# Supramolecular Polymers Constructed from Macrocycle-Based Host−Guest Molecular Recognition Motifs

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CONSPECTUS: Supramolecular polymers, fabricated via the combination of supramolecular chemistry and polymer science, are polymeric arrays of repeating units held together by reversible, relatively weak noncovalent interactions. The introduction of noncovalent interactions, such as hydrogen bonding, aromatic stacking interactions, metal coordination, and host−guest interactions, endows supramolecular polymers with unique stimuli responsiveness and self-adjusting abilities. As a result, diverse monomer structures have been designed and synthesized to construct various types of supramolecular polymers. By changing the noncovalent interaction types, numbers, or chemical structures of functional groups in these monomers, supramolecular polymeric materials can be prepared with tailored chemical and physical properties. In recent years, the interest in supramolecular polymers has been extended from the preparation of intriguing topological structures to the discoveries of potential applications as functional materials. Compared with traditional polymers, supramolecular polymers show some advantages in the fabrication of reversible or responsive materials. The development of supramolecular polymers also offers a platform to construct complex and sophisticated materials with a bottom-up approach.

Macrocylic hosts, including crown ethers, cyclodextrins, calixarenes, cucurbiturils, and pillararenes, are the most commonly used building blocks in the fabrication of host−guest interaction-based supramolecular polymers. With the introduction of complementary guest molecules, macrocylic hosts demonstrate selective and stimuli-responsive host−guest complexation behaviors. By elaborate molecular design, the resultant supramolecular polymers can exhibit diverse structures based on the self-selectivity of host−guest interactions. The introduction of reversible host−guest interactions can further endow these supramolecular polymers with interesting and fascinating chemical/physical properties, including stimuli responsiveness, self-healing, and environmental adaptation. It has been reported that macrocycle-based supramolecular polymers can respond to pH change, photoirradition, anions, cations, temperature, and solvent. Macrocycle-based supramolecular polymers have been prepared in solution, in gel, and in the solid state. Furthermore, the solvent has a very important influence on the formation of these supramolecular polymers. Crown ether- and pillararene-based supramolecular polymers have mainly formed in organic solvents, such as chloroform, acetone, and acetonitrile, while cyclodextrin- and cucurbituril-based supramolecular polymerizations have been usually observed in aqueous solutions. For calixarenes, both organic solvents and water have been used as suitable media for supramolecular polymerization. With the development of supramolecular chemistry and polymer science, various methods, such as nuclear magnetic resonance spectroscopy, X-ray techniques, electron microscopies, and theoretical calculation and computer simulation, have been applied for characterizing supramolecular polymers. The fabrication of macrocycle-based supramolecular polymers has become a currently hot research topic. In this Account, we summarize recent results in the investigation of supramolecular polymers constructed from macrocycle-based host−guest molecular recognition motifs. These supramolecular polymers are classified based on the different macrocycles used in them. Their monomer design, structure control, stimuli-responsiveness, and applications in various areas are discussed, and future research directions are proposed. It is expected that the development of supramolecular polymers will not only change the way we live and work but also exert significant influence on scientific research.
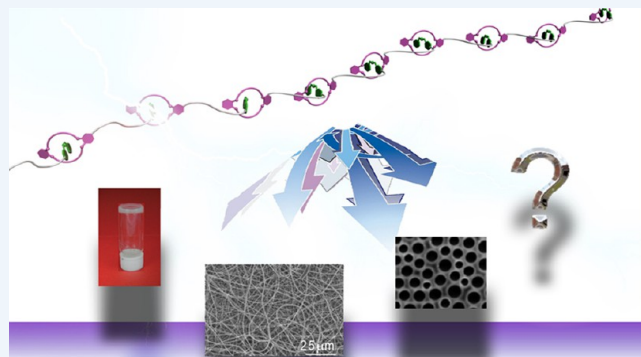
■ INTRODUCTION

