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# Cucurbituril-Modulated Supramolecular Assemblies: From Cyclic Oligomers to Linear Polymers

Hai Qian, Dong-Sheng Guo, and Yu Liu*[a]

**Abstract:** Employing bis(*p*-sulfonatocalix[4]arenes) (bisSC4A) and *N*′,*N*″-hexamethylenebis(1-methyl-4,4′-bipyridinium) ($HBV^{4+}$) as monomer building blocks, the assembly morphologies can be modulated by cucurbit[*n*]uril (CB[*n*]) (*n* = 7, 8), achieving the interesting topological conversion from cyclic oligomers to linear polymers. The binary supramolecular assembly fabricated by $HBV^{4+}$ and bisSC4A units, forms an oligomeric structure, which was characterized by NMR spectroscopy, atomic force microscopy (AFM), transmission electron microscopy (TEM), dynamic light scattering (DLS), isothermal titration calorimetry (ITC), and gel permeation chromatography (GPC) experiments. The ternary supramolecular polymer participated by CB[8] is constructed on the basis of host–guest interactions by bisSC4A and the [2]pseudorotaxane $HBV^{4+}$@CB[8], which is characterized by means of AFM, DLS, NMR spectroscopy, thermogravimetric analysis (TGA), UV/Vis spectroscopy, and elemental analysis. CB[*n*] plays vital roles in rigidifying the conformation of $HBV^{4+}$, and reinforcing the host–guest inclusion of bisSC4A with $HBV^{4+}$, which prompts the formation of a linear polymer. Moreover, the CB[8]-participated ternary assembly could disassemble into the molecular loop $HBV^{2+}$@CB[8] and free bisSC4A after reduction of $HBV^{4+}$ to $HBV^{2+}$, whereas the CB[7]-based assembly remained unchanged after the reduction. CB[8] not only controlled the topological conversion of the supramolecular assemblies, but also improved the redox-responsive assembly/disassembly property practically.

**Keywords:** calixarenes · cucurbiturils · redox response · supramolecular chemistry · polymers

## Introduction

Supramolecular polymers, defined as polymeric arrays of monomer units brought together by noncovalent interactions, coalesce the advantages of both polymer science and supramolecular chemistry.[1] Comparing with the covalent polymerization and/or cross-linking, the noncovalent route has been demonstrated as a promising approach towards novel smart design principle for responsive materials capable of self-repairing and self-healing.[2] In this context, it emerges to be a significantly interesting topic to construct supramolecular polymers with different topologies, and endow them with responsive capability to external stimuli.[3]

Host–guest interactions are an alternative, robust candidate for supramolecular polymerization among the family of noncovalent forces, ascribing to their diverse binding selectivity.[4] It is also well known that macrocyclic hosts always show distinguishable inclusion affinities to different substrates, even to homologues and isomers.[5] Among these macrocyclic compounds, crown ethers and cyclodextrins (CDs) have been extensively studied to build various supramolecular polymers.[6] In early 1999, Reinhoudt and co-workers reported molecular threads composed of interconnective, linear host–guest complexation of β-CD-calix[4]arene couples.[7] Recently, Harada and co-workers described supramolecular fibrils based on host–guest interactions of modified CDs, which could disassemble by adding competitive guests or hosts.[8] The same group prepared a stilbene-bridged bis(β-CD) dimer and firstly achieved the conformational change from pinching-type dimer to supramolecular polymer triggered by photoirradiation.[9] Thus, it can be seen that host–guest-directed supramolecular polymers can be not only smoothly switched between assembly and disassembly, but also tuned to topological conversion by adjusting their binding affinities and/or geometries.

Calixarenes,[10] composed of phenolic units linked by methylene groups, represent the third generation of supramolecular host molecules. It remains an immature project to construct supramolecular polymers based on calixarenes, compared to construct cyclodextrin-based supramolecular polymers. Only a few examples have been occasionally reported,[11] where the cavities of calixarenes were not sufficiently exploited.[12] Haino and co-workers reported supramolecular polymeric nano networks based on strong binding between ditopic calix[5]arene and dumbbell $C_{60}$.[13] Parisi and co-workers outlined a general strategy for constructing noncovalent assemblies from modular calix[5]arenes with iterative inclusion of alkylammonium components.[14] In our

[a] H. Qian, Dr. D.-S. Guo, Prof. Dr. Y. Liu
Department of Chemistry
State Key Laboratory of Elemento-Organic Chemistry
Nankai University, Tianjin, 300071 (P.R. China)
Fax: (+86) 22-2350-3625
E-mail: yuliu@nankai.edu.cn

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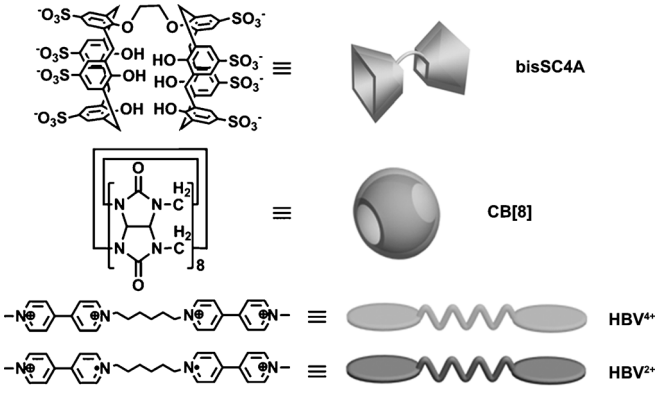
previous works,[15] we also fabricated nano-supramolecular linear/netlike assemblies from the bis(*p*-sulfonatocalix[5]arenes) and porphyrins, and more recently, electrochemical stimulus-responsive supramolecular polymers from bis(*p*-sulfonatocalix[4]arenes) and viologen dimers. Cucurbit[*n*]urils (CB[*n*]s), a family of novel pumpkin-shaped macrocyclic hosts, containing a different number of glycoluril units, were extensively exploited in host–guest chemistry.[16] Especially, CB[8] has been occasionally employed for supramolecular polymerization and cross-linking[17] by utilizing multiple host-stabilized charge-transfer interactions.[18]

