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Supramolecular Polymers

Water-Soluble Supramolecular Polymerization Driven by Multiple Host-Stabilized Charge-Transfer Interactions**

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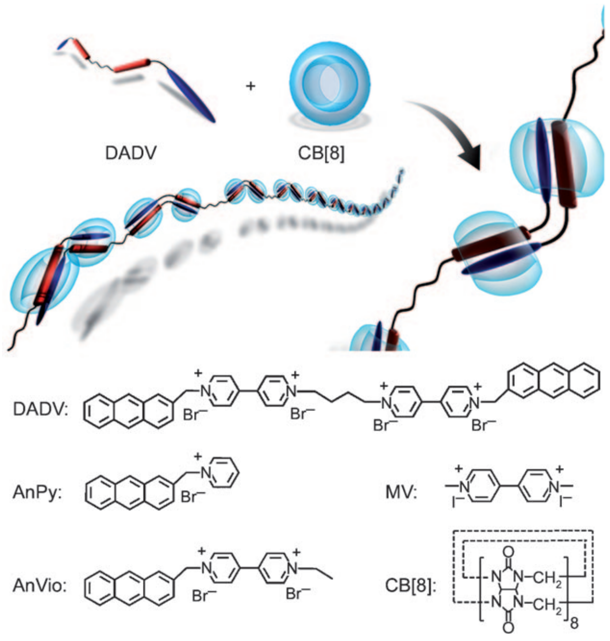
Supramolecular polymers are defined as polymeric arrays of monomeric units that are brought together by reversible and highly directional secondary interactions.[1] Owing to the dynamic and reversible nature of noncovalent interactions, supramolecular polymers are endowed with new structures and functions, for example degradability, reversibility, stimuli-responsiveness, and self-healing.[2] In principle, different directional intermolecular interactions can be employed to fabricate supramolecular polymers; however, the interactions must be strong enough to obtain polymers with high degree of polymerization. Among the noncovalent interactions for constructing supramolecular polymers, hydrogen bonding[3] and metal–ligand interactions[4] are the most commonly used because of their high binding constants. The construction of supramolecular polymers by charge-transfer interactions is not feasible owing to the low strength of these interactions. Moreover, owing to the generally low solubility in water of the charge-transfer components, the preparation of supramolecular polymers based on charge-transfer interactions in water is a challenge.

Herein, we have developed the new idea of utilizing multiple host-stabilized charge transfer (HSCT) interactions for fabricating supramolecular polymers. HSCT is a concept that was established by Kim et al. in which donor and acceptor are both encapsulated in the cavity of the host cucurbit[8]uril (abbrieviated to CB[8]).[5] Due to the short distance between the donor and the acceptor, the CT interaction is greatly enhanced. Furthermore, encapsulation gives the CT complex considerable solubility in water. However, attempts to obtain supramolecular polymers with a high degree of polymerization utilizing only single HSCT interactions have been unsuccessful[5c,e,f] for the following reasons: 1) The strength of single HSCT interactions was not sufficient; and 2) single HSCT interactions do not have high orientation selectivity, thus leading to the formation of cyclic species (Supporting Information, Figure S1) and suppressing the formation of polymeric species.

To overcome these two problems, we designed and synthesized a multifunctional monomer that is able to form multiple HSCT interactions. The monomer is 1′,1′′-(butane-1,4-diyl)bis(1-(anthracen-2-ylmethyl)-4,4′-bipyridine-1,1′-diium)bromide (DADV; Scheme 1). DADV contains two viologen moieties as electron acceptors and two anthracene moieties as electron donors. The double HSCT interactions can drive the monomers to join together in head to tail fashion when encapsulated in CB[8]. Moreover, butylidene is employed as a spacer, and formation of the 1:1 cyclic complex is inhibited due to the short length of the spacer. Furthermore, because of the charge repulsion between the two viologen moieties, the 2:2 cyclic complex can also be prevented (Supporting Information, Figure S2). Consequently, such a design of molecular building blocks can successfully suppress cyclization, thus favoring the formation of supramolecular polymers.



Scheme 1. Representation of the formation of the supramolecular polymer based on multiple host-stabilized charge-transfer interactions, and the structures of monomers DADV and CB[8] as well as the model molecules AnPy, MV, and AnVio.

