

Supramolecular Polymers

Synthesis of Doubly Ethyl-Bridged Bis(*p*-sulfonatocalix[4]arene) and Its Supramolecular Polymerization with Viologen DimerKun-Peng Wang, Dong-Sheng Guo, Hong-Xia Zhao, and Yu Liu*^[a]

Abstract: A water-soluble supramolecular polymer with a high degree of polymerization and viscosity has been constructed based on the strong host–guest interaction between *p*-sulfonatocalix[4]arenes (SC4As) and viologen. A homoditopic doubly ethyl-bridged bis(*p*-sulfonatocalix[4]arene) (*d*-SC4A) was prepared and its binding behavior towards methyl viologen compared with the singly ethyl-bridged bis(*p*-sulfonatocalix[4]arene) (*s*-SC4A) by NMR spectroscopy and isothermal titration calorimetry. By employing a viologen dimer (bisMV⁴⁺) as the homoditopic guest, two linear AA/BB-type supramolecular polymers, *d*-SC4A⊃bisMV⁴⁺ and

s-SC4A⊃bisMV⁴⁺, were successfully constructed. Compared with *s*-SC4A⊃bisMV⁴⁺, *d*-SC4A⊃bisMV⁴⁺ shows much higher solubility and viscosity, and has also been characterized by viscosity, diffusion-ordered NMR spectroscopy, dynamic light scattering, and atomic force microscopy measurements. Furthermore, the polymer is responsive to electrostimulus as viologen is electroactive, which was studied by cyclic voltammetry. This study represents a proof-of-principle as the polymer can potentially be applied as a self-healing and degradable polymeric material.

Introduction

Supramolecular polymers^[1] directed by the molecular recognition of host–guest pairs have gained increasing attention in the last two decades.^[2] Host–guest complexation events involving substrates based on cyclodextrin, sulfonatocalixarene, and cucurbituril macrocycles commonly occur in aqueous media, in which some noncovalent interactions are not always effective.^[3] Zhang and co-workers prepared a novel supramolecular polymer hydrogel with a high degree of polymerization that is based on multiple host-stabilized charge-transfer interactions of cucurbit[8]uril.^[4] In addition, host–guest interactions are susceptible to external stimuli, especially light and electricity. For example, Harada and co-workers prepared a stilbene-bridged bis(β -cyclodextrin) dimer and achieved the conformational change from pinching-type dimer to supramolecular polymer through photoirradiation.^[5] We previously reported a supramolecular polymer based upon a homoditopic singly ethyl-bridged bis(*p*-sulfonatocalix[4]arene) (*s*-SC4A) receptor prepared by iterative complexation with a homoditopic viologen connector, its assembly process being reversibly controlled by electrochemical stimulus.^[6] Thus, host–guest interactions have advantages in the building of environmentally

friendly, biocompatible, and smart polymeric materials. Recently, Harada and co-workers demonstrated the specific and stimuli-responsive macroscopic assembly of cyclodextrin- and guest-functionalized hydrogels.^[7] In addition, Kim and co-workers reported the synthesis of supramolecular “Velcro”, a new approach for achieving strong and reversible underwater adhesion based on the ultrahigh affinity of the host–guest binding pair of cucurbit[7]uril and ferrocenes.^[8]

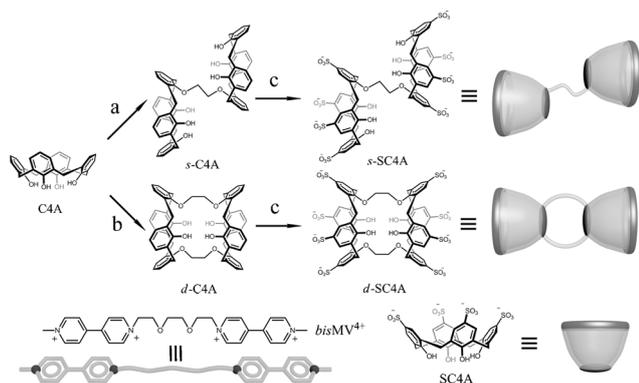
Calixarenes,^[9] composed of phenolic units linked by methylene groups, represent the third generation of supramolecular host molecules. Calixarene-based molecular recognition has also been used in supramolecular polymerization in recent years, for example, the complexation of calix[5]arene with ammonium salts^[10] and fullerene,^[11] and *p*-sulfonatocalix[4,5]arenes with organic cations.^[12] In addition, Pappalardo and co-workers reported an applicable proton-driven homoditopic host–guest pairing of modular homoditopic bis-calix[5]arenes and long-chain r,ω -alkanediyl diammonium components for the preparation of supramolecular polymers^[10c] and Haino and co-workers employed ditopic calix[5]arene to construct supramolecular polymers with dumbbell C₆₀ and further supramolecular cross-linkage with [60]fullerene-tagged polyphenylacetylene.^[11] We fabricated a series of water-soluble supramolecular polymers based on homoditopic *s*-SC4A.^[6,13] Subsequent to our study, Tian and co-workers reported a dual-stimuli-responsive supramolecular polymer based on the iterative intermolecular inclusion of *s*-SC4A and a heteroditopic flexible guest.^[14] More recently, they reported a novel, light-driven, linear, chiral supramolecular polymer formed by the molecular-recognition-directed self-assembly of *s*-SC4A and an α -cyclodextrin-based pseudo[3]rotaxane containing axially chiral 1,1'-binaphthyl and photoresponsive azobenzene moieties.^[15] Although supra-

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Supporting information for this article is available on the WWW under
<http://dx.doi.org/10.1002/chem.201303344>.

molecular polymerization directed by the host–guest interactions of calixarenes has been increasingly pursued in recent years, materials with truly typical polymeric features have been reported much less frequently^[16] due to complex stability and solubility issues.