As a natural evolution of our ongoing program concerning supramolecular polymers based on calixarene macrocycles, we report here the fascinating topological conversion of assemblies, controlled by the complexation of additional CB[8]. The complexation of *N*′,*N*″-hexamethylenebis(1-methyl-4,4′-bipyridinium) ($HBV^{4+}$) with bis(*p*-sulfonatocalix[4]arenes) (bisSC4A) leads to binary cyclic oligomeric assemblies (Scheme 1). Although interestingly, upon addition




Scheme 1. Structural illustration of bis(*p*-sulfonatocalix[4]arenes) (bisSC4A), *N*′,*N*″-hexamethylenebis(1-methyl-4,4′-bipyridinium) ($HBV^{4+}$) and cucurbit[8]uril (CB[8]) (counterions are omitted for clarity).

of CB[*n*] ($n=7$, 8), a ternary supramolecular linear polymer was formed by the complexation of bisSC4A with [2]pseudorotaxane ($HBV^{4+}$@CB[*n*]). Moreover, we can operate practically the assembly/disassembly of the obtained polymer by redox stimulus, benefiting from the introduction of CB[8].

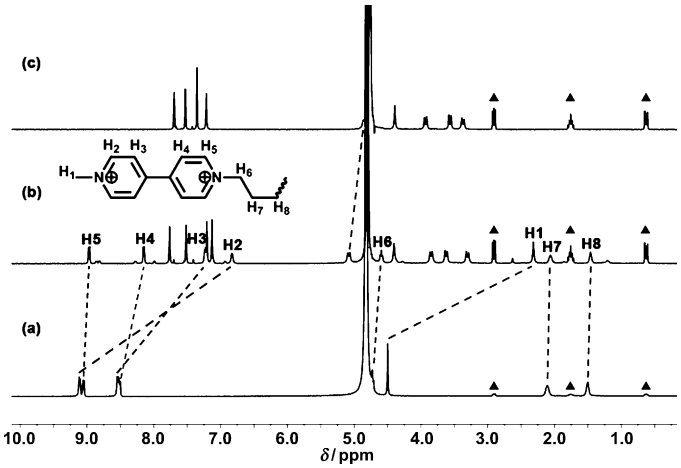



Figure 1. $^1$H NMR spectra of 1.0 mM $HBV^{4+}$ in the a) absence and b) presence of one equivalent bisSC4A, and c) 1.0 mM free bisSC4A. The solvent is $D_2O$ and "▲" represents the proton of 2,2-dimethyl-2-silapentane-5-sulfonate (DSS), which was added as an external reference.

lene-bridged bisviologen ($HBV^{4+}$), a species with a longer spacer. The obvious evidence for host–guest complexation between bisSC4A and $HBV^{4+}$ was initially presented by $^1$H NMR experiments (Figure 1). The aromatic and methyl protons ($H^{1-4}$) of $HBV^{4+}$ undergo pronounced upfield chemical shifts owing to the ring current effect of the aromatic nuclei of calixarene. The $\Delta\delta$ values are 2.18 for $H^1$, 2.28 for $H^2$, 1.30 for $H^3$, and 0.36 ppm for $H^4$. However, the aliphatic spacer protons ($H^{5-8}$) have almost negligible shifts. The $\Delta\delta$ values are 0.12 for $H^5$, 0.13 for $H^6$, 0.04 for $H^7$, and 0.04 ppm for $H^8$. It indicates that $HBV^{4+}$ is captured by bisSC4A with methyl-pyridinium moieties deeply immersed into the cavity,[19] whereas the hexamethylene spacer is located outside.

Isothermal titration calorimetry (ITC) measurements supplied the quantitative information (Table 1) for the host–guest complexation, both binding affinity and thermodynamic origin. The high association constant of bisSC4A with $HBV^{4+}$ was obtained as $(1.15\pm0.01)\times10^6\,M^{-1}$, fitted by using the "one set of binding sites" model (assuming that all the binding sites for the interacting species are identical, *n*:*n* complexation is dealt with a 1:1 binding model; $\Delta H°$ and $T\Delta S°$ represent the values per host site, in which the experi-

## Results and Discussion

**Construction of a binary supramolecular cyclic oligomer based on bisSC4A and $HBV^{4+}$**: Viologens, one class of dicationic redox couples, are strongly included by *p*-sulfonatocalix[*n*]arene (SC*n*A) ($n=4$, 5) to form a stable complex.[19] Previously, we built a supramolecular linear polymer based on the complexation of bisSC4A with ethylene-bridged bisviologen ($EBV^{4+}$).[15b] We studied herein the binding and assembly behavior of bisSC4A with hexamethy-

Table 1. Complex stability constant ($K_S$), enthalpy ($\Delta H°$), and entropy changes ($T\Delta S°$) for the intermolecular complexation of bisSC4A with $HBV^{4+}$, SC4A with $MV^{2+}$[a], and bisSC4A with $HBV^{4+}$@CB[*n*] in aqueous solution (pH 7.0) at 298.15 K.

| Complex | $K_S$ [$M^{-1}$] | $\Delta H°$ [kJ mol$^{-1}$] | $T\Delta S°$ [kJ mol$^{-1}$] |
|---|---|---|---|
| $HBV^{4+}$@bisSC4A | $(1.15\pm0.01)\times10^6$ | (−29.6±0.2) | (4.96±0.18) |
| $MV^{2+}$@SC4A | $(9.26\pm0.08)\times10^5$ | (−27.2±0.2) | (6.79±0.18) |
| $HBV^{4+}$@CB[8]/bisSC4A[b] | $(1.85\pm0.01)\times10^6$ | (−47.9±0.4) | (−12.1±0.4) |
| $HBV^{4+}$@CB[7]/bisSC4A[b] | $(1.86\pm0.21)\times10^7$ | (−42.0±0.6) | (−0.543±0.290) |

