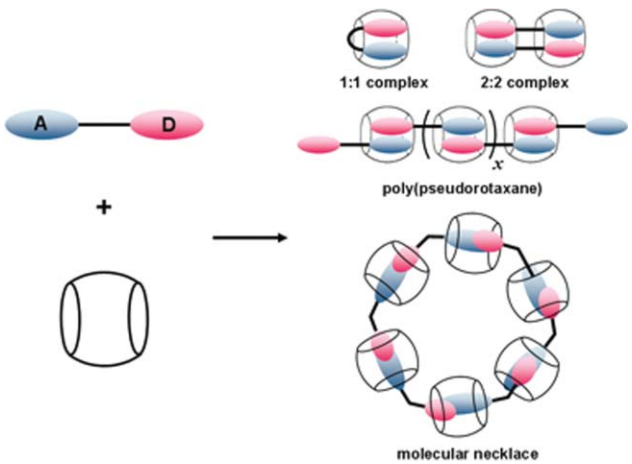
Fig. 2 X-Ray crystal structure of a CT complex stabilized inside CB[8].



In characterizing the resulting supramolecular assemblies we used various NMR techniques extensively, including COSY and ROESY, and mass spectrometry. In particular, the pulsed field gradient (PFG) NMR technique[17] turned out to be very useful to characterize them. It allows the measurement of the self-diffusion coefficient of a supramolecular species generated, from which we can estimate its size. Furthermore, in the case of multiple components, it provides an additional dimension to distinguish them by their mobility.[17]

3.1. Host-stabilized intramolecular charge-transfer complexes

A D–A molecule with a flexible linker can easily fold to bring its donor and acceptor units into close proximity, resulting in the formation of a stable intramolecular CT complex inside the CB[8] cavity. The D–A molecule $\mathbf{1}^{2+}$, in which electron-donor and acceptor units are linked by a four-atom bridge, forms a 1 : 1 complex ($\mathbf{5}^{2+}$) with CB[8] by intramolecular CT interaction.[15] When 1 equivalent of CB[8] is added to the guest $\mathbf{1}^{2+}$, the solution turns violet (λ_{max} = 566 nm), indicating the formation of a CT complex. The formation of 1 : 1 complex $\mathbf{5}^{2+}$ was further confirmed by NMR and mass



Scheme 2 Possible supramolecular assemblies built with CB[8] and D–A molecules containing both electron-donor and electron-acceptor units connected by a suitable linker.

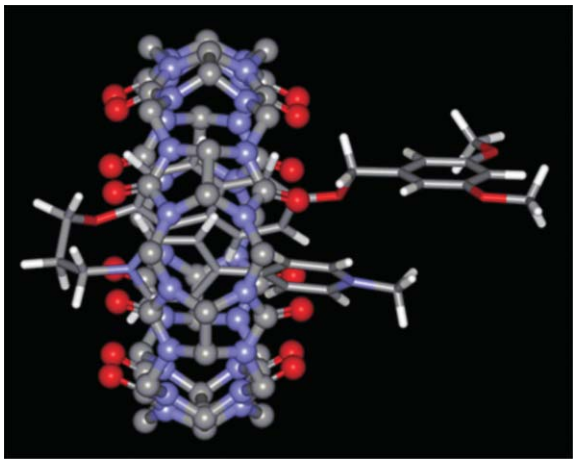


Fig. 3 Energy-minimized structure of 1 : 1 complex $\mathbf{5}^{2+}$. Color codes: oxygen: red; nitrogen: blue; carbon: grey; hydrogen: white.

spectroscopy. The size of $\mathbf{5}^{2+}$ estimated by the PFG NMR technique is 1.3 times larger than that of CB[8] itself. The energy-minimized structure of $\mathbf{5}^{2+}$ (Fig. 3) obtained by molecular modeling is consistent with the proposed structure.

To gain further insight into the nature of $\mathbf{5}^{2+}$, we investigated the interaction of $\mathbf{5}^{2+}$ with competing electron-donor and -acceptor molecules. When **HN** or $\mathbf{MV}^{2+}$ is added to $\mathbf{5}^{2+}$ in D_2O, no change in color or in ^{1}H NMR spectrum is observed. However, the addition of $\mathbf{MPE}^{2+}$, which is a stronger electron-acceptor than $\mathbf{MV}^{2+}$, results in complete conversion of $\mathbf{5}^{2+}$ to a ternary complex $\mathbf{6}^{4+}$, in which $\mathbf{MPE}^{2+}$ forms a CT complex with the naphthalene unit of $\mathbf{1}^{2+}$, inside CB[8], by replacing the bipyridinium unit of $\mathbf{1}^{2+}$ with $\mathbf{MPE}^{2+}$ (Fig. 4). This experiment demonstrates that the guest in the supramolecular system changes its conformation from a folded form to an extended form in response to an external chemical stimulus.

D–A molecule $\mathbf{2}^{2+}$, in which a but-2-enyloxy unit containing a double bond links its acceptor and donor units, also forms an intramolecular CT complex inside the cavity of CB[8] ($\mathbf{7}^{2+}$). We had first thought that the but-2-enyloxy linker would be rigid enough to prevent the intramolecular CT complex formation inside CB[8]. However, it turned out that $\mathbf{2}^{2+}$ folds back to form 1 : 1 complex $\mathbf{7}^{2+}$ whose structure is similar to

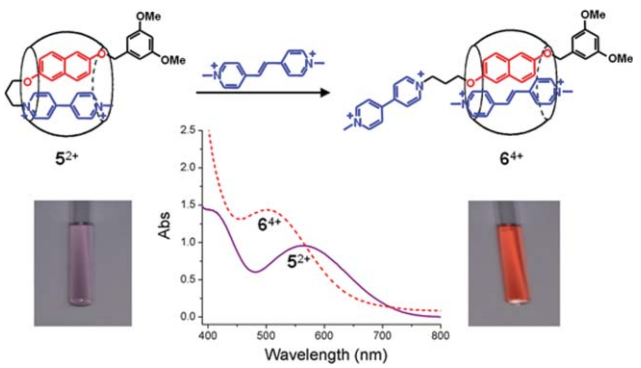


Fig. 4 Competitive host–guest interaction of 1 : 1 complex $\mathbf{5}^{2+}$ with electron-acceptor $\mathbf{MPE}^{2+}$ leading to ternary complex $\mathbf{6}^{4+}$, and associated changes in the CT band.

that of $\mathbf{5}^{2+}$, as evidenced by NMR and ESI-mass spectrometry.[18] In the structure of $\mathbf{7}^{2+}$, $\mathbf{2}^{2+}$ is folded in such a way that the inner pyridinium ring of the dipyridyliumylethylene unit interacts with the naphthalene unit inside the CB[8] cavity, as revealed by ^{1}H NMR spectroscopy. These host-stabilized intramolecular CT complexes provided an insight into designing molecular machines triggered by external stimuli, as described in Section 4.