As a natural evolution of our ongoing program concerning supramolecular polymers based on calixarene macrocycles, we prepared in this work a new homoditopic bis(*p*-sulfonatocalix[4]arene) with dual bridging spacers (*d*-SC4A; Scheme 1). In comparison with the flexible conformation of *s*-SC4A



Scheme 1. Synthetic routes to *s*-SC4A and *d*-SC4A. Structures of *s*-SC4A, *d*-SC4A, bisMV⁴⁺, and SC4A. Reagents and conditions: a) TsOCH₂CH₂OTs, acetonitrile, NaOMe; b) BrCH₂CH₂Br, acetonitrile, potassium carbonate; c) 98% H₂SO₄, NaOH.

has a fixed conformation and shows improved molecular rigidity. It is well established that the flexibility of spacers between two (self-)complementary recognition sites plays a crucial role in directing supramolecular polymerization.^[1,16,17] We therefore envisaged that *d*-SC4A would be more favorable for constructing supramolecular polymers than *s*-SC4A. Homoditopic triglycol-bridged bis(methyl viologen) (bisMV⁴⁺) was employed as a model guest for a comparative evaluation of the supramolecular polymerization of *s*-SC4A and *d*-SC4A. As expected, the *d*-SC4A⊃bisMV⁴⁺ polymer clearly exhibits a much higher viscosity and degree of polymerization than *s*-SC4A⊃bisMV⁴⁺. In addition, the electrostimulus response was investigated.

Results and Discussion

Syntheses of building blocks and conformational analyses

To fabricate water-soluble supramolecular polymers with a high degree of polymerization, strong host–guest interactions are always demanded. *p*-Sulfonatocalixarenes, a robust family of water-soluble calixarene derivatives, show a strong binding affinity and high molecular selectivity towards organic cations, driven by the synergistic effect of the intrinsic cavities as well as the additional anchoring points provided by the sulfonate groups.^[12] A minimum of two interacting sites is needed to form supramolecular polymers from two complementary monomers, driven by iterative complexation, and therefore we synthesized *d*-SC4A and *s*-SC4A in two steps from

the mother *p*-H-calix[4]arene (C4A), as shown in Scheme 1. *s*-SC4A was prepared according to our previous work^[6] and *d*-SC4A was prepared as a new compound by the following process. C4A was treated with 1 equiv 1,2-dibromoethane in a mixture of acetonitrile and potassium carbonate to generate the symmetric, doubly ethyl-bridged bis(*p*-H-calix[4]arene) (*d*-C4A) in 41% yield. Subsequent sulfonation of *d*-C4A with conc. H₂SO₄ and neutralization with NaOH afforded the water-soluble sodium salt of *d*-SC4A in 63% yield.

The bridging methylene protons of the parent SC4A show a single peak in its ¹H NMR spectrum, which broadens or splits into a doublet upon complexation with guest molecules, indicating that SC4A itself has a flexible conformation in aqueous solution but becomes a rigidified cone upon complexation.^[18] The ¹H NMR spectrum of *d*-SC4A shows two doublets for the bridging methylene protons of the skeleton (the axial and equatorial species; see Figure S5 in the Supporting Information), which shows that the framework of *d*-SC4A is much more rigid than that of the parent SC4A because the lower-rim dual bridging spacers restrain the random flipping motion of the aromatic rings. As a result, it was deduced that *d*-SC4A assumes a “pinched” cone conformation.

The energy-minimized structures of *s*-SC4A and *d*-SC4A were also simulated in a molecular modeling study (Figure 1). *s*-SC4A has a flexible and unfixed conformation with the two calixarene units in a “*trans*” manner.^[19] In *d*-SC4A, the two calixarene units are fixed well by the two ethyl bridges. Compared with *s*-SC4A, *d*-SC4A has a more rigid and symmetric confor-

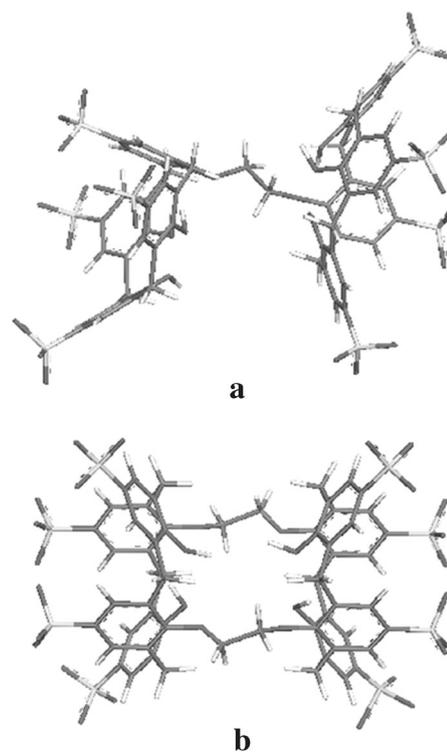


Figure 1. Energy-minimized structures of a) *s*-SC4A and b) *d*-SC4A obtained by molecular modeling. The geometries were optimized by the molecular mechanics method employing a Dreiding force field.

mation. In addition, the calixarene cavities in *d*-SC4A are pinched to a greater extent than in *s*-SC4A. The S...S distances of the distal sulfonates are 9.0 and 12.9 Å in *s*-SC4A, and 5.1 and 12.9 Å in *d*-SC4A.