[a] Methyl viologen. [b] ITC titrations of ternary supramolecular polymers based on bisSC4A with $HBV^{4+}$@CB[*n*] revealed relatively large associated errors due to limited solubility of the ternary complexes.

mental $\Delta H°$ value was divided by the number of sites of host).[20] Such high binding constant is a prerequisite for the construction of a supramolecular polymer.[1b,e] The experimental "$N$" value of 1.036 (binding molar ratio) is close to the expected value of 1. Resembling the 1:1 complexation case of SC4A with $MV^{2+}$ in aqueous solution, the assembly process of supramolecular progress is also typically driven by a favorable enthalpy change, accompanied with a positive entropy contribution. The sulfonate groups attract organic cations electrostatically, which may cause a large degree of desolvation of the host and guest molecules.[21] This favorable contribution to the entropy will compensate the loss of conformational freedom arising from the complexation of bisSC4A with $HBV^{4+}$. In our previous result,[15b] the entropy term of complexation by bisSC4A with $EBV^{4+}$ is twice more as unfavorable as that of SC4A with $MV^{2+}$, reflecting the formation of supramolecular polymer. However, in the present case, the entropy change of bisSC4A with $HBV^{4+}$ is more unfavorable than that of SC4A with $MV^{2+}$, probably indicating lower degree of polymerization than previous systems, such as supramolecular oligomers.

The shape, size, and size distribution of the binary supramolecular nanoarchitecture were investigated by atomic force microscopy (AFM), transmission electron microscopy (TEM), and cryo-TEM, showing the direct morphology of supramolecular assembly. As shown in Figure 2a, all these

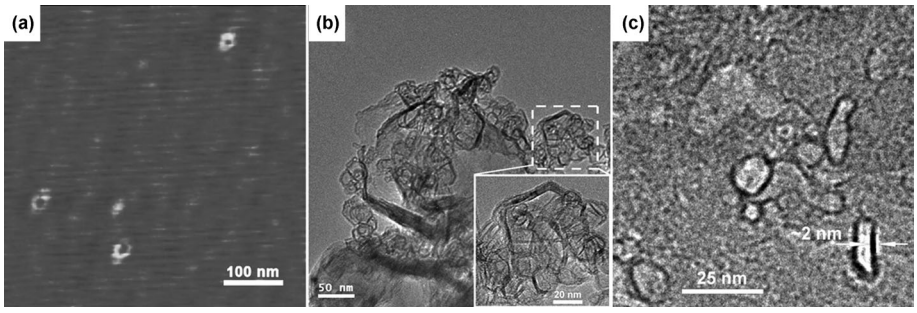



Figure 2. a) AFM image, b) TEM image (scale bar = 50 nm, inset scale bar = 20nm), and c) cryo-TEM image of the supramolecular cyclic assembly of $HBV^{4+}$@bisSC4A.

2D nanostructures are mainly cyclic, and have diameters of 25–45 nm according to a statistical representation of the cyclic assembly dimensions (Figure S3 in the Supporting Information).[22] The average height is 1.1 nm, representing the upper-rim size of SC4A (Figure S4a in the Supporting Information).[15b] TEM images gave similar insight into the size and shape of $HBV^{4+}$@bisSC4A binary assembly, where large numbers of irregular cyclic assemblies with heterogeneous sizes no larger than 50 nm overlap together (Figure 2b). A cryo-TEM image (Figure S5 in the Supporting Information),[23] which provides direct visual information from a vitrified aqueous solution ($c = 0.5$ mM), reveals the formation of different sizes and shapes of a confined cyclic assembly. The dimensions of an irregular cyclic assembly in water are the same with the results observed from the TEM image. The estimated thickness of the oligomeric structure in Figure 2c ($\approx$2 nm) was somewhat larger than the upper-rim size of SC4A ($\approx$1.2 nm), probably ascribing to guest counterions at the profile of oligomeric assembly.

To investigate the hydrodynamic diameter and the concentration dependence of $HBV^{4+}$@bisSC4A, we performed dynamic light scattering (DLS) and viscosity measurements at different concentrations. On one hand, the discrete DLS data reflect that no scattering intensity has been detected even at the concentration of 1.0 mM (aqueous solution) of $HBV^{4+}$@bisSC4A (Figure S7 in the Supporting Information), implying no large-size assembly was formed. In contrast, the reported supramolecular polymer of $EBV^{4+}$ with bisSC4A yielded relatively high scattering intensity at the same concentration.[15b] Thus, it is suggested that the mixture of $HBV^{4+}$ and bisSC4A cannot form supramolecular polymers. On the other hand, the absolute light scattering intensity of a $HBV^{4+}$@bisSC4A solution remained unchanged with increasing concentrations (Figure S6 in the Supporting Information), indicating that $HBV^{4+}$@bisSC4A formed a small supramolecular assembly, which is different from the concentration-dependent supramolecular polymers (see discussion below). This hypothesis was supported by viscosity measurement in aqueous solution by using a micro-Ubbelohde viscometer. As shown in Figure S8 in the Supporting Information, the specific viscosity of a binary assembly varied linearly with its concentrations. A double-logarithmic curve of the specific viscosity versus the concentration exhibits a slope of 0.87, which is close to 1.[24] This indicates that non-interacting assemblies of possibly cyclic oligomer with constant size are formed in the low concentration region (0.1–1.5 mM). We cannot perform the experiments at much higher concentration due to the limit solubility of the assembly.