3.2. Host-stabilized intermolecular CT complexes

The introduction of a rigid and/or short linker between the donor and the acceptor units leads to a 2 : 2 complex or polymer (or poly(pseudorotaxane)) by preventing the intramolecular CT complex formation inside CB[8].[16,18] Reaction of CB[8] with D–A molecule $\mathbf{3}^{2+}$, containing a rigid *p*-xylylene linker, resulted in quantitative formation of stable 2 : 2 complex $\mathbf{8}^{4+}$, which was characterized by PFG NMR as well as 2D NMR spectroscopy such as COSY and ROESY.[18] The hydrodynamic volume of $\mathbf{3}^{2+}$ is 3.1 times that of CB[8] itself, supporting the formation of the 2 : 2 complex, which was finally confirmed by ESI-mass spectrometry. The inclusion geometry of the energy-minimized structure of $\mathbf{8}^{4+}$ (Fig. 5) is consistent with the changes in chemical shifts of $\mathbf{3}^{2+}$ upon complex formation, and the intermolecular NOE between the protons of the two guests. The 2-naphthol unit of one guest interacts with the terminal pyridinium unit of the dipyridyliumylethylene of the other guest molecule inside the cavity of CB[8].

On the other hand, treatment of D–A molecule $\mathbf{4}^{2+}$, containing 4,4′-bipyridinium as an acceptor unit, with CB[8] produced a polymeric (oligomeric) species as well as a 2 : 2 complex. Upon addition of 1 equivalent of CB[8] to $\mathbf{4}^{2+}$ in H_2O the color of the solution changed from yellow to red with the appearance of a strong absorption band at ~482 nm, indicating formation of a CT complex. NMR spectroscopy, using COSY, NOESY and DOSY techniques, established that the complex between CB[8] and $\mathbf{4}^{2+}$ formed in aqueous solution (2 mM) is a mixture of a 2 : 2 complex and a

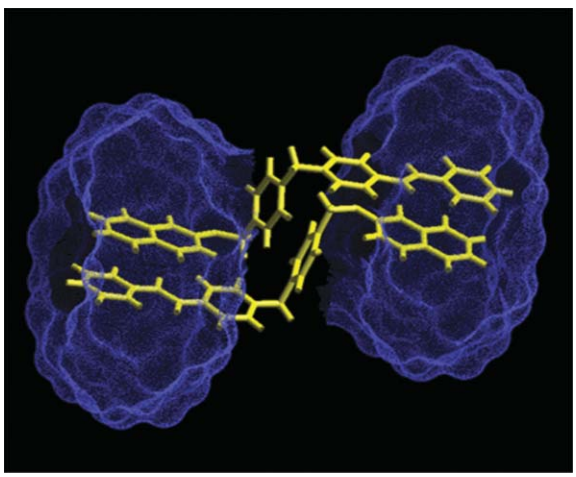


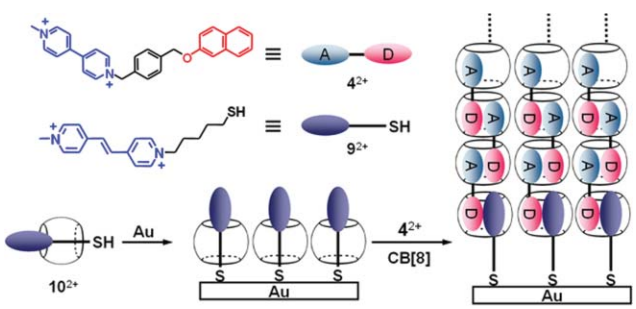
Fig. 5 Energy-minimized structure of a 2 : 2 complex of $\mathbf{3}^{2+}$ and CB[8]. CB[8] is represented by a Connolly surface and the guest by a stick model.

polymeric (oligomeric) species in a 3 : 2 ratio. The hydrodynamic volume of the polymeric species estimated by DOSY suggested a degree of polymerization of ~4. The failure to observe species with a higher degree of polymerization in solution was most likely due to their poor solubility.

Having established the existence of a polymeric species in solution, we decided to grow the poly(pseudorotaxane) on gold, which was carried out in two steps.[16] We first anchored pseudorotaxane $\mathbf{10}^{2+}$, comprising CB[8] threaded on $\mathbf{9}^{2+}$, which contains a dipyridyliumylethylene unit and a thiol terminal, on the surface. Using the immobilized pseudorotaxane as a "seed", a linear poly(pseudorotaxane) was then grown on the surface, utilizing the host-stabilized CT interaction as "glue" (Scheme 3). After a self-assembled monolayer (SAM) of $\mathbf{10}^{2+}$ on gold was formed by dipping a gold substrate in a solution containing $\mathbf{10}^{2+}$, a poly(pseudorotaxane) was grown by soaking the substrate in an aqueous solution containing CB[8] and $\mathbf{4}^{2+}$. The growth of the poly(pseudorotaxane) was monitored by reflectance FT-IR spectroscopy and the surface plasmon resonance (SPR) technique, which revealed that the growth of the poly(pseudorotaxane) on the surface can be reversibly controlled by the concentration of the monomer solution and the immersion time. The poly(pseudorotaxane) grown on gold by dipping the substrate in 1 mM monomer solution for a day has a degree of polymerization of ~4. The AFM image of the poly(pseudorotaxane) grown on gold showed large grains (Fig. 6) with a height increase of 3.9 nm, which was consistent with the IR and SPR results. This is a rare example of noncovalent polymers grown on a solid surface.