To construct an AA/BB polymer based on the molecular recognition of the SC4A dimer, bisMV⁴⁺ was employed as a model guest, which was prepared according to a literature procedure.^[20] Viologens, a class of dicationic redox couples, are strongly included by SC4As to form stable complexes. More recently, we studied the binding behavior between SC4A and homoditopic guests possessing different spacer lengths and rigidities, as well as sizes, shapes, and charges of terminal groups,^[21] and found that viologen-terminated homoditopic guests are much more favorable for supramolecular polymerization than other species, such as imidazolium, pyridinium, and quinolinium. On the other hand, the spacer is also important in supramolecular polymerization. With diglycol as spacer, calixarene exhibits a binding affinity towards the spacer and the binding geometry transforms with the gradual addition of calixarene, which is unfavorable for supramolecular polymerization. With tri- and tetraglycol as spacers, calixarene clearly includes the terminal viologen portion rather than the spacer portion, which is a prerequisite for *n*:*n* iterative complexation. The tetraglycol spacer is longer and more flexible, which may prompt an undesired ring-chain equilibrium in some cases^[13a,22] and therefore triglycol was selected as the spacer to link two viologen units together.

Host-guest complexation

¹H NMR spectroscopy was used to provide evidence for the host-guest complexation of bisMV⁴⁺ with *s*-SC4A and *d*-SC4A (Figure 2). The complex-induced chemical shifts of bisMV⁴⁺ resulting from complexation by *s*-SC4A and *d*-SC4A are similar, and therefore we inferred that almost the same binding events occur. Taking *d*-SC4A⊃bisMV⁴⁺ as an example, the ar-

omatic and methyl protons (H₁₋₄) of bisMV⁴⁺ underwent pronounced upfield chemical shifts upon addition of calixarene due to the ring current effect of the aromatic nuclei of calixarene.^[13,23] The $\Delta\delta$ values are 1.90 ppm for H₁, 2.02 ppm for H₂, 1.12 ppm for H₃, and 0.33 ppm for H₄. The protons H₅₋₈ underwent almost negligible complex-induced shifts, the $\Delta\delta$ values being 0.09 ppm for H₅, 0.14 ppm for H₆, 0.09 ppm for H₇, and 0.06 ppm for H₈. This shows that bisMV⁴⁺ is captured by calixarene with the methylpyridinium moieties deeply immersed in the cavity^[24] and the spacer located outside. However, some slight changes were observed in the shifts of the *s*-SC4A protons upon complexation, whereas no appreciable changes were observed for the *d*-SC4A protons. One reasonable explanation is that the conformation of *s*-SC4A changes to some extent on binding the viologen guest, whereas *d*-SC4A maintains its original conformation. It further validates the fact that *d*-SC4A adopts a more rigid pinched-cone conformation than *s*-SC4A.

Isothermal titration calorimetry (ITC) measurements supplied further quantitative information (Table 1) for the host-guest complexation relating to the binding affinity and thermodynamics. The MV²⁺ monomer was chosen as a model to determine the binding ability of *s*-SC4A and *d*-SC4A. Possessing two cavities, both *s*-SC4A and *d*-SC4A form 1:2 complexes with MV²⁺ as expected, as shown by the experimental *N* values of 1.96 and 1.94, respectively. The binding constants of *s*-SC4A

Complex	<i>N</i>	K_s [M ⁻¹]	ΔH° [kJ mol ⁻¹]	$T\Delta S^\circ$ [kJ mol ⁻¹]
SC4A⊃MV ²⁺ ^[b]	1	$(9.26 \pm 0.08) \times 10^5$	-27.2 ± 0.2	6.8 ± 0.2
<i>d</i> -SC4A⊃MV ²⁺	1.94 ± 0.01	$(3.59 \pm 0.06) \times 10^6$	-33.2 ± 0.1	4.2 ± 0.1
<i>s</i> -SC4A⊃MV ²⁺	1.96 ± 0.02	$(1.23 \pm 0.04) \times 10^7$	-41.0 ± 0.4	-0.5 ± 0.3

[a] Methyl viologen. [b] Data are taken from ref. [13a].

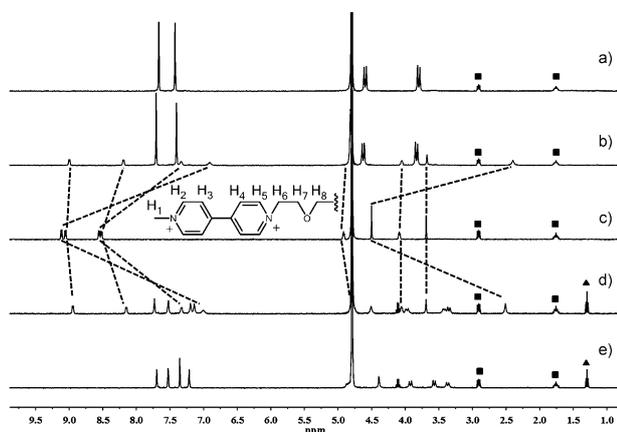


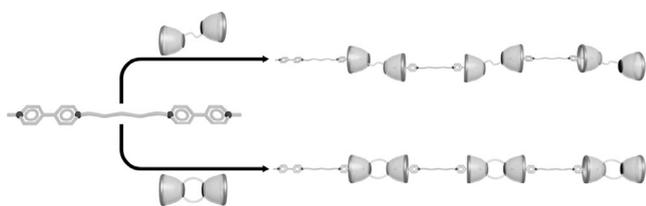
Figure 2. ¹H NMR spectra (400 MHz, D₂O, 298 K) of a) *d*-SC4A (1.0 mM), b) bisMV⁴⁺ (1.0 mM) with 1 equiv *d*-SC4A, c) bisMV⁴⁺ (1.0 mM), d) bisMV⁴⁺ (1.0 mM) with 1 equiv *s*-SC4A, and e) *s*-SC4A (1.0 mM). "■" represents the signals of DSS protons and "▲" represents the signals of ethanol protons.