Apart from introducing multiple HSCT interactions, we have chosen anthracene as an electron donor to achieve a

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high binding constant. Anthracene is planar and electron-rich, and it can have higher affinity with MV-CB[8] than naphthalene or tryptophan, which have been extensively reported in the literature.[6] The affinity of anthracene and MV-CB[8] was confirmed by isothermal titration calorimetry (ITC) experiments. Taking 1-(anthracen-2-ylmethyl)pyridinium bromide (AnPy) and 1,1′-dimethyl-4,4′-bipyridine-1,1′-diium iodide (MV) as model molecules, MV first binds to CB[8] in 1:1 ratio to form the MV-CB[8] complex with a binding constant K_1 on the order of 10^5 L mol^{-1}.[6a] The MV-CB[8] complex can further bind with AnPy with binding constant K_2. MV-CB[8] was found to bind with AnPy in 1:1 molar ratio with $K_2 = 1.1 \times 10^6$ (Supporting Information, Figure S3). This value is indeed higher than the corresponding value for naphthalene or tryptophan (10^3–10^5). The stronger binding facilitates the formation of a supramolecular polymer with a high degree of polymerization.

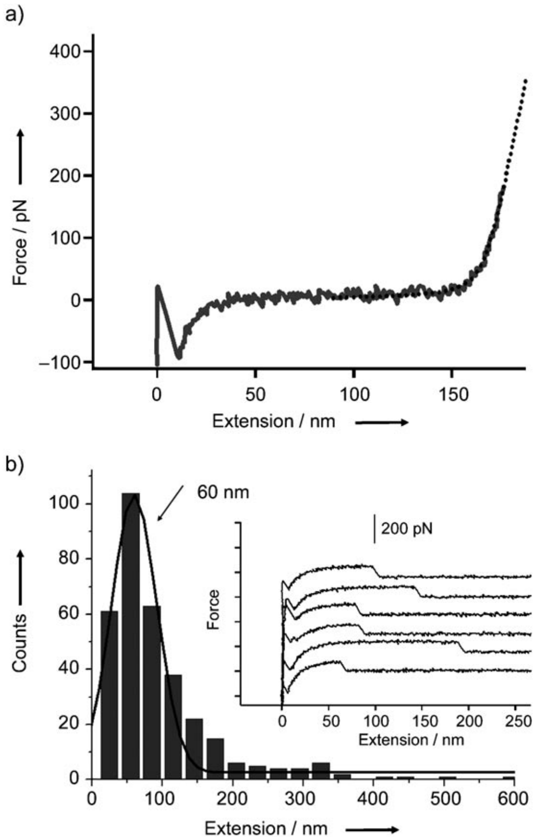

Figure 1. a) A typical force–extension curve with a peak (——) obtained by single-molecule force spectroscopy, which indicates the existence of long-chain supramolecular polymer. Parameters that embody the mechanical properties of the supramolecular polymer chain were calculated through M-FJC model fitting (•••••): $l_k = 2.2 \pm 0.1$ nm, $K_{segment} = 1250 \pm 50$ pN nm^{-1}. b) Histogram of the lengths of plateaus. The most probable length was determined by Gaussian fitting. Inset: Force–extension curves with a long plateau corresponding to desorption of supramolecular polymer chains from the substrate. These curves have been shifted vertically for clarity.

The solubility of DADV in water is very limited, and the solubility of CB[8] is even smaller. However, when they were dissolved together at 1:2 molar ratio in water, their solubility was remarkably enhanced and a purple solution was obtained, suggesting that water-soluble DADV-2CB[8] HSCT complexes were formed. The stoichiometry between DADV and CB[8] was confirmed to be 1:2 by a Job plot (Supporting Information, Figure S4a), in agreement with the molecular design.

To confirm that chain-like supramolecular polymers were formed on the basis of HSCT complexes of DADV-2CB[8] in solution, we utilized AFM-based single-molecule force spectroscopy (SMFS)[7] to provide evidence. Figure 1 a shows a representative force–extension curve (in brief, force curve) obtained in the solution of DADV-2CB[8] (0.10 mM), which is similar to the force curves for stretching of traditional polymer chains. As a control experiment, no force curve appeared when we carried out the SMFS experiment in the solution of AnPy-MV-CB[8]. The modified freely-jointed-chain (M-FJC) model[7d,8] was found to fit the curves very well, suggesting that the mechanical properties of the HSCT complex are similar to those of traditional polymers. The fitting gave the Kuhn length (l_k) 2.2 ± 0.1 nm and the segment elasticity ($K_{segment}$) $(1.25 \pm 0.05) \times 10^3$ pN nm^{-1}. l_k is slightly larger than that of a traditional flexible polymer,[9] showing that the supramolecular polymer chains are not as flexible as traditional polymer chains, whereas the value of $K_{segment}$ is much smaller than that of a traditional polymer,[9] showing that the supramolecular polymer chains are easily lengthened as a spring, which is rationalized by considering the nature of non-covalent bonds. Zou et al. reported that supramolecular polymers based on multiple hydrogen bonding can show a stretching peak in SMFS,[7a] which is similar to the force curves obtained in our experiment. The results above indicate that we obtained long-chain supramolecular polymers, and the supramolecular polymer chains show mechanical properties comparable with those of traditional polymers.