Gel permeation chromatography (GPC) measurement also shows assembly characterization of $HBV^{4+}$@bisSC4A. Although the binary assembly is typically dynamic on account of the supramolecular nature and will fall apart under the high shear forces on the GPC column, we can still recognize results of the formation of supramolecular oligomers based on data measured by four detectors. As shown in Figure 3, retention volumes of $HBV^{4+}$@bisSC4A obtained by the refractive index (RI), right-angle light scattering (RALS), and viscometer DP (DP) detectors remain almost same. The major peak at 7.98 mL represents the $HBV^{4+}$@bisSC4A assembly. The minor peak at 9.37 mL is assumed to be the fragments when the sample eluted from the column. These give the weight-average molecular weight, where two $M_w$ (Da) values ($2.2\times10^5$ and $1.0\times10^5$) were obtained, indicating, on average, 50–115 alternating host and guest units in the cyclic assembly. Additionally, the 4-capillary differential viscometer DP re-

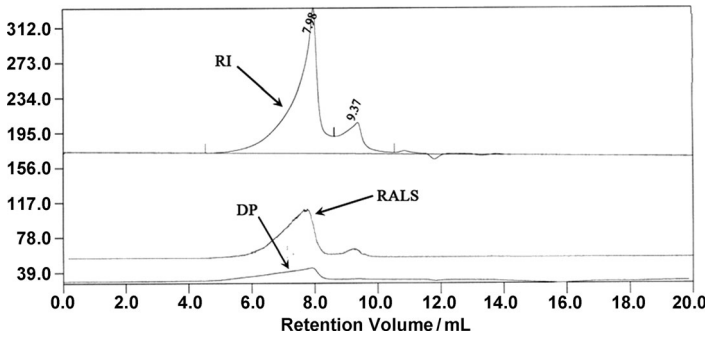



Figure 3. GPC trace of 0.5 mM aqueous solution of binary oligomer $HBV^{4+}$@bisSC4A at 298 K.

sponds to the viscosity of the sample as it elutes from GPC, indicating the formation of a higher-order assembly from the host–guest blocks. Based on all of the aforementioned AFM, TEM, DLS, GPC, and viscosity results, we infer that the complexation of $HBV^{4+}$ and bisSC4A is more likely to form a cyclic oligomeric assembly with certain size distribution, than linear polymer. The deduced topological structure of the binary assembly is illustrated in Figure 4. Compared with $EBV^{4+}$, $HBV^{4+}$ with a more flexible spacer results in cyclic oligomers, rather than linear polymers.

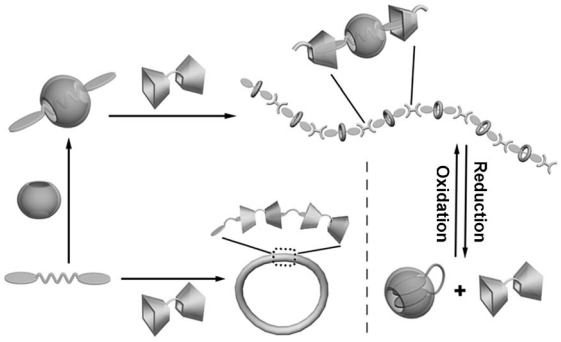



Figure 4. Schematic representation of CB[8]-modulated assembly structures and the redox stimulus-response of the $HBV^{4+}$@CB[8]/bisSC4A supramolecular polymer.

**Construction of a ternary supramolecular linear polymer**: To obtain the supramolecular polymer as we anticipated, CB[$n$] ($n=7$, 8) was employed as it can bind the aliphatic spacer of $HBV^{4+}$ tightly,[25] and therefore, improve the molecular rigidity. Upon addition of CB[8], large upfield shifts of the aliphatic proton ($H^{6-8}$) signals indicate that CB[8] is on the hexamethylene parts, due to the hydrophobic binding affinity between the aliphatic chain of $HBV^{4+}$ and the inner cavity of CB[8] (Figure S1 in the Supporting Information).[25b] The $\Delta\delta$ values are 0.31 for $H^6$, 0.68 for $H^7$, and 0.69 ppm for $H^8$. We obtained the NMR spectrum of the ternary assembly $HBV^{4+}$@CB[8]/bisSC4A at 0.2 mM by using a water suppression sequence (Figure S1c in the Supporting Information). Upon the addition of bisSC4A to $HBV^{4+}$@CB[8], the pronounced upfield shifts of the aromatic and methyl protons ($H^1$, $H^2$, and $H^4$) indicated that $HBV^{4+}$ was captured by bisSC4A with the methyl-pyridinium moieties deeply immersed into the cavity. The hexamethylene protons ($H^{6-8}$) showed negligible downfield shifts, which indicated that the aliphatic spacer was still located in the cavity of CB[8]. One should note that, the precipitation appears when the solutions of $HBV^{4+}$@CB[8] and bisSC4A (with concentrations higher than 0.2 mM) were mixed together. A similar phenomenon can be observed in $HBV^{4+}$@CB[7]/bisSC4A system.[25a] Because both bisSC4A and $HBV^{4+}$@CB[$n$] are soluble, we can preliminarily estimate the components of precipitations, $HBV^{4+}$, CB[$n$], and bisSC4A.

To further identify the components of precipitation of $HBV^{4+}$@CB[8]/bisSC4A, we performed thermogravimetric analysis (TGA) (Figure 5) and elemental analysis. The result

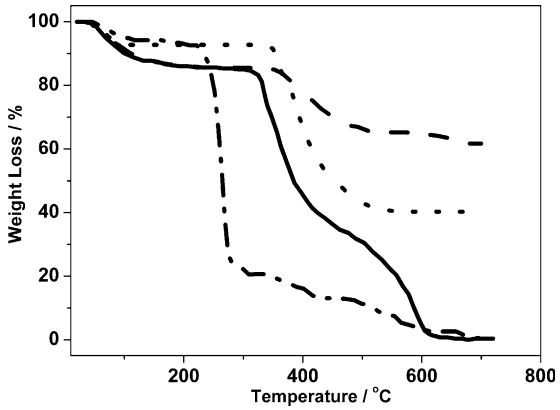



Figure 5. TGA curves of $HBV^{4+}$·4$Br^-$ (dash dot), CB[8] (dot), bisSC4A·8$Na^+$ (dash), and $((HBV^{4+}@CB[8])_2$·bisSC4A$)_n$ (solid).