3.3. Designed self-assembly of molecular necklaces

We then extended this effort to build cyclic oligomers (molecular necklaces) *via* the host-stabilized intermolecular CT complex formation using a carefully designed D–A molecule.[19] D–A molecule $\mathbf{11}^{2+}$ contains a naphthalene unit and a dipyridyliumylethylene unit connected by a methylene bridge. The short, bent linker prevents the intramolecular CT complex formation inside CB[8] while setting a stage for the formation of a cyclic oligomer *via* the host-stabilized intermolecular CT complex formation. Since the angle between the electron-donor and -acceptor units of $\mathbf{11}^{2+}$ set by the methylene bridge is close to the vertex angle of an equilateral pentagon, we thought that five CB[8] molecules and five $\mathbf{11}^{2+}$ molecules would form a cyclic pentamer (molecular



Scheme 3 Growth of a poly(pseudorotaxane) on gold using the host-stabilized CT interaction.

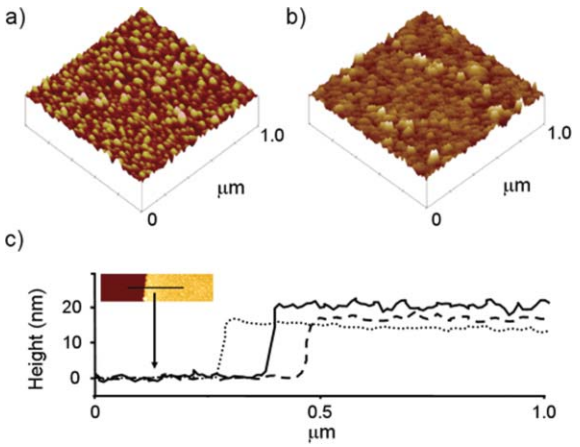
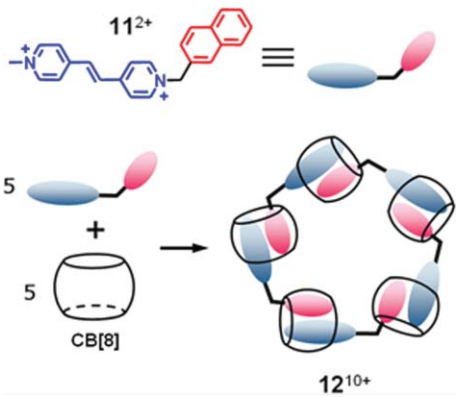


Fig. 6 AFM images of (a) bare gold surface and (b) the poly(pseudorotaxane) grown on gold by dipping in a 1 mM monomer solution. (c) The height profiles near a step edge of gold/Si(100) surface: bare gold (···), SAM of pseudorotaxane $\mathbf{10}^{2+}$ (---) on gold, and the poly(pseudorotaxane) grown on gold (—).

necklace [6]MN) as shown in Scheme 4. Indeed, the D–A molecule and CB[8] self-assembled into a molecular necklace [6]MN ($\mathbf{12}^{10+}$) quantitatively *via* the host-stabilized intermolecular CT interaction, which was characterized by NMR and mass spectrometry and X-ray crystallography. The NMR data hinted that the product is most likely a cyclic oligomer. The hydrodynamic volume of the complex measured by the PFG NMR technique is 8.7 times that of CB[8] itself. A molecular mechanical calculation[13] established that a cyclic pentameric structure ([6]MN) is the most stable one (Fig. 7), which was eventually confirmed by ESI-mass spectrometry and X-ray crystallography. In the structure, five molecules of $\mathbf{11}^{2+}$ form a cyclic framework by the intermolecular CT interaction, on which five CB[8] molecules are threaded with an arrangement reminiscent of a five-fold propeller. Despite some disorder in the cyclic framework, the X-ray crystal structure of $\mathbf{12}^{10+}$ closely matched the calculated structure shown in Fig. 7. The molecular necklace measures ~3.7 nm in diameter and ~1.8 nm in thickness. Other molecular necklaces with different sizes, shapes, and numbers of molecular beads may be synthesized by varying the length and angle of the linker of the guest molecule.



Scheme 4 Self-assembly of molecular necklace $\mathbf{12}^{10+}$ from five $\mathbf{11}^{2+}$ and five CB[8].

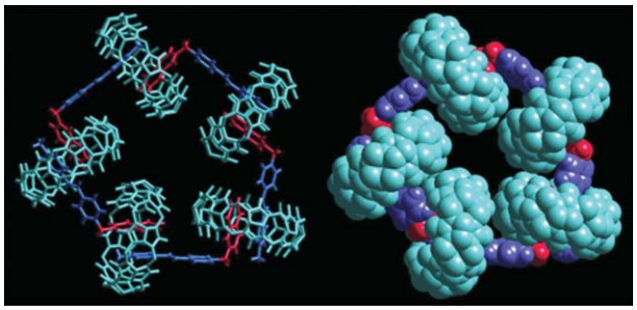
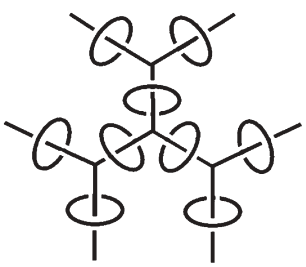


Fig. 7 Energy-minimized structure of molecular necklace $\mathbf{12}^{10+}$ shown in stick (left) and space-filling (right) models.