and *d*-SC4A with MV²⁺ were determined to be 1.23×10^7 and 3.59×10^6 M⁻¹, respectively, by using the "one set of binding sites" model (assuming that all of the binding sites for the interacting species are identical).^[13a,25] Compared with the SC4A monomer, *s*-SC4A and *d*-SC4A exhibit stronger binding affinities towards MV²⁺, dominated by the more favorable enthalpy term. All three host-guest complexes are mainly dominated by the negative enthalpy changes, which are a result of charge, hydrogen-bonding, π -stacking, and van der Waals interactions.^[18] The enthalpy term for SC4A is much less favorable than those for *s*-SC4A ($\Delta\Delta H^\circ = 13.8$ kJ mol⁻¹) and *d*-SC4A ($\Delta\Delta H^\circ = 6.0$ kJ mol⁻¹), which should originate from the π -stacking factor. *s*-SC4A and *d*-SC4A show a relatively pinched cone conformation, which is more preorganized for capturing the planar MV²⁺ guest than SC4A, and therefore the complexation of *s*-SC4A and *d*-SC4A affords stronger π -stacking interactions with MV²⁺ than SC4A.^[18] Such high complexation stabilities for *s*-SC4A and *d*-SC4A with MV²⁺ render them able to build truly

polymeric materials. Another insightful comparison concerns the entropy terms between *s*-SC4A and *d*-SC4A. The entropy change for *s*-SC4A is less favorable than that for *d*-SC4A owing to its loss of conformational degree of freedom. In solution, the conformation of free *s*-SC4A is unfixed so that the two calixarenes can randomly swing around the ethyl bridge. Upon complexation with MV^{2+} , the intramolecular rotation is somewhat restricted, thereby leading to a loss of conformational freedom. In contrast, the conformation of free *d*-SC4A is well fixed by the two ethyl bridges and therefore the conformational loss before and after complexation is not as significant as it is for *s*-SC4A. The ITC results agree well with the aforementioned NMR and molecular simulation results.

Construction and identification of supramolecular polymers

Combining the homoditopic host *d*-SC4A (or *s*-SC4A) with homoditopic guest $bisMV^{4+}$, supramolecular polymers can be generated by iterative host-guest complexation, as shown in Scheme 2. Notably, the *d*-SC4A \supset $bisMV^{4+}$ polymer possesses



Scheme 2. Schematic illustration of the formation of supramolecular polymers of *s*-SC4A \supset $bisMV^{4+}$ and *d*-SC4A \supset $bisMV^{4+}$.

higher solubility than the *s*-SC4A \supset $bisMV^{4+}$ polymer and complex 2SC4A \supset $bisMV^{4+}$ (Figure 3). The solubilities of *s*-SC4A \supset $bisMV^{4+}$ and 2SC4A \supset $bisMV^{4+}$ are around 7 and 2 mM, whereas the solubility of *d*-SC4A \supset $bisMV^{4+}$ is hundreds of times higher. Previously we developed a series of water-soluble supramolecular polymers based on *s*-SC4A but never obtained

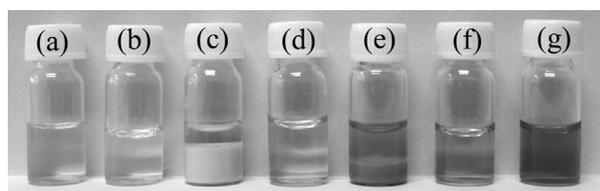


Figure 3. Images of 15.0 mM aqueous solutions of a) $bisMV^{4+}$ (solution), b) SC4A (solution), c) 2SC4A \supset $bisMV^{4+}$ (precipitation), d) *s*-SC4A (solution), e) *s*-SC4A \supset $bisMV^{4+}$ (precipitation), f) *d*-SC4A (solution), and g) *d*-SC4A \supset $bisMV^{4+}$ (solution) at 298 K.

truly polymeric materials with high viscosity due to the poor solubilities of the assemblies.^[6,13] The reason for the differences in solubility is not clear, and the high water solubility of *d*-SC4A \supset $bisMV^{4+}$ solves the problem of building highly viscous supramolecular polymeric materials.

Viscosity measurements were performed to validate the formation of two supramolecular polymers in aqueous solution. The solubility of *s*-SC4A \supset $bisMV^{4+}$ is about 7 mM at 298 K, so the specific viscosities of two polymers were compared up to 6.0 mM. As shown in Figure 4a, the *s*-SC4A \supset $bisMV^{4+}$ polymer shows lower specific viscosity than the *d*-SC4A \supset $bisMV^{4+}$ polymer even though their binding structures and stabilities are

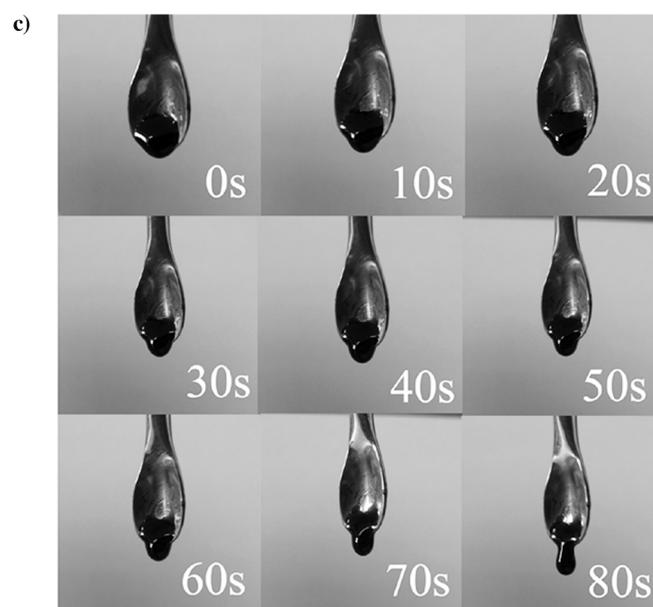
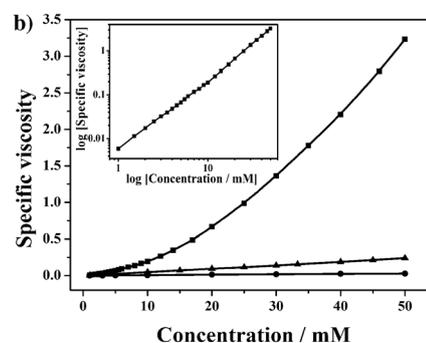
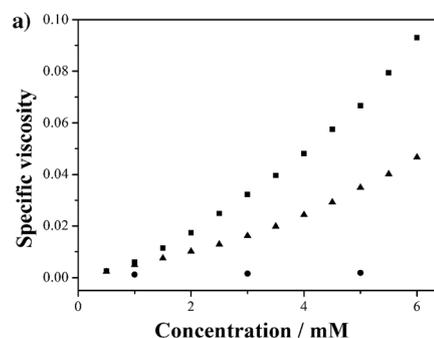