of elemental analysis identified the binding ratio between $HBV^{4+}$@CB[8] and bisSC4A in the solid-state species as 2:1. The complex species is water rich, and TGA exhibits initial 14.2% weight loss corresponding to dehydration from 25 to approximately 330°C; in this region none of $HBV^{4+}$·4$Br^-$, CB[8], and bisSC4A·8$Na^+$ decompose. Elemental analysis also suggests the presence of 14.4% crystal-water molecules in the complex, which is in good accordance with the TGA. The $HBV^{4+}$@CB[8]/bisSC4A supramolecular assembly loses 99.6% of its original weight at approximately 640°C, corresponding to the unique decomposition of $HBV^{4+}$@CB[8] and bisSC4A. The decomposition temperature of the ternary supramolecular assembly increases as the number of monomer units increases due to strong host–guest interaction,[26] and the components are $HBV^{4+}$@CB[8] and bisSC4A with the ratio of 2:1 attributed to charge conservation.

To gain a better understanding of the morphology of the CB[8] assembly, an AFM measurement was performed. Employing $HBV^{4+}$@CB[8] and bisSC4A as building blocks, the resultant supramolecular polymer was a 1D linear structure with a length in the micron range (Figure 6 and Figure S4b in the Supporting Information). The 1D nanostructure

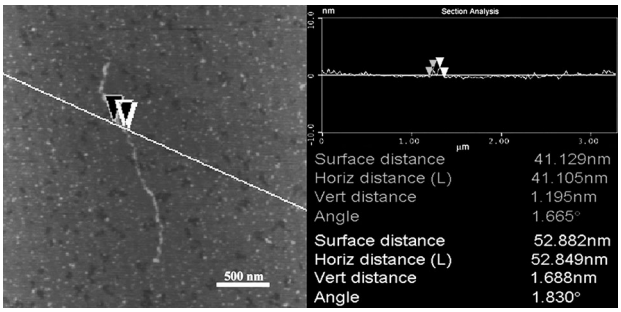



Figure 6. AFM image of the ternary supramolecular polymer of $HBV^{4+}$@CB[8]/bisSC4A scale bar = 500 nm.

shows two heights of 1.2 and 1.7 nm, which are identical to the upper-rim size of SC4A and the outer diameter of CB[8], respectively.[15b,16b] The ditopic guest $HBV^{4+}$ possesses a flexible aliphatic spacer, which prompts the formation of cyclic oligomer upon complexation with bisSC4A. Whereas with CB[8] threading on $HBV^{4+}$, the $HBV^{4+}$@CB[8]/bisSC4A complex forms a linear polymer. The topological conversion triggered by CB[*n*] is essentially owing to the change of the molecular flexibility of $HBV^{4+}$ before and after complexation with CB[*n*]. These results suggest that building blocks with more rigid spacer groups favor the formation of linear polymers, not cyclic oligomers.[27]

DLS measurements (Figure 7a) show pronounced scattering intensity of the large size polymer $HBV^{4+}$@CB[*n*]/bisSC4A only at 0.2 mM (the aqueous solution become lightly cloudy as the ternary complexes precipitates at higher concentration.), and the DLS data are shown in Figure S9 in the Supporting Information. Two hydrodynamic diameter distributions of $HBV^{4+}$@CB[8]/bisSC4A were observed. One was centered at 92 nm, which could be ascribed to the chains with low degree of polymerization. The other, centered at 490 nm, was contributed by polymer chains of high molecular weight. The diameter distribution of $HBV^{4+}$@CB[7]/bisSC4A was remarkably narrower than that of $HBV^{4+}$@CB[8]/bisSC4A. The average hydrodynamic diameters were 336 and 614 nm for CB[8] and CB[7], respectively. One possible explanation for this difference is that CB[7], possessing smaller cavity than CB[8],[16b] can make the hexamethylene spacer of $HBV^{4+}$ conformationally rigid to a higher extent. This indicates that the more rigid the spacer, the narrower the distribution and the larger the size of the supramolecular polymer. The other explanation is that bisSC4A has a higher binding affinity for $HBV^{4+}$@CB[7] than for $HBV^{4+}$@CB[8] (Table 1). It can be seen in Figure 7b that the hydrodynamic diameter of the supramolecular polymer $HBV^{4+}$@CB[8]/bisSC4A increases from 0 to 336 nm when the concentration increases from 0.001 to 0.2 mM. This indicates that the formation of the supramolecular polymer is intrinsically concentration dependent, the higher the concentration, the larger the polymer size.[28] Therefore, by introducing CB[*n*], the binary cyclic oligomer $HBV^{4+}$@bisSC4A can be transferred to the ternary linear polymer $HBV^{4+}$@CB[*n*]/bisSC4A, as shown in Figure 4.

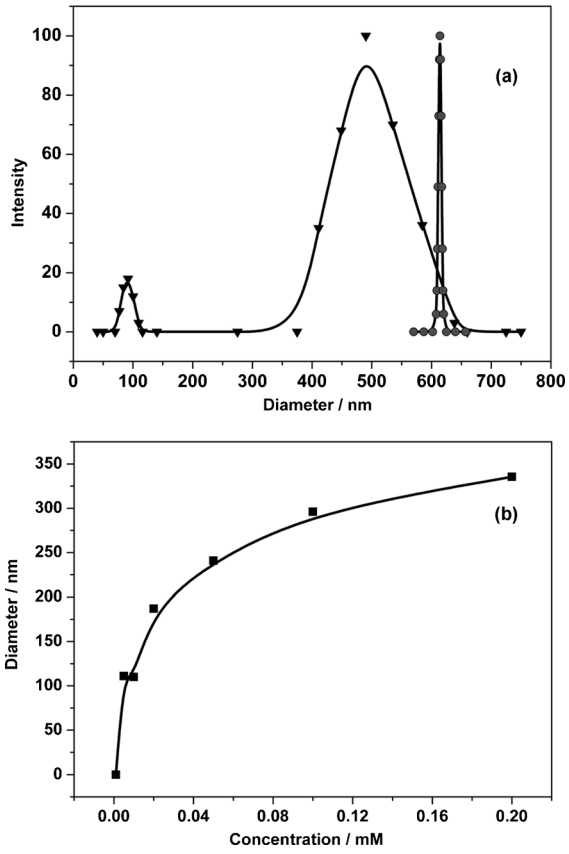



Figure 7. a) Hydrodynamic diameter distribution of ternary supramolecular polymers at the concentration of 0.2 mM. b) Dependence of the supramolecular polymer concentration on the hydrodynamic diameter of $HBV^{4+}$@CB[8]/bisSC4A at 298 K.