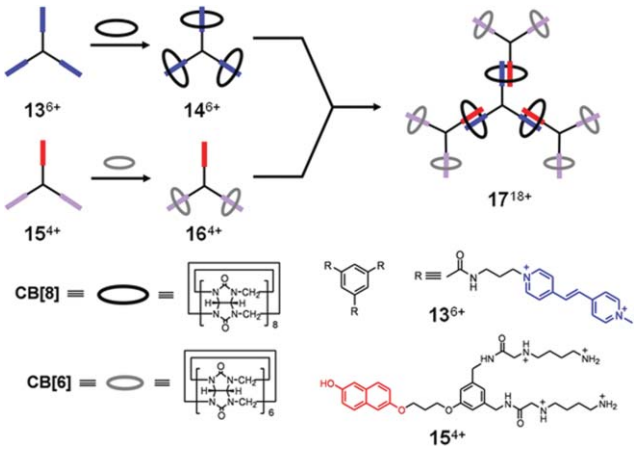
3.4. Noncovalent synthesis of rotaxane dendrimers

Rotaxane dendrimers are dendritic molecules containing rotaxane-like mechanical bonds to link their components. Combining many attractive features of conventional dendrimers with properties that result from the mechanical bonds, they are not only structurally appealing but also hold great promise for applications in many areas including materials science. Rotaxane dendrimers are classified into three types depending on where rotaxane-like moieties appeared—Type I, II, and III rotaxane dendrimers, which incorporate rotaxane-like features at the core, terminal and branches, respectively.[20] The synthesis of Type I and II rotaxane dendrimers is relatively straightforward, whereas that of well-defined Type III rotaxane dendrimers (Scheme 5), particularly second and higher generations, still remains challenging. Therefore, we decided to build high generation Type III rotaxane dendrimers using CB[*n*] as ring components.

As a part of this effort, we decided to synthesize a dendritic [10]pseudorotaxane, or a second generation Type III pseudorotaxane dendrimer, in which the ring components reside on the branches, by combining the remarkable host–guest behavior of CB[6] and CB[8].[21] As shown in Scheme 6, the strategy for the construction of a dendritic [10]pseudorotaxane using noncovalent interactions involves (1) threading a CB[8] bead onto each of three electron-deficient ''arms'' of a triply branched core to make a [4]pseudorotaxane, or G1 pseudorotaxane dendrimer, (2) at the same time synthesizing a triply branched wedge ligand containing one electron-donor ''arm'' and two amine ''arms'' on each of which a CB[6] bead is threaded, and (3) linking the first generation (G1) pseudorotaxane dendrimer with three of the wedge ligands *via* CB[8]-stabilized CT interactions to form a dendritic [10]pseudorotaxane, or G2 Type III pseudorotaxane dendrimer (Fig. 8). The triply branched core molecule $\mathbf{13}^{6+}$ contains a *trans*-1,2-bis(1-methyl-4-pyridinio)ethylene unit (as an acceptor) on each branch. Stirring a mixture of $\mathbf{13}^{6+}$ and three equivalents of CB[8] in water resulted in formation of stable [4]pseudorotaxanes ($\mathbf{14}^{6+}$), which may be considered as a G1 pseudorotaxane dendrimer. Stirring an aqueous solution containing $\mathbf{15}^{4+}$ and 2 equivalents of CB[6] yields the wedge ligand $\mathbf{16}^{4+}$ in which a CB[6] bead is threaded onto each of the protonated diaminobutane units. Finally, mixing $\mathbf{14}^{6+}$ with 3 equivalents of $\mathbf{16}^{4+}$ produced dendritic [10]pseudorotaxane (or G2 rotaxane dendrimer) $\mathbf{17}^{18+}$, which was characterized by UV-visible and NMR spectroscopy. The dendritic [10]pseudorotaxane was the first example of a G2 Type III-A (pseudo) rotaxane dendrimer in which 13 molecular components are held together by noncovalent interactions. Since the host-stabilized CT interaction is weakened by reduction of electron-acceptor units or oxidation of electron-donor units, the dendritic [10]pseudorotaxane is disassembled upon addition of redox stimuli.



Scheme 5 Type III rotaxane dendrimer (second generation).



Scheme 6 Synthetic scheme for [10]pseudorotaxane (G2 pseudorotaxane dendrimer) $\mathbf{17}^{18+}$.

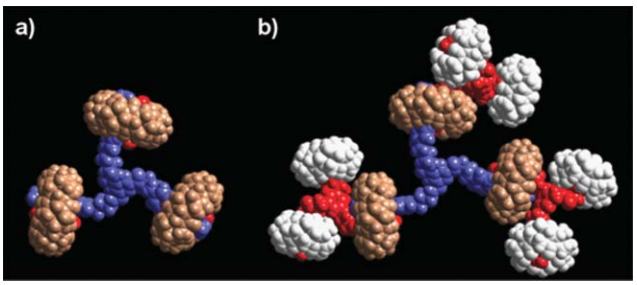


Fig. 8 Energy-minimized structures: (a) [4]pseudorotaxane $\mathbf{14}^{6+}$ (G1 pseudorotaxane dendrimer) and (b) [10]pseudorotaxane $\mathbf{17}^{18+}$ (G2 pseudorotaxane dendrimer). Color code: core: blue; wedge: red; CB[8]: light brown; CB[6]: white.

4. Molecular machines based on the CT complex formation inside CB[8]

The interplay between the redox and inclusion processes of host-stabilized CT complexes has been studied and exploited in designing molecular machines.