Figure 4. a) Specific viscosities of aqueous solutions of $bisMV^{4+}$ (●), *s*-SC4A \supset $bisMV^{4+}$ (▲), and *d*-SC4A \supset $bisMV^{4+}$ (■) versus concentration (0.5–6.0 mM) at 298 K. b) Specific viscosities of $bisMV^{4+}$ (●), *d*-SC4A (▲), and *d*-SC4A \supset $bisMV^{4+}$ (■) versus concentration (1.0–50.0 mM) in aqueous solutions at 298 K. Inset: Slope of a double logarithmic plot of the specific viscosity of *d*-SC4A \supset $bisMV^{4+}$ versus concentration. c) A series of digital photographs showing the flowability of *d*-SC4A \supset $bisMV^{4+}$ (250.0 mM).

similar. We inferred that the conformation of the host leads to the difference in the viscosity. *d*-SC4A possesses the more rigid and fixed conformation, as mentioned above, and thereby the *d*-SC4A⊃bisMV⁴⁺ assembly tends to stretch in solution. The degree of supramolecular polymerization increases with increasing concentration, and then the solubility is a significant factor in building supramolecular polymers with good performance.^[1] We also performed viscosity measurements on *d*-SC4A⊃bisMV⁴⁺ at higher concentrations. As shown in Figure 4b, the specific viscosity of *d*-SC4A⊃bisMV⁴⁺ varies exponentially with its concentration, which indicates the formation of a supramolecular polymer of increasing size.^[26] Control experiments showed that the bisMV⁴⁺ and *d*-SC4A subunits have markedly lower viscosity. Linear relationships between specific viscosity and concentration were observed for free bisMV⁴⁺ and *d*-SC4A, which indicates no significant physical entanglement. The double logarithmic plot of specific viscosity versus concentration gives a linear relationship with a slope of 1.7 (inset in Figure 4b). This sharp rise proves the high degree of polymerization. The high viscosity partially results from the polyelectrolyte effect. It is known that ionic species on polyelectrolyte chains repel each other, thus resulting in the expansion of the polymer coil and consequently an increase in the viscosity.^[27] As shown in Figure 4c, the polymer *d*-SC4A⊃bisMV⁴⁺, an excellent viscous liquid, drips slowly by force of gravity at a concentration of 250.0 mM, which reveals the nature of the polymer in solution.

Diffusion ordered spectroscopy (DOSY) can correlate ¹H NMR signals with the diffusion coefficient (*D*) in solution and has recently been used to characterize supramolecular polymers.^[28] According to the Stokes–Einstein relation, $D = k_B T / (6\pi\eta R)$, in which *T* denotes the temperature, *k_B* the Boltzmann constant, and η the dynamic viscosity of the solvent, the diffusion coefficient of a molecular species is inversely proportional to the hydrodynamic radius *R* of a molecule. For highly aggregated species, which have much larger *R* values than monomers, clearly, a change in the values of *D* should be observed in the DOSY spectra. Thus, to substantiate the formation of the *d*-SC4A⊃bisMV⁴⁺ assembly, DOSY experiments were also performed^[29] (see Figures S10–S12 in the Supporting Information). The corresponding *D* values are recorded in Table 2. The DOSY experiment on *d*-SC4A⊃bisMV⁴⁺ (100.0 mM) shows the same diffusion rate ($D = 0.16 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) for *d*-SC4A and bisMV⁴⁺, that is, complexed *d*-SC4A and bisMV⁴⁺ diffuse together as one entity but with a diffusion rate one order of magnitude less than those of free *d*-SC4A and bisMV⁴⁺ subunits ($D = 1.30 \times 10^{-10}$ and $3.59 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 100.0 mM). The decrease

Sample	<i>D</i> [$10^{-10} \text{ m}^2 \text{ s}^{-1}$]	<i>N</i>
<i>d</i> -SC4A⊃bisMV ⁴⁺ (100.0 mM)	0.16	1472
2SC4A⊃bisMV ⁴⁺ (2.0 mM)	1.82	1
<i>d</i> -SC4A (100.0 mM)	1.30	–
bisMV ⁴⁺ (100.0 mM)	3.59	–

in diffusion rate implies the formation of large polymeric aggregates.

Moreover, the average degree of supramolecular polymerization can be estimated from the obtained diffusion coefficients according to the Stokes–Einstein equation by simplistically assuming that all assemblies are hydrodynamically spherical.^[30] We can obtain the average polymerization number *N* as the cube root of the molecular weight of polymers has been suggested to be proportional to the reciprocal of the diffusion coefficient, $N \approx 1/(D/D_{\text{ref}})^3$, in which *D* and *D_{ref}* are the diffusion coefficients obtained from the DOSY measurements for polymer and reference complex, respectively. In this work we employed 2SC4A⊃bisMV⁴⁺ as the reference complex, which has a similar size and molecular weight as the repeating unit of the polymer. The value of *D_{ref}* obtained is listed in Table 2 (see also Figure S13 in the Supporting Information). The average polymerization number was calculated to be 1472, which indicates that the molecular weight of the *d*-SC4A⊃bisMV⁴⁺ polymer is up to 3×10^6 at 100.0 mM. Although such a calculation is merely a rough approximation because the hydrodynamic shape of the aggregates deviates from the spherical shape, it confirms that supramolecular polymerization has been effectively achieved.