The previous $EBV^{4+}$@bisSC4A polymer gave a relatively broad DLS peak with an average diameter of 141 nm at a concentration of 1.0 mM.[15b] We observed sizes of the ternary $HBV^{4+}$@CB[*n*]/bisSC4A polymers that were 2–4 times larger than that of the binary $EBV^{4+}$@bisSC4A polymer at a concentration of only 0.2 mM (Figure 7a). This is due to the fact that bisSC4A has a much stronger binding affinity for $HBV^{4+}$@CB[*n*] pseudorotaxanes than for free $HBV^{4+}$, which is in turn ascribed to cooperative enhancement between CB[*n*] and bisSC4A. The complex stability constants between bisSC4A and $HBV^{4+}$@CB[*n*] were determined by ITC experiments (Table 1). Such cooperative enhancement between macrocyclic hosts is reasonably acceptable according to a previous report.[29] The complexation of bisSC4A with $HBV^{4+}$@CB[*n*] shows remarkably negative entropy changes, indicating a pronounced loss of degrees of system freedom. This is due to the formation of ternary $HBV^{4+}$@CB[*n*]/bisSC4A polymers with higher degree of polymerization. Thus, the larger polymer size should result from the introduction of supramolecular positive co-operativity of bisSC4A with CB[*n*].

**Redox stimulus-responsive CB[8]-assisted supramolecular polymer**: Another significant point regarding CB[8] is their

extremely strong affinity to $HBV^{2+}$, the radical cation form of $HBV^{4+}$. Although viologen can reversibly change its redox state in response to chemical or electrochemical redox stimuli, it cannot be released from the cavity of SC4A until reduced to the water-insoluble neutral state.[15b] In the present ternary system, we anticipate that, the ternary polymer disassemble to free bisSC4A and molecular loop $HBV^{2+}$@CB[8] once $HBV^{4+}$ is reduced to $HBV^{2+}$, which is more practically operational. The disassembly process of the linear assembly of $HBV^{4+}$@CB[8]/bisSC4A upon reduction was monitored by UV/Vis absorption spectroscopy. As shown in Figure 8, when excess hydrazine was added to the solution of $HBV^{4+}$, a new absorption band, corresponding to its radical cationic state, appeared at about $\lambda = 600$ nm. This state is formed by the two-electron reduction.[30] Similar absorption bands also emerge in both UV/Vis spectra of $HBV^{2+}$@bisSC4A and $HBV^{2+}$@CB[7]/bisSC4A, whereas the observed absorbance of both solutions at $\lambda = 475$–550 nm region are more intensive than that of the free $HBV^{2+}$ radical cation, probably due to the strong host–guest interaction between bisSC4A and $HBV^{2+}$.[19] However, in the case of the aqueous solution of $HBV^{4+}$@CB[8]/bisSC4A when hydrazine was added, it showed the characteristic absorption band at approximately $\lambda = 549$ nm, indicating that $HBV^{2+}$ undergoes a rapid dimerization process inside the cavity of CB[8] to form the stable molecular loop $HBV^{2+}$@CB[8].[25b,31] The solution of $HBV^{2+}$@CB[8]/bisSC4A is purple as shown in Figure S13 in the Supporting Information, which is different from the light blue solutions of $HBV^{2+}$@bisSC4A and $HBV^{2+}$@CB[7]/bisSC4A. Meanwhile, the purple solution is much more stable than the other two when exposed to air. A control experiment was carried out with $HBV^{4+}$@CB[8] in the absence of bisSC4A, and remarkable enhancement of the $\lambda = 549$ nm absorption band was observed after reduction by hydrazine, along with a notable diminishment of the absorption band at $\lambda =$ 600 nm. Thus, the absorbance of $HBV^{2+}$@CB[8]/bisSC4A is close to that of $HBV^{2+}$@CB[8], which implies that the $HBV^{4+}$@CB[8]/bisSC4A system exhibits nearly complete disassembly after reduction of $HBV^{4+}$ to $HBV^{2+}$. More powerful evidence for the disassembly process of the ternary polymer $HBV^{4+}$@CB[8]/bisSC4A comes from the DLS results. Figure S11 in the Supporting Information shows that no scattering intensity has been detected upon the addition of excess hydrazine to the ternary system. The reversible assembly/disassembly of $HBV^{4+}$@CB[8]/bisSC4A, which can be controlled by the redox method, was further monitored by UV/Vis spectroscopy (Figure S12 in the Supporting Information).

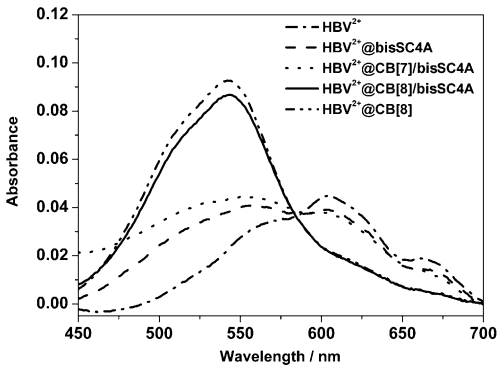



Figure 8. UV/Vis absorption spectra of 0.01 mM aqueous solutions in the presence of excess hydrazine at 298 K.