The development of new polymers not only has changed the way we live and work but also exerts significant influence on scientific research. Inspired by the amazing properties of polymeric structures with high molecular weights, scientists try to expand the concepts of polymers and thereby obtain novel materials with specific structures and properties.[1,2] Supramolecular polymers, first defined by J.-M. Lehn, are the fruits of the perfect combination between polymer science and supramolecular chemistry.[3,4] Engendered by the above two fields, supramolecular polymers possess a variety of advantages
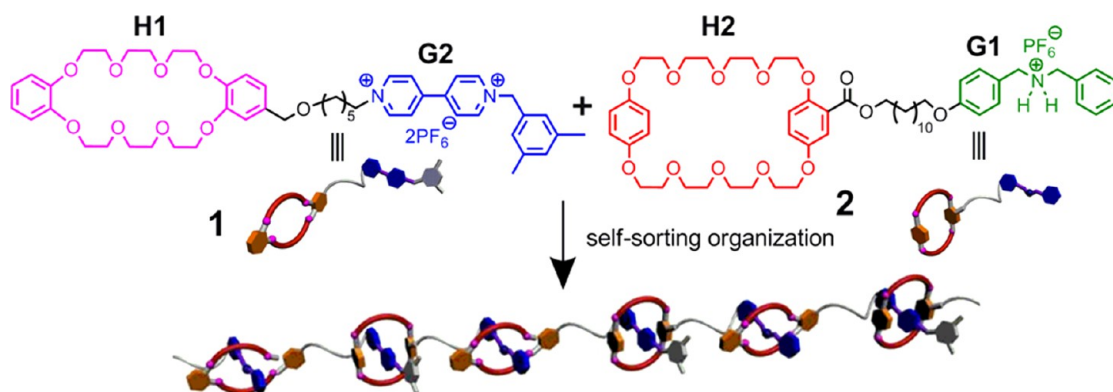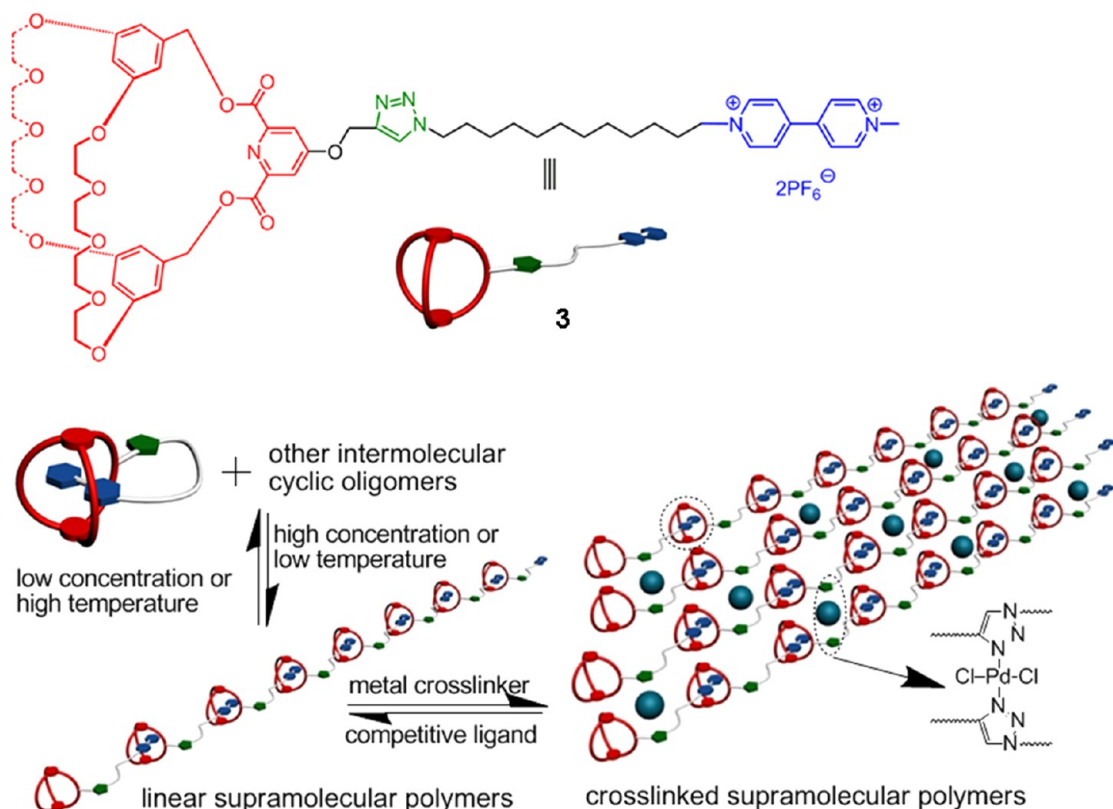
Figure 1. Formation of supramolecular alternating copolymers from self-sorting organization of two heteroditopic monomers. Adapted with permission from ref 27. Copyright 2008 American Chemical Society.