Dynamic light scattering (DLS) measurements were performed to identify the hydrodynamic diameter of *d*-SC4A⊃bisMV⁴⁺ (Figure 5). One relatively wide peak was observed from 174 to 460 nm at 5.0 mM, which indicates the formation of highly polymerized supramolecular assemblies, and another was centered below 10 nm, which can be ascribed to

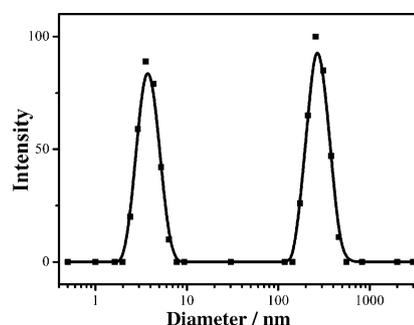


Figure 5. Hydrodynamic diameter distribution of the *d*-SC4A⊃bisMV⁴⁺ polymer (5.0 mM).

the existence of oligomers with low degrees of polymerization. The morphology of the *d*-SC4A⊃bisMV⁴⁺ assembly was also investigated by atomic force microscopy (AFM). As shown in Figure 6, several linear objects with lengths in the micron range were observed. The 1D nanostructure shows a height of 1.2 nm, which is identical to the average height of calixarene.

The electrochemical properties of the supramolecular polymers were also studied by cyclic voltammetry (CV) as viologen is electroactive (see Figure S15 in the Supporting Information).^[31] Upon complexation with calixarenes, both its reduction peaks exhibit negative shifts, which indicates that the complexation of calixarenes makes the reduction of bisMV⁴⁺

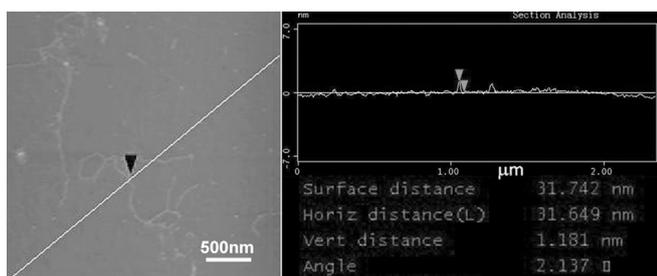


Figure 6. AFM image of the linear $d\text{-SC4A}\supset\text{bisMV}^{4+}$ polymer.

more difficult and also that the stability of the complex decreases gradually upon reduction.^[6,32] It was also observed that the second re-oxidation peak of the complexed bisMV^{4+} splits into two peaks, which means two different re-oxidation processes occur concurrently. Taking $d\text{-SC4A}$ as an example, two peaks located at -946 and -820 mV were assigned to the oxidation of complexed and uncomplexed bisMV^0 to bisMV^{2+} , respectively. To discuss the process of neutral bisMV^0 escaping from the SC4A cavity, CV experiments were performed on $d\text{-SC4A}\supset\text{bisMV}^{4+}$ at different scan rates (see Figure S15b); the minor re-oxidation peak (-946 mV) weakened with decreasing scan rate and disappeared completely at a scan rate of 5 mVs^{-1} . This means that bisMV^0 can escape completely from the calixarene cavity at a slow scan rate.

Conclusion

We have prepared a novel bis(*p*-sulfonatocalix[4]arene), $d\text{-SC4A}$, with two ethyl bridges at the lower rim, with an improved molecular conformation and rigidity for supramolecular polymerization in comparison with $s\text{-SC4A}$, a bis(*p*-sulfonatocalix[4]arene) with a single ethyl bridge. A highly soluble, linear polymer was then constructed by the complexation of $d\text{-SC4A}$ with bisMV^{4+} in water. The resulting $d\text{-SC4A}\supset\text{bisMV}^{4+}$ polymer exhibits a high degree of polymerization and high viscosity. Benefiting from the redox nature of viologen, assembly/disassembly can be effected by electrostimulus. In comparison with the water-soluble calixarene-based supramolecular polymers reported before, the present example is optimized for building truly polymeric materials.

Experimental Section

Materials

All chemicals used were reagent grade unless noted otherwise. *p*-H-calix[4]arene,^[33] *p*-sulfonatocalix[4]arene (SC4A),^[34] and the singly ethyl-bridged bis(*p*-sulfonatocalix[4]arene) ($s\text{-SC4A}$)^[6] were synthesized and purified according to previously reported procedures. All other chemicals were commercially available and of reagent grade without further purifications.

Characterization

NMR data were recorded on a Bruker AV400M or 600M spectrometer. Mass spectra were recorded on a Varian 7.0T FTMS (MALDI)

spectrometer. Elemental analyses were measured by using an elemental vario EL CUBE element analyzer. Viscometer measurements were carried out on a SCHOTT-Ubbelohde micro capillary viscometer (DIN 53810, 0.40 mm inner diameter) at 298 K in deionized water.

Isothermal titration calorimetry (ITC)

All microcalorimetric data were acquired on a thermostatted and fully computer-operated isothermal calorimetry (VP-ITC) instrument, purchased from MicroCal, Northampton, MA. The VP-ITC instrument was calibrated chemically by measurement of the complexation reaction of β -cyclodextrin with cyclohexanol (the thermodynamic data obtained were in good agreement (error $< 2\%$) with the literature data^[35]) and also by measurement of the complexation reaction of SC4A with methyl viologen (the obtained thermodynamic data were in good agreement (error $< 5\%$) with the literature data^[24]). All microcalorimetric titrations were performed in deionized water at atmospheric pressure and 298 K. Each solution was degassed and thermostatted by using a ThermoVac accessory before the titration experiment. Twenty-eight successive injections were made for each titration experiment. A constant volume ($2\ \mu\text{L}$ for the first injection and then $10\ \mu\text{L}$ per injection) of guest solution in a $0.272\ \text{mL}$ syringe was injected into the reaction cell ($1.4227\ \text{mL}$) charged with the host molecule solution in the same aqueous solution. A representative titration curve is shown in Figure 7.