Apart from the normal curves, force curves with a long plateau were also obtained (Figure 1 b, insert), which is another type of typical curve for a traditional polymer. The plateau indicates that part of the supramolecular polymer chain adsorbs on the substrate with a train-like conformation,[7c] and the adsorbing part is desorbed continuously from the substrate at higher forces. By statistically analyzing the lengths of the plateaus in all the curves, the most probable length was determined, by Gaussian fitting, to be 60 nm (Figure 1 b). The result means the average length of the supramolecular polymer chains is larger than 60 nm.[7c]

Dynamic light-scattering (DLS) experiments were performed to provide further evidence for the existence of supramolecular polymers of DADV-2CB[8]. The solution of DADV-2CB[8] exhibits a hydrodynamic radius R_h of about 30 nm (Supporting Information, Figure S5a), which indicates the existence of long supramolecular polymer chains. As a comparison, AnPy-MV-CB[8] supramolecular complex has a R_h of about 0.4 nm, indicating that no supramolecular polymers are formed (Supporting Information, Figure S5b).

Formation of the supramolecular polymers was also supported by the ^{1}H NMR spectra (Supporting Information, Figure S6) of DADV and its HSCT complex with CB[8]. The spectrum of the model molecule 1-(anthracen-2-ylmethyl)-1′-ethyl-4,4′-bipyridine-1,1′-diium bromide (AnVio) was used as a comparison. Upon formation of the HSCT complex with CB[8], signals corresponding to the hydrogen atoms of the anthracene and viologen moieties of DADV broadened. Correspondingly, the signal intensity of AnVio-CB[8] remained sharp and clear. Such a contrast also confirms the supramolecular polymerization of DADV-2CB[8].

UV/Vis spectroscopy was employed to answer the question of whether binding occurred as expected in the polymerization process. A series of aqueous solutions of 0.1 mM DADV with different molar ratios of CB[8] were prepared. Figure 2 shows that upon addition of CB[8], a broad absorption band at wavelength higher than 400 nm emerged, corresponding to the characteristic absorption of a charge-transfer interaction.[5] Notably, when a smaller amount of CB[8] was added, the CT absorption band peaked at about 540 nm, and the absorbance increased with increase of CB[8] concentration. However, as the ratio of CB[8] to DADV was increased from 1:1 to 1:2, the CT band showed a hypochromatic shift, eventually to about 490 nm.

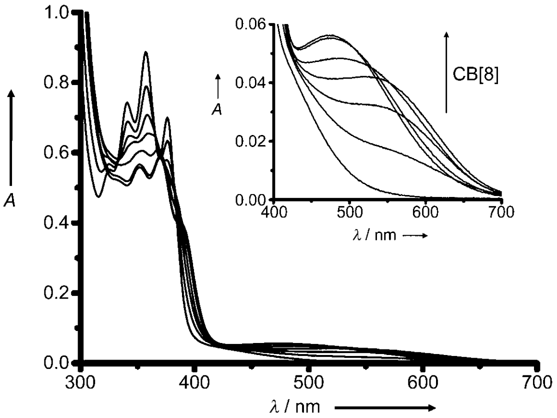

Figure 2. UV/Vis spectra of DADV (0.10 mM) with different ratios of CB[8] (CB[8]/DADV = 0, 1:3, 2:3, 1:1, 4:3, 5:3, 2:1). Inset: Magnification of the region 400–700 nm.

Two model systems were employed to clarify the situation. AnPy-MV-CB[8] and AnVio-CB[8] were used as single and dual HSCT interaction systems, respectively. Figure 3 a shows that upon addition of an increasing ratio of MV-CB[8] to a 0.2 mM AnPy solution, the characteristic CT absorption band with peak at about 540 nm increased concomitantly. Similarly, in the UV/Vis spectra on AnVio (0.2 mM) with different ratios of CB[8] (Figure 3 b), the CT absorption band was found at about 490 nm. On the basis of the information provided by these two model systems, the CT bands of DADV with different ratio of CB[8] have been analyzed by software that can separate overlapped peaks. Single and double HSCT interactions were found to coexist at the very beginning (Supporting Information, Figure S7); with an increase in the ratio of CB[8], the proportion of complex driven by double HSCT interactions becomes larger. When two equivalents of CB[8] is added, only complex is found, driven by double HSCT interactions.