## Conclusion

In conclusion, we successfully built two species of supramolecular assemblies: the binary cyclic oligomer of $HBV^{4+}$@bisSC4A and the ternary linear polymers of $HBV^{4+}$@CB[*n*]/bisSC4A. The intriguing conversion of topological structures is modulated by CB[*n*]; the threading of CB[*n*] on the flexible spacer of $HBV^{4+}$ improves its molecular rigidity, as well as enhances the binding affinity between bisSC4A and $HBV^{4+}$. In addition, benefiting from grafting CB[8], we can control the assembly/disassembly of the supramolecular polymer by redox stimulus between $HBV^{4+}$ and $HBV^{2+}$. The ternary polymer disassembles to molecular loop $HBV^{2+}$@CB[8] and free bisSC4A, undergoing a two-electron reduction. Therefore, CB[8] cannot only modulate the topology of the supramolecular assemblies of bisSC4A and $HBV^{4+}$, but can also stimulate their switching between assembly and disassembly more practically operational. The present results pave an alternative way for constructing smart supramolecular materials with diverse structures and self-mending capability.

## Experimental Section

**Materials**: The tetrabromide salt of *N*′,*N*″-(hexylene)bis(1-methyl-4,4′-bipyridinium) ($HBV^{4+}$·4$Br^-$) was prepared by the literature procedure[32] with counterion exchanged by $PF_6^-$ and then $Br^-$. Bis(*p*-sulfonatocalix[4]-arene)octasodium (bisSC4A·8$Na^+$) was synthesized and purified according to the literature procedure.[15b] Hydrazine was purchased from Aladdin, and cucurbit[7]uril (CB[7]) and cucurbit[8]uril (CB[8]) were purchased from Aldrich and all of them were used without further purifications. All other chemicals were commercially available and were reagent grade without further purifications. Aqueous solutions of pH 7.0 was prepared with distilled, deionized water, adjusted with hydrochloric acid (1 M) or sodium hydroxide (1 M), and verified on a Sartorius pp-20 pH-meter calibrated with two standard buffer solutions.[21]

**Supramolecular polymer of $HBV^{4+}$@CB[8]/bisSC4A**: $HBV^{4+}$·4$Br^-$ (7.5 mg, 0.01 mmol) and CB[8] (13.3 mg, 0.01 mmol) were mixed in distilled, deionized water (10 mL) to prepare an aqueous solution of $HBV^{4+}$@CB[8] after heating and stirring for 2 h, then filtered to get rid of unsolved solid. BisSC4A·8$Na^+$ (17.0 mg, 0.01 mmol) was dissolved in distilled, deionized water (3 mL). The two solutions were mixed, giving a yellow precipitate of the supramolecular aggregate immediately. The precipitate was separated by centrifugation, washed with water twice, dried under vacuum at 60 °C, and further characterized by AFM, TGA, and elemental analysis. Elemental analysis calcd. (%) for $(C_{58}H_{42}O_{32}S_8)\cdot(C_{76}H_{82}N_{36}O_{16})_2\cdot(H_2O)_{50}\cdot(H_2SO_4)_3$ ($M_w = 6213.84$ g mol$^{-1}$): C 40.59, H 5.06, N 16.23; found: C 40.39, H 5.09, N 16.57.

**Instruments**: $^1$H NMR spectra were recorded on a Bruker AV400 spectrometer. The thermogravimetric analysis was recorded with a RIGAKU Standard type TG analyzer. The samples were put into platinum pans, which were hung in the heating furnace. The weight percentage of material remaining in the pan was recorded, while the temperature was increased from room temperature to 800 °C at a heating rate of 10 °C min$^{-1}$. Elemental analysis was recorded on Elementar Vario EL instrument. Viscometer measurements were carried out on a SCHOTT-Ubbelohde micro capillary viscometer (DIN 53810, 0.40 mm inner diameter) at 25 °C in deionized water.

**AFM measurements**: The samples were performed by using a multimode IIIa AFM (Veeco Metrology, USA) in tapping mode in air at room temperature. Sample solutions of $1.0\times10^{-7}$ M (calculated from the repeat units) were dropped onto newly clipped mica and then dried in air.

**TEM measurements**: Sample solutions of $5.0\times10^{-6}$ M (calculated from the repeat units) were dropped onto a copper grid. The grid was then dried in air. The samples were examined by a high-resolution TEM (Philips Tecnai G2 20S-TWIN microscope) operating at an accelerating voltage of 200 kV. Droplets of the sample solution ($5.0\times10^{-4}$ M) were applied to perforated (1 μm hole diameter) 200 mesh grids covered with a carbon film. The sample was immediately vitrified by propelling the grids into liquid ethane with a guillotine-like plunging device (FEI Vitrobot Mark IV). The vitrified samples were subsequently transferred under liquid nitrogen into a Tecnai 20 microscope (FEI, Oregon, USA) by using the Gatan (Gatan Inc., California, USA) cryoholder and cryostage (Model 626) and operating an accelerating voltage of 100 kV.

**UV/Vis measurements**: UV/Vis spectra were recorded in a quartz cell (light path 10 mm) on a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller to keep the temperature at 25 °C.

**DLS measurements**: The samples were performed on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-9000AT) at $\lambda = 532$ nm at 25 °C. All DLS measurements were performed at the scattering angle of 90°. The sample solutions were prepared by filtering each component solution (2 mL in total volume) through a 220 nm syringe filter into a clean scintillation vial at the different concentrations.

**GPC measurements**: The measurement of weight-average molecular weights ($M_w$) was performed on a four detection size exclusion chromatograph (Four-SEC) containing a Waters 1525 separation module (Waters Corp.) connected with a M302 four detector array (Viscotek Corp., Houston, Texas), a combination of refractive index, light scattering (LS angle, 7 and 90°, laser wavelength, $\lambda = 532$ nm), viscosity detector, and UV/Vis detector. Two mixed bed SEC columns ($GMH_{HR}$-M, $GMH_{HR}$-H, Viscotek Corp.) were used. Poly(ethylene oxide) (PEO) was used as calibration standard and water was used as mobile phase at a flow rate of 1.0 mL min$^{-1}$ and an operating temperature of 25 °C.