As can be seen in Figures 7, S8, and S9, each titration of MV^{2+} into the sample cell gave an apparent reaction heat caused by the formation of an inclusion complex. The reaction heat decreases after each injection of MV^{2+} because less and less host molecules are available to form inclusion complexes. A control experiment was carried out for each run to determine the dilution heat by injecting an aqueous solution of the guest into a pure aqueous solution containing no host 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) to simultaneously compute the binding stoichiometry (N), complex stability constant (K_s), standard molar reaction enthalpy (ΔH°), and standard deviation from the titration curve. In general, the first point of the titration curve was removed on the basis that the concentration of the host in the cell far exceeded the concentration of the guest. Knowledge of the complex stability constant (K_s) and molar reaction enthalpy (ΔH°) enabled calculation of the standard free energy (ΔG°) and entropy changes (ΔS°) according to $\Delta G^\circ = -RT\ln K_s = \Delta H^\circ - T\Delta S^\circ$, in which R is the gas constant and T is the absolute temperature.

Typical curve fitting results for the complexation of MV^{2+} with $s\text{-SC4A}$ and $d\text{-SC4A}$ are shown in Figure 7. To check the accuracy of the observed thermodynamic parameters, two independent titration experiments were carried out to afford self-consistent thermodynamic parameters; their average values are listed in Table 1.

DLS measurements

Samples were analyzed on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-9000AT) at $\lambda = 636\ \text{nm}$ at 25°C . All DLS measurements were performed at a scattering angle of 90° . Sample solutions were prepared by filtering

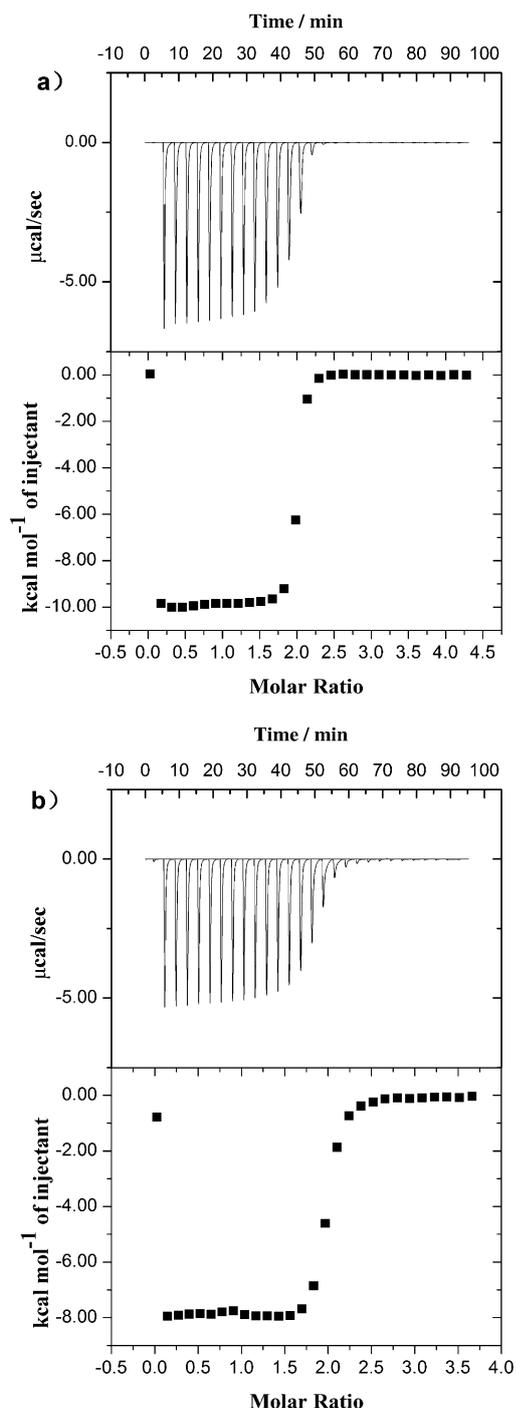


Figure 7. ITC data for sequential twenty-eight injections (2 μL for the first injection and then 10 μL per injection) of a) a MV^{2+} solution (1.80 mM) injected into an *s*-SC4A solution (0.103 mM) and b) a MV^{2+} solution (1.82 mM) injected into a *d*-SC4A (0.104 mM) solution in aqueous solution (pH 7.0) at 298 K.

each component solution (2 mL in total volume) through a 220 nm syringe filter into a clean scintillation vial.

AFM measurements

Sample solutions were dropped onto newly clipped mica and then dried in air. The samples were performed by using a multi-mode

Illa AFM instrument (Veeco Metrology, USA) in tapping mode in air at room temperature.

Cyclic voltammetry measurements

Cyclic voltammetry was carried out on a BAS Epsilon electrochemical analyzer with C3-cell stand. All solutions were prepared in a 50 mM NaCl solution at 298 K and deoxygenated by purging with dry nitrogen for at least 15 min before each experiment. The glassy carbon working electrode was polished to a mirror with a 0.05 mm BAS alumina suspension on a brown texmet polishing pad, sonicated in distilled water for a few minutes to remove any residual alumina particles, and then rinsed with ethanol before use. A platinum wire was used as the counter electrode. The potentials were recorded with respect to an Ag/AgCl reference electrode (immersed in a solution containing 3 M sodium chloride).