4.1. Interconversion of hetero- and homo-guest pair inclusion in CB[8]

One-electron reduction of $\mathbf{MV}^{2+}$ leads to cation radical $\mathbf{MV}^{+\bullet}$, which has moderate tendency to dimerize and therefore exists as a monomer and a dimer in equilibrium in aqueous solution. However, one-electron reduction of $\mathbf{MV}^{2+}$ in the presence of CB[8] results in the rapid generation of 2 : 1 inclusion complex $(\mathbf{MV}^{+\bullet})_2\subset$CB[8], comprising a dimer of the monocation radical $\mathbf{MV}^{+\bullet}$ encapsulated in CB[8]. The dimerization constant of $\mathbf{MV}^{+\bullet}$ in the presence of equimolar CB[8] is estimated to be $2 \times 10^7\ M^{-1}$, which is about 10^5 times larger than that of $\mathbf{MV}^{+\bullet}$ alone in aqueous media.[12d]

As described in section 2, $\mathbf{MV}^{2+}$ and **HN** form a stable CT complex inside the CB[8] cavity to form the stable 1 : 1 : 1 complex $(\mathbf{MV}^{2+}\cdot\mathbf{HN})\subset$CB[8]. However, treatment of a 1 : 1 mixture of $\mathbf{MV}^{2+}$ and the ternary complex with a reducing agent such as sodium dithionite ($Na_2S_2O_4$) resulted in near-quantitative formation of 2 : 1 inclusion complex $(\mathbf{MV}^{+\bullet})_2\subset$CB[8],[12d] and free **HN** (Scheme 7). This guest exchange is completely reversible since electrochemical oxidation reinstates the hetero-guest pair inclusion complex and $\mathbf{MV}^{2+}$.[22] This result demonstrated the reversible conversion of hetero- and homo-guest pair inclusion inside CB[8] triggered by a redox stimulus. The redox-coupled guest exchange process was also investigated by cyclic voltammetry and spectroelectrochemistry, which suggested that the reduction of $(\mathbf{MV}^{2+}\cdot\mathbf{HN})\subset$CB[8] initially generates the one-electron reduced species containing $\mathbf{MV}^{+\bullet}$ and **HN** encapsulated in CB[8], which then reacts with free $\mathbf{MV}^{+\bullet}$ to undergo the rapid guest exchange leading to $(\mathbf{MV}^{+\bullet})_2\subset$CB[8] and free **HN**.

As described in Section 2, **TTF** derivatives readily form a stable CT complex with $\mathbf{MV}^{2+}$ inside CB[8] ($(\mathbf{MV}^{2+}\cdot\mathbf{TTF})\subset$CB[8]) in aqueous solution. Recently, we also reported the first stable π-dimer of **TTF** cation radical encapsulated in the cavity of CB[8] ($(\mathbf{TTF}^{+\bullet})_2\subset$CB[8]), which has been isolated at room temperature and fully characterized.[12e] Furthermore, the ternary complex $(\mathbf{MV}^{2+}\cdot\mathbf{TTF})\subset$CB[8] is reversibly converted to $(\mathbf{MV}^{+\bullet})_2\subset$CB[8] + 2**TTF** or $(\mathbf{TTF}^{+\bullet})_2\subset$CB[8] + $2\mathbf{MV}^{2+}$ upon reduction or oxidation, respectively.[14] The interconversion of hetero- and homo-guest pair inclusion in CB[8] provided an operating principle of molecular machines triggered by redox stimuli as described below.

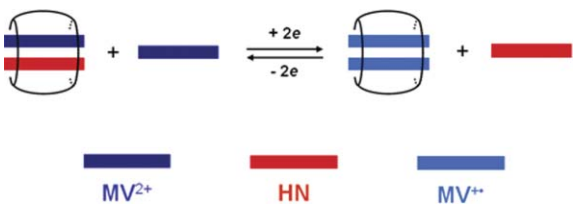
4.2. Molecular loop-lock: a redox-driven molecular machine

The discovery of the redox-coupled guest-exchange process prompted us to design and synthesize a redox-driven molecular machine behaving as a molecular loop lock that can be "locked" and "unlocked" with a key and a redox stimulus (Scheme 8).[22] The D–A molecule $\mathbf{18}^{3+}$ contains a naphthalene-2-yloxy (**Np**) unit and a viologen ($\mathbf{V}^{2+}$) unit linked to each other by a flexible tether, along with a bulky cationic "stopper" unit. Treatment of $\mathbf{18}^{3+}$ with 1 equivalent of CB[8] in aqueous solution resulted in exclusive formation of the stable 1 : 1 complex $\mathbf{19}^{3+}$ through the intramolecular CT complex formation between the **Np** and $\mathbf{V}^{2+}$ units inside CB[8] with the formation of a molecular loop[15] with a "closed" or "folded" conformation (Scheme 8). The NMR spectrum of $\mathbf{19}^{3+}$ is not affected by addition of 1 equivalent of $\mathbf{MV}^{2+}$, indicating that the 1 : 1 host–guest complex formed by the intramolecular CT interaction is much more stable than the ternary complex formed by the intermolecular CT interaction between the **Np** unit of $\mathbf{18}^{3+}$ and $\mathbf{MV}^{2+}$ inside CB[8].

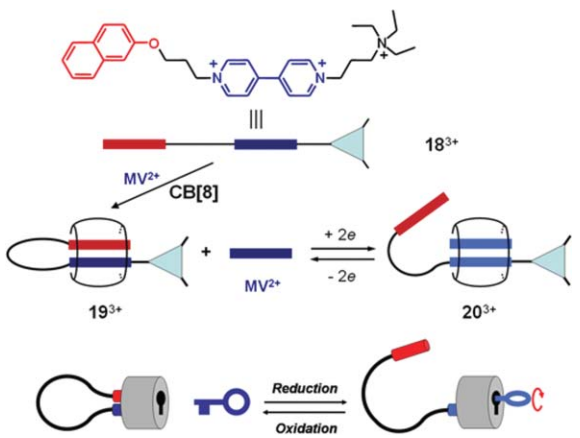
However, electrochemical reduction of the solution containing $\mathbf{19}^{3+}$ and 1 equivalent of $\mathbf{MV}^{2+}$ resulted in formation of the ternary complex $\mathbf{20}^{3+}$ (Scheme 8) in which the one-electron reduced viologen unit of $\mathbf{18}^{2+\bullet}$ interacts with $\mathbf{MV}^{+\bullet}$ inside CB[8] as confirmed by UV-visible spectroscopy. NMR spectroscopy also revealed that the **Np** unit is now located outside CB[8], which means that $\mathbf{20}^{3+}$ has an "open" or "unfolded" conformation. Introduction of O_2 into the solution of $\mathbf{20}^{3+}$ regenerates $\mathbf{19}^{3+}$ and $\mathbf{MV}^{2+}$. Taken together, $\mathbf{19}^{3+}$ with a "closed" conformation is converted to $\mathbf{20}^{3+}$ with an "open" conformation upon reduction in the presence of $\mathbf{MV}^{2+}$, and the process can be reversed by oxidation. This system thus behaves as a molecular loop lock that can be "locked" and "unlocked" with a key and a redox stimulus (Scheme 8), where $\mathbf{19}^{3+}$ and $\mathbf{20}^{3+}$ represent the locked and unlocked states, respectively, and $\mathbf{MV}^{2+}$ plays the role of the key which is activated by reduction. One may regard it as a "safeguarded" lock since it requires not only a key but also an activation process to open.