Figure 2. Controlling supramolecular polymer topologies. Adapted with permission from ref 28. Copyright 2010 John Wiley and Sons, Inc.

such as highly dynamic, multiple stimuli responsive, and self-adjusting properties.[5,6]

Macrocylic hosts, including crown ethers,[7] cyclodextrins,[8,9] calixarenes,[2] cucurbiturils,[10,11] and pillararenes,[12] are important building blocks in host–guest and supramolecular chemistry. Over the past 2 decades, many charged and neutral molecules have been designed and synthesized to complex macrocyclic hosts with high binding affinities and specific selectivities.[13–17] Due to the reversibility and responsiveness of host–guest interactions, these artificial host–guest complexes, especially pseudorotaxanes and rotaxanes, form the basis of macrocycle-based host–guest supramolecular polymers.[1,18,19]

In this Account, we mainly focus on the supramolecular polymerization of low molecular weight monomers and summarize recent progress for the preparation and function-alization of macrocycle-based supramolecular polymers. Specif-ically, we classify the resulting supramolecular polymers depending on the types of macrocyclic hosts. Special attention is paid to two aspects: (1) topological control of supra-molecular polymers by elaborate molecular design; (2) the performance of supramolecular polymeric materials in the bulk state.[2,18–20] Although many beautiful examples of supra-molecular polymers based on host–guest interactions have been reported up to now, not all of them can be highlighted in this Account due to the space limitation.