**ITC measurements**: A thermostated and fully computer-operated isothermal calorimetry (VP-ITC) instrument, purchased from Microcal Inc., Northampton, MA, was used for all microcalorimetric experiments. The VP-ITC instrument was calibrated chemically by measurement of the complexation reaction of β-cyclodextrin with cyclohexanol, and the obtained thermodynamic data were in good agreement (error $<2\%$) with the literature data.[33] All microcalorimetric titrations between bisSC4A and $HBV^{4+}$ were performed in aqueous solution (pH 7.0) at atmospheric pressure and 298.15 K. Each solution was degassed and thermostated by a ThermoVac accessory before the titration experiment. Twenty-five successive injections were made for each titration experiment. A constant

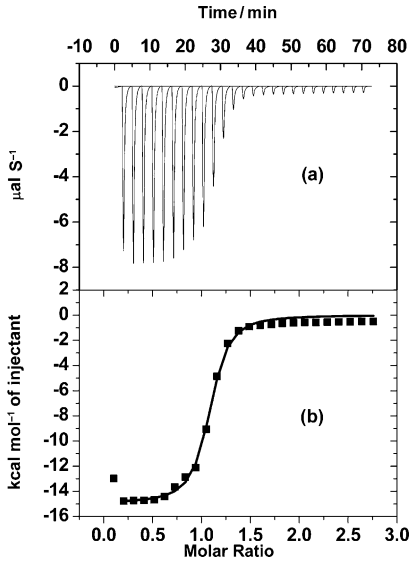



Figure 9. Microcalorimetric titration of bisSC4A with $HBV^{4+}$ in aqueous solution (pH 7.0) at 298.15 K. a) Raw ITC data for sequential twenty-five injections (10 μL per injection) of bisSC4A solution (1.88 mM) injecting into $HBV^{4+}$ solution (0.131 mM). b) Apparent reaction heat obtained from the integration of calorimetric traces.

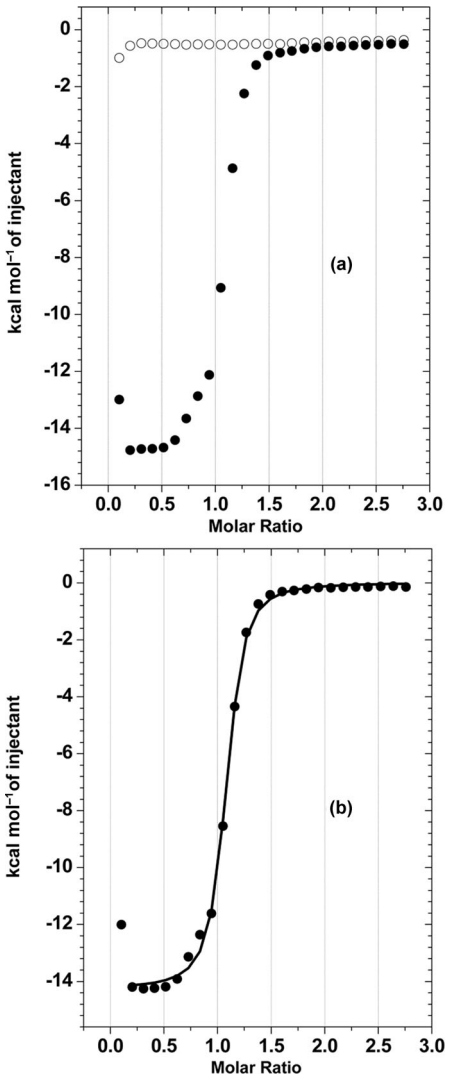



Figure 10. a) Heat effects of the dilution and of the complexation reaction of bisSC4A with $HBV^{4+}$ for each injection during the titration microcalorimetric experiment. b) "Net" heat effects of complexation of bisSC4A with $HBV^{4+}$ for each injection, obtained by subtracting the dilution heat from the reaction heat, which was fitted by computer simulation by using the "one set of binding sites" model.

volume (10 μL per injection) of host solution in a syringe (0.250 mL) was injected into the reaction cell (1.4227 mL) charged with guest molecule solution in the same aqueous solution. A representative titration curve is shown in Figure 9. As can be seen from Figure 9, each titration of bisSC4A into the sample cell gave an apparent reaction heat caused by the formation of an inclusion complex between bisSC4A and $HBV^{4+}$. The reaction heat decreases after each injection of bisSC4A because less and less guest molecules are available to form inclusion complexes. A control experiment was carried out in each run to determine the dilution heat by injecting an aqueous solution of the host into a pure aqueous solution containing no guest molecules. The dilution heat determined in these control experiments was subtracted from the apparent reaction heat measured in the titration experiments to give the net reaction heat.

The net reaction heat in each run was analyzed by using the "one set of binding sites" model (ORIGIN software, Microcal Inc.) to simultaneously compute the binding stoichiometry ($N$), complex stability constant ($K_S$), standard molar reaction enthalpy ($\Delta H°$), and standard deviation from the titration curve. Generally, the first point of the titration curve was disregarded, as some liquid mixing near the tip of the injection needle is known to occur at the beginning of each ITC run. Knowledge of the complex stability constant ($K_S$) and molar reaction enthalpy ($\Delta H°$) enabled calculation of the standard free energy ($\Delta G°$) and entropy changes ($\Delta S°$) according to Equation (1):

$$\Delta G^\circ = -RT\ln K_S = \Delta H^\circ - T\Delta S^\circ \quad (1)$$

where $R$ is the gas constant and $T$ is the absolute temperature.

A typical curve fitting result for the complexation of bisSC4A with $HBV^{4+}$ in aqueous solution (pH 7.0) is shown in Figure 10. To check the accuracy of the observed thermodynamic parameters, two independent titration experiments were carried out to afford self-consistent thermodynamic parameters, and their average values with associated errors are listed in Table 1.

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