4.3. Molecular loop-lock with a built-in key

A molecular loop lock with a built-in key was also designed and synthesized (Scheme 9).[23] The D–A molecule $\mathbf{21}^{4+}$ contains a naphthalene unit and a viologen unit linked to each other by a rigid phenanthroline unit. In addition, another



Scheme 7 Interconversion of hetero- and homo-guest pair inclusion in CB[8] triggered by a redox stimulus.



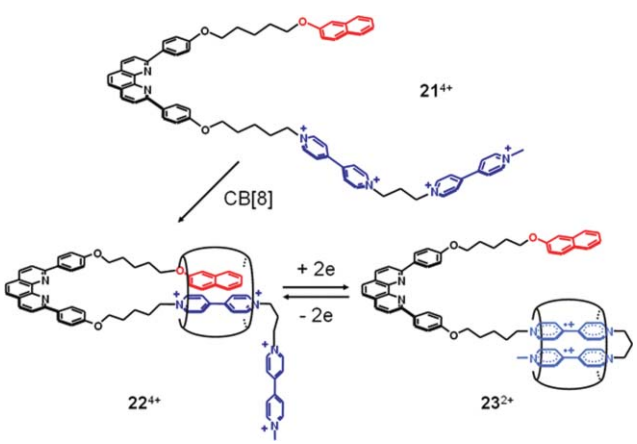
Scheme 8 Formation of molecular loop lock $\mathbf{19}^{3+}$ (locked state) and redox-induced formation of ternary complex $\mathbf{20}^{3+}$ (unlocked state) along with an illustration of the working mode of a molecular loop lock with a key.

viologen unit, which behaves as a key, is linked to the above-mentioned viologen unit by a flexible tether. Treatment of $\mathbf{21}^{4+}$ with 1 equivalent of CB[8] results in formation of the stable 1 : 1 complex $\mathbf{22}^{4+}$, with a folded conformation, through the intramolecular CT interaction between the naphthalene and viologen units insides the host (''closed'' or ''locked'' state). The ''locked'' and ''unlocked'' states of the molecular loop lock with a built-in key can be controlled by a redox stimulus. Two-electron reduction of $\mathbf{22}^{4+}$ results in formation of $\mathbf{23}^{2+}$, with intramolecular pairing of the viologen cation radical units inside CB[8], leaving the naphthalene unit outside CB[8] (''open'' or ''unlocked'' state). This process is reversible; upon oxidation, $\mathbf{22}^{4+}$, with a ''locked'' conformation, is regenerated.

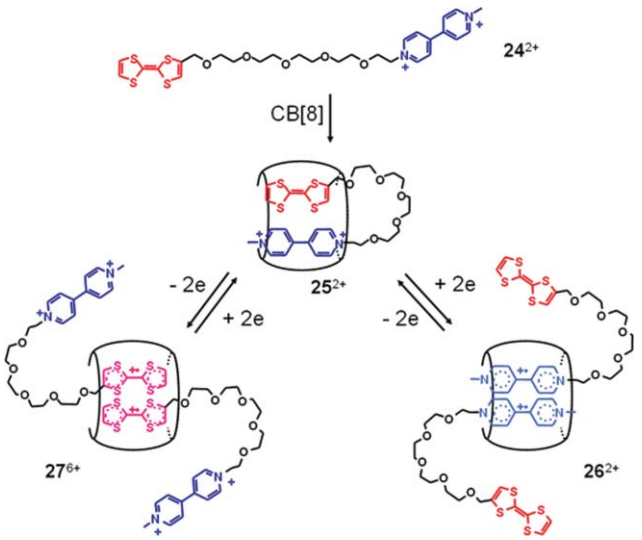
4.4. Molecular machines based on TTF and viologen

As described in Section 4.1, electron-deficient $\mathbf{MV}^{2+}$ and electron-rich **TTF** derivatives form a stable CT complex inside CB[8], which undergoes a guest exchange reaction upon reduction or oxidation. Based on this observation, a molecular machine working in response to reduction as well as oxidation was designed. The D–A molecule $\mathbf{24}^{2+}$ contains **TTF** and viologen ($\mathbf{V}^{2+}$) units connected by the penta(ethylene glycol) chain.[14]

When 1 equivalent of CB[8] is added to $\mathbf{24}^{2+}$, the $\mathbf{V}^{2+}$ and **TTF** units of $\mathbf{24}^{2+}$ form a stable intramolecular CT complex inside CB[8] as expected. Reduction or oxidation of the 1 : 1 complex $\mathbf{25}^{2+}$ generates a radical cation of the viologen unit or **TTF** unit, respectively, which then rapidly dimerize to form an intermolecular 2 : 1 inclusion complex, (**24**-$\mathbf{V}^{+\bullet}$)$_2$⊂CB[8] ($\mathbf{26}^{2+}$) or (**24**-$\mathbf{TTF}^{+\bullet}$)$_2$⊂CB[8] ($\mathbf{27}^{6+}$), respectively, with a conformational change from a folded form to an extended form (Scheme 10). For example, treatment of $\mathbf{25}^{2+}$ with $Fe(ClO_4)_3$ in aqueous solution results in formation of the ternary complex $\mathbf{27}^{6+}$, in which the **TTF** radical cation units of two D–A molecules form a dimer inside CB[8] as confirmed by the appearance of the new absorption bands characteristic of a CB[8]-stabilized **TTF** radical cation dimer. Similarly, reduction of $\mathbf{25}^{2+}$ with sodium dithionite ($Na_2S_2O_4$) produces the 2 : 1 inclusion complex $\mathbf{26}^{2+}$.