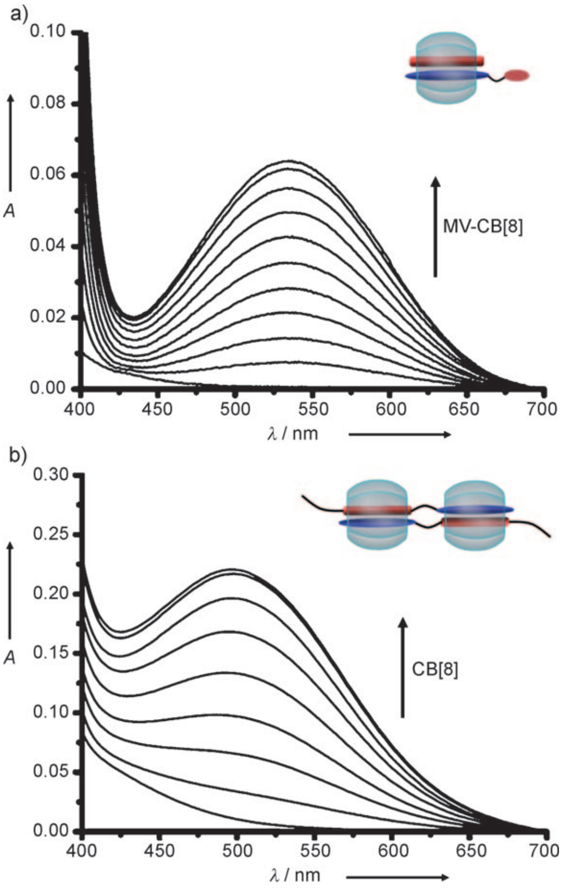

Figure 3. Partial UV/Vis spectra of the complexation of a) AnPy (0.20 mM) with different ratios of MV-CB[8] (MV-CB[8]/AnPy = 0, 1:8, 1:4, 3:8, 1:2, 5:8, 3:4, 7:8, 1:1, 9:8, 5:4); b) AnVio (0.20 mM) with different ratios of CB[8] (CB[8]/AnVio = 0, 1:8, 1:4, 3:8, 1:2, 5:8, 3:4, 7:8, 1:1).

A further interesting finding is that a deep purple gel was formed when the concentration of DADV was increased to 4 mM and two equivalents of CB[8] were added (Figure 4). A possible explanation of this behavior is that when the concentration of monomer reaches 4 mM, supramolecular polymers with much higher degree of polymerization are formed, and further assemble to form supramolecular polymer gels. This hypothesis was supported by a series of control experiments. When an 8 mM AnVio-CB[8] sample which contains similar components to 4 mM DADV-2CB[8] (the

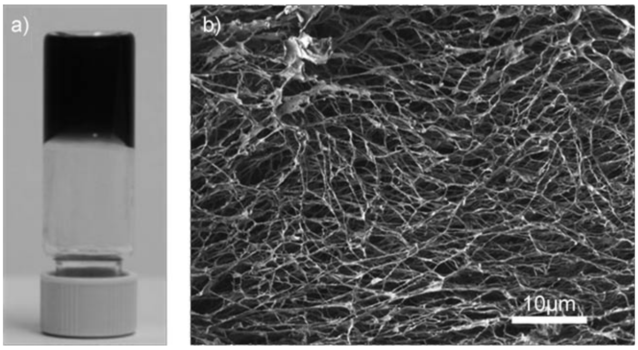

Figure 4. a) Gel formed by DADV-2CB[8]. b) SEM image of the gel.

amount of anthracene, viologen moieties, and CB[8]) was dissolved in water, gelation did not occur (Supporting Information, Figure S8a). The most likely reason is that AnVio-CB[8] cannot form a polymeric structure. Moreover, when MV, the polymerization inhibitor, was added to the gel, the gel collapsed in a very short time (Supporting Information, Figure S8b). Both of these control experiments indicate that polymeric structure is crucial to gel formation. Furthermore, interactions between supramolecular polymer chains are needed to form a gel. It is thought that the interactions between carbonyl group portals and hydronium ions of CB[8] and also between CB[8] themselves are the main driving force for gelation, as observed previously for the CB[7] system.[10] Upon addition of K^+, the interactions can be easily destroyed and the gel collapses, owing to the binding of potassium ions with the carbonyl groups (Supporting Information, Figure S8c).

In conclusion, we prepared a novel water soluble supramolecular polymer with high degree of polymerization that is based on multiple HSCT interactions. It was demonstrated that multiple HSCT interactions, which possess a high binding constant and orientation selectivity, can be used as the driving force to construct a supramolecular polymer. This study enriches the field of supramolecular polymerization with new building blocks and driving forces, and the concept is expected to be used as a new effective method for fabricating supramolecular materials.

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