■ SUPRAMOLECULAR POLYMERS CONSTRUCTED FROM CROWN ETHER-BASED HOST–GUEST MOLECULAR RECOGNITION MOTIFS

With the development of crown ether chemistry, many organic salts have been investigated for the complexation with crown ethers.[7,13,14] In earlier studies, researchers found that rigid
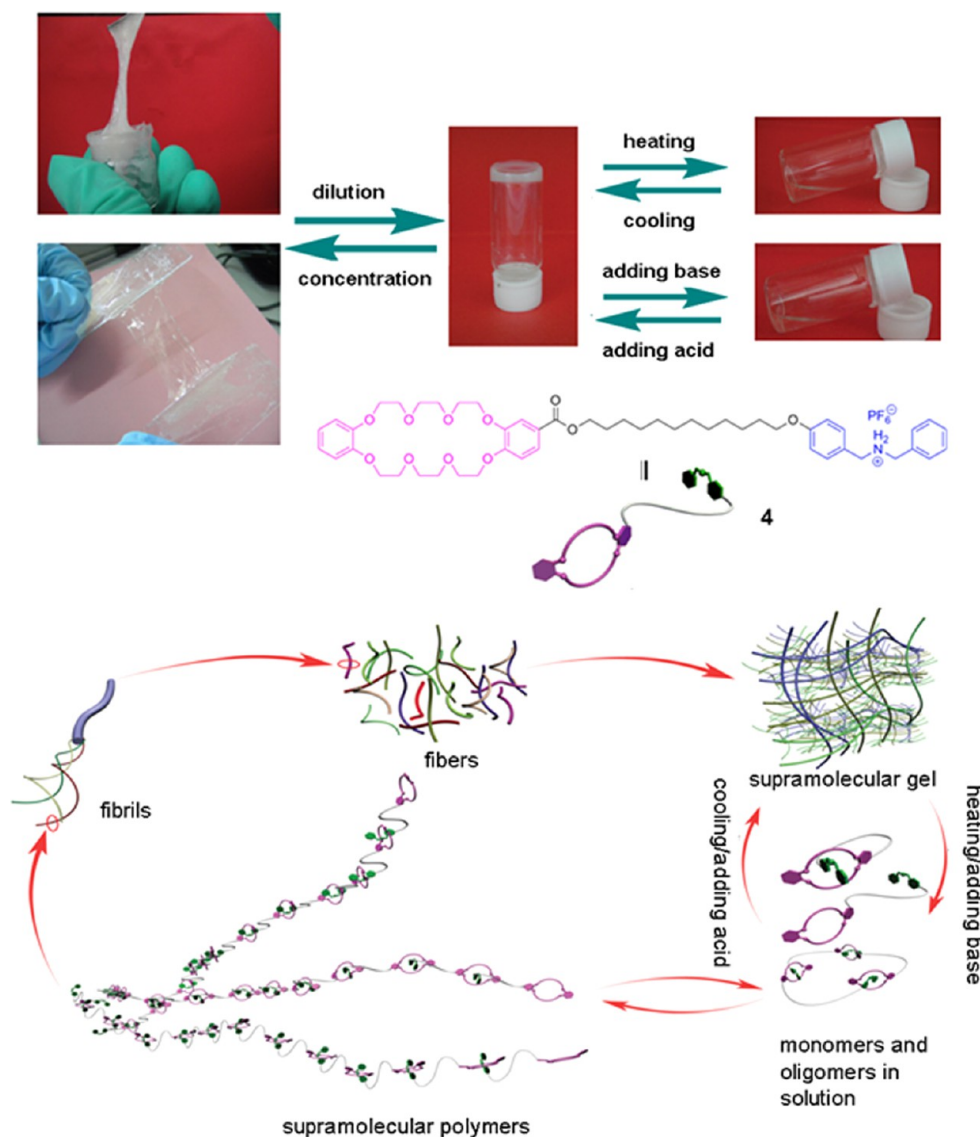
Figure 3. A dual-responsive supramolecular organogel via a crown ether-based molecular recognition motif and the cartoon representation for its formation. Adapted with permission from ref 29. Copyright 2011 John Wiley and Sons, Inc.

heteroditopic monomers made by directly linking the host–guest moieties favored forming low molecular weight oligomers. As a result, linear supramolecular polymers could be obtained only at very high monomer concentrations.[21–23] Later on, Gibson's group and our group demonstrated that introducing a flexible aliphatic spacer in the monomer destabilizes the cyclic oligomers and thereby favors the linear extension, resulting in a relatively low critical polymerization concentration (CPC) for the supramolecular polymerization process.[18,23–26]

We endeavor to utilize a multicomponent self-assembly strategy to achieve more complicated and hierarchical supramolecular polymers. Therefore, we prepared alternating supramolecular copolymers by integration of the "self-sorting" concept (Figure 1).[27] In order to accomplish self-sorting self-assembly for the supramolecular polymerization process, it is necessary to realize high selectivity and specific stoichiometry for the host–guest recognition process. Luckily, we found that DB24C8 (H1)/DBA (G1) complex and BPP34C10 (H2)/paraquat (G2) complex are a pair of building blocks with "self-sorting" recognition behavior in solution. Subsequently, we

designed and synthesized two AB-type heteroditopic monomers **1** and **2**. Monomer **1** possesses DB24C8 and paraquat units, while monomer **2** contains BPP34C10 and DBA moieties on two ends. On the basis of concentration-dependent ^{1}H NMR spectra, we proved that at low monomer concentration, cyclic oligomeric