Scheme 9 A redox-driven molecular loop lock with a built-in key.



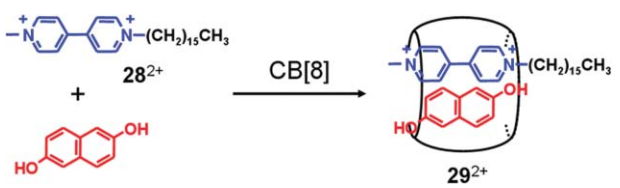
Scheme 10 Formation of intramolecular CT complex $\mathbf{25}^{2+}$ (folded) inside CB[8], and its conversion to intermolecular 2 : 1 inclusion complex (**24**-$\mathbf{MV}^{+\bullet}$)$_2$·CB[8] $\mathbf{26}^{2+}$ or (**24**-$\mathbf{TTF}^{+\bullet}$)$_2$·CB[8] $\mathbf{27}^{6+}$ upon reduction or oxidation, respectively.

5. Other applications of the host-stabilized CT interactions

The host-stabilized CT complex formation not only provided an operating principle of molecular machines, but also found other applications such as the development of smart materials and detection of biologically important molecules.

5.1. Hierarchical self-assembly of vesicles triggered by CT complex formation in a host

We recently demonstrated the hierarchical self-assembly of giant vesicles triggered by the formation of a CT complex inside CB[8].[24] When a long alkyl tail is tethered to viologen, the viologen part of the guest forms a stable CT complex with an electron-donor molecule such as **HN** inside the CB[8] cavity, leaving the alkyl tail extended into the solution (Scheme 11). For example, sonication of an equimolar mixture of CB[8], a viologen with a long alkyl chain ($\mathbf{28}^{2+}$), and **HN** in water produces a violet turbid solution with a broad absorption band centered at ~550 nm, indicating the formation of a CT complex inside CB[8] ($\mathbf{29}^{2+}$), which was further confirmed by NMR and mass spectrometry. The SEM images of the complex $\mathbf{29}^{2+}$ show relatively large spherical objects with diameters of 0.02–1.2 μm, which turned out to be vesicles (Fig. 9). The vesicles are exceptionally robust as they maintain the spherical shape even under the SEM experiment conditions. Their hollow structures were confirmed



Scheme 11 Formation of a stable ternary complex $\mathbf{29}^{2+}$.

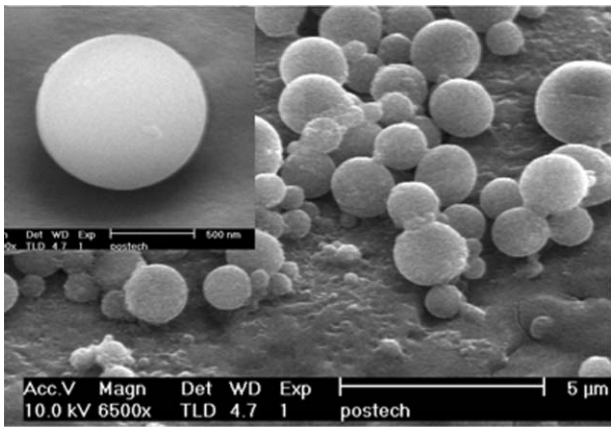


Fig. 9 SEM image of the vesicle formed with a CB[8]-stabilized CT complex.

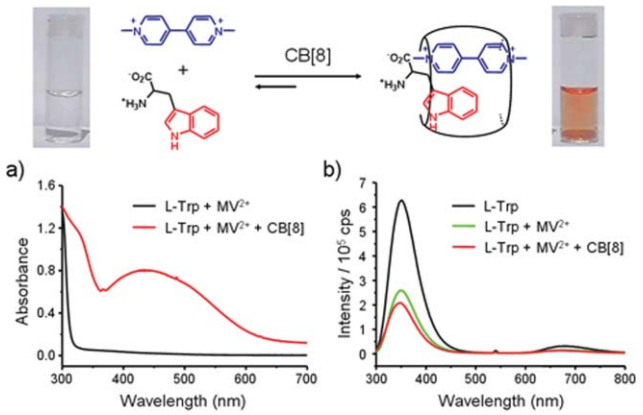


Fig. 10 Formation of a charge-transfer complex between $\mathbf{MV}^{2+}$ and tryptophan in CB[8]. (a) UV-visible spectra of tryptophan in the presence of $\mathbf{MV}^{2+}$ (black) or $\mathbf{MV}^{2+}\subset$CB[8] (red). (b) Fluorescence emission spectra of tryptophan unbound (black) and in the presence of $\mathbf{MV}^{2+}$ (green) or $\mathbf{MV}^{2+}\subset$CB[8] (red).

by high-resolution TEM. Encapsulation of a fluorescent dye within the interior of the vesicles, which can be visualized by confocal microscopy, provides another evidence for the vesicle formation. Although the exact mechanism of the hierarchical self-assembly is not clear, the first step involves the formation of a ternary complex $\mathbf{29}^{2+}$ from the viologen derivative with a tail, **HN** and CB[8], which behaves as a supramolecular amphiphile with a large polar head group and a hydrophobic tail, which in turn self-assembles into a large vesicle. Since the ternary complex is stabilized by CT interaction of an electron-donor–acceptor pair inside the host, redox chemistry can be used to trigger the collapse of the vesicles. Addition of cerium(IV) ammonium nitrate oxidizes **HN** to the quinone, which disrupts the CT complex and results in the collapse of the vesicles, which was confirmed by SEM. This supramolecular, redox-controllable vesicle system may find useful applications in many areas including development of smart materials and drug delivery.

5.2. Recognition of biologically important molecules using the host-stabilized CT interactions

The design of artificial receptors capable of recognizing biologically important molecules in aqueous solution is an important problem in the chemical and biomedical sciences.[25] The unique phenomenon of the CT complex formation inside CB[8] can be utilized for the detection of biologically important molecules containing aromatic side chains.[26,27] We have shown that small biomolecules with aromatic residues form stable ternary complexes with an electron-acceptor molecule and CB[8] that are easily recognized by the pronounced color development as well as fluorescence quenching owing to the CT interaction.[7,26] Aromatic amino acids, tyrosine and tryptophan, and dopamine form stable CT complexes ($K = \sim 10^3$–10^5 M^{-1}) with $\mathbf{MV}^{2+}$ inside CB[8], as indicated by color, UV-visible, emission and ^{1}H NMR spectral changes (Fig. 10).[26a,26b] The 1 : 1 inclusion complex $\mathbf{MPE}^{2+}\subset$CB[8] binds the biomolecules more tightly than $\mathbf{MV}^{2+}\subset$CB[8]. For example, the binding affinity of the former ($K_a = 2.9 \times 10^5$ M^{-1}) to tryptophan is around 6 times higher than that of the latter ($K_a = 5.1 \times 10^4$ M^{-1}), as measured by isothermal titration calorimetry (ITC) in aqueous solution.[26c]

Similarly, stable complex formation with neurotransmitters such as epinephrine and serotonin was also observed.[26c]

Recently, the potential of $\mathbf{MV}^{2+}\subset$CB[8] to recognize specific amino acids and peptides was further examined by Urbach *et al.*[27a] The binding affinities of $\mathbf{MV}^{2+}\subset$CB[8] to the natural aromatic amino acids were measured using ITC in a pH 7.0 buffer, which showed that $\mathbf{MV}^{2+}\subset$CB[8] binds tryptophan ($K_a = 4.3 \times 10^4$ M^{-1}) selectively over phenylalanine and tyrosine with 8-fold and 19-fold specificity, respectively. No binding was observed for histidine. They also tested the recognition of specific tripeptides by $\mathbf{MV}^{2+}\subset$CB[8], which showed that $\mathbf{MV}^{2+}\subset$CB[8] binds to N-terminal tryptophan residues with higher binding affinity than C-terminal or internal tryptophan residues: it binds Trp–Gly–Gly ($K_a = 1.3 \times 10^5$ M^{-1}) with 6-fold and 40-fold specificity over Gly–Trp–Gly, and Gly–Gly–Trp, respectively. They suggested that peptide recognition is mediated by the electrostatic charge(s) proximal to the indole. The complex formation is accompanied by the growth of a visible CT band and quenching of indole fluorescence. These optical properties, combined with the stability and selectivity of this system, make this system potentially useful in sensing and separating specific peptides.

Kaifer *et al.* reported the recognition of neurotransmitters such as dopamine using the host-stabilized CT interaction.[27b] The 1 : 1 inclusion complex $\mathbf{MDAP}^{2+}\subset$CB[8] ($\mathbf{MDAP}^{2+}$ = 2,7-dimethyldiazapyrenium; Scheme 1) was used as a "fluorescent host" to bind substrates with aromatic residues. The presence of CB[8] markedly increased the sensitivity of the $\mathbf{MDAP}^{2+}$ probe for the detection of catechol and dopamine. Increased fluorescence quenching in the presence of the host may be explained by static quenching due to the short lifetime of the excited state of the diazapyrenium dication and the close proximity to the π-donor inside the hydrophobic cavity of CB[8]. To explore further the sensing ability of the $\mathbf{MDAP}^{2+}\subset$CB[8] inclusion complex, they fabricated a fluorescent sensor by anchoring a $\mathbf{DAP}^{2+}$ derivative on the surface of silica nanoparticles and investigated the response of the fluorescent nanoparticles to dopamine and catechol in the presence and absence of CB[8]. Resembling the results

obtained in solution, the observed level of fluorescence quenching was considerably more pronounced when CB[8] was present. Thus, this supramolecular host system may be useful for sensitive fluorescence detection of catecholamines and related neurotransmitters.

6. Summary and outlook

In this *feature article* we described the host-stabilized CT interactions and supramolecular assemblies built with these interactions. Particularly, the CB[8]-stabilized CT complexes are thermodynamically stable, but can be readily disassembled into their components when treated with redox stimuli. The high thermodynamic stability of the CB[8]-stabilized CT interactions allowed us to build various supramolecular assemblies ranging from molecular necklaces to vesicles. Furthermore, the reversibility of the CT complex formation inside CB[8] led us to design redox-driven molecular machines such as molecular loop locks based on this chemistry. It has also been demonstrated that the host-stabilized CT interactions are useful in the detection of biologically interesting molecules containing aromatic residues. Very recently, Mori *et al.* reported that, upon formation of an intramolecular CT complex inside the CB[8] cavity, a chiral D–A molecule greatly enhances the anisotropy factor due to the confinement of the guest in the host,[28] which suggests that the host-stabilized CT interactions may be useful in chiral recognition as well.

Using carefully designed components one may be able to design and create other elaborate supramolecular assemblies in the solid state, on surfaces as well as in solution, based on the CB[8]-stabilized CT interactions. For example, sophisticated molecular machines with unidirectional rotatory motion, and/or working on surfaces may be developed. The work described here can be extended further using other host systems such CB[10][10c] and coordination nanocages[29] that can accommodate two (or more) π-conjugated molecules to form a stable CT complex. In fact, Fujita *et al.* recently reported stacking of two or more large π-conjugated molecules within organic-pillared coordination cages, stabilized by CT interactions.[30] The use of CB[10] with a large cavity and functionalized CB[8] with tailored properties[31] may provide a new dimension to the chemistry of the host-stabilized CT interactions.

The application perspectives of supramolecular assemblies based on host-stabilized CT interactions are great. For example, the polyrotaxanes built with the host-stabilized CT interactions may display interesting electrical and optical properties. The redox-controllable vesicles may find useful applications in the development of smart materials and drug delivery. The studies of the molecular machines may lead to the development of new sensors and actuators. Practical sensors detecting biogenic molecules such as neurotransmitters may be developed. With these exciting developments and perspectives, the future of the chemistry of the host-stabilized CT interactions looks bright.

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