Synthesis of bisMV⁴⁺

BisMV⁴⁺ was synthesized and purified according to a literature procedure.^[20a] 4,4'-Dipyridyl (4.0 mmol) was dissolved in anhydrous CH_3CN (10 mL) and heated at reflux in a 50 mL three-necked round-bottomed flask under a nitrogen atmosphere. Then oligoether glycol diiodide (1 mmol) in anhydrous CH_3CN (10 mL) was dropped into the flask whilst stirring, and the reaction mixture was maintained under reflux for an additional 24 h. Upon cooling the mixture to room temperature, it was added dropwise into Et_2O (250 mL) and a precipitate formed immediately. After cooling to 0 °C and allowing to stand for several hours, the precipitate produced was filtered and recrystallized from anhydrous CH_3CN to afford the product as a solid and then dried under vacuum (yield: 53%). This product (0.4 mmol) was dissolved in dimethylformamide (DMF; 10 mL) and then the CH_3I (2.0 mmol) was added. The reaction mixture was stirred at 90 °C for 24 h. The solids were then collected and washed with anhydrous CH_3CN . The product was dried under vacuum overnight (yield: 75%). ¹H NMR (400 MHz, D_2O , 298 K): δ = 9.123 (d, J = 6.8 Hz, Ar-H, 4H), 9.059 (d, J = 6.4 Hz, Ar-H, 4H), 8.565 (d, J = 6.0 Hz, Ar-H, 4H), 8.545 (d, J = 6.0 Hz, Ar-H, 4H), 4.821 (t, J = 4.4 Hz, N- CH_2 , 4H), 4.501 (s, N- CH_2 , 6H), 4.091 (t, J = 4.8 Hz, O- CH_2 , 4H), 3.692 ppm (s, CH_2 - CH_2 , 4H).

Synthesis of d-C4A

A mixture of *p*-H-calix[4]arene (4.0 g, 9.4 mmol) and K_2CO_3 (2 g, 14.5 mmol) was heated at reflux in acetonitrile (60 mL) for 0.5 h under a nitrogen atmosphere. 1,2-Dibromoethane (3.5 g, 18.8 mmol) was added and the solution was heated at reflux for 18 h. After cooling to room temperature, the solvent was removed by rotatory evaporation. The residue was dissolved in CH_2Cl_2 , washed with 0.1 M HCl solution (3 \times 50 mL), dried over anhydrous MgSO_4 , and concentrated in vacuum. The crude solid was purified by chromatography on silica gel using CH_2Cl_2 /petroleum ether (60–90 °C) as eluent to give a pure white product in 18% yield (0.78 g). ¹H NMR (400 MHz, TMS, CDCl_3): δ = 8.07 (s, ArOH, 4H), 7.03 (d, J = 7.6 Hz, Ar-H, 8H), 6.96 (d, J = 7.6 Hz, Ar-H, 8H), 6.78 (t, J = 7.6 Hz, Ar-H, 4H), 6.60 (t, J = 7.6 Hz, Ar-H, 4H), 4.65 (s, $\text{OCH}_2\text{CH}_2\text{O}$, 8H), 4.57 (d, J = 12.8 Hz, Ar CH_2 Ar, 4H), 3.46 ppm (d, J = 12.8 Hz, Ar CH_2 Ar, 4H); ¹³C NMR (100 MHz, TMS, CDCl_3): δ = 153.64 (Ar-O), 153.45 (Ar-OH), 132.88 (Ar- CH_2), 129.18 (Ar- CH_2), 128.37 (Ar-H), 127.89 (Ar-H), 125.29 (Ar-H), 118.70 (Ar-H), 76.37 (OCH_2), 32.10 ppm (Ar CH_2 Ar); HRMS (MALDI-TOF): calcd for 923.3560 $[\text{M}+\text{Na}]^+$; found: 923.3550.

Synthesis of d-SC4A

d-SC4A was prepared according to a similar procedure previously reported by our group. d-C4A (0.5 g, 0.56 mmol) suspended in conc. H₂SO₄ (2 mL, 98%) was stirred at 50 °C for 24 h. After cooling to room temperature, the solution was added to cold diethyl ether dropwise. The resulting sticky precipitate was collected by filtration, washed with diethyl ether (3 × 50 mL), and dissolved in distilled water (250 mL). Following neutralization by 1 M NaOH solution to pH 7, the solvent was removed in vacuum. The crude solid obtained was later subjected to recrystallization (water/ethanol = 1:1) to give the title product as a light-gray powder (0.6 g, 63% yield). ¹H NMR (400 MHz, D₂O, DSS): δ = 7.67 (s, Ar-H, 8H), 7.43 (s, Ar-H, 8H), 4.78 (s, OCH₂CH₂O, 8H), 4.59 (d, J = 13.6 Hz, Ar-CH₂-Ar, 8H), 3.80 ppm (d, J = 13.6 Hz, Ar-CH₂-Ar, 8H); ¹³C NMR (100 MHz, D₂O): δ = 155.40, 155.31 (Ar-SO₃⁻), 139.47, 133.75, 132.89, 127.54, 126.59 (Ar-H), 76.07 (O-CH₂CH₂-O), 31.44 ppm (Ar-CH₂-Ar); elemental analysis calcd (%) for C₆₀H₄₂O₃₂S₈Na₁₀·(H₂O)₁₈: C 34.55, H 3.77; found: C 34.41, H 3.71.

Acknowledgements

This work was supported by the 973 Program (Grant 2011CB932502) and the National Natural Science Foundation of China (Grants 91227107, 21172119 and 21322207), which is gratefully acknowledged.

Keywords: calixarenes · cyclic voltammetry · host-guest systems · polymers · supramolecular chemistry

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Received: August 27, 2013

Published online on February 26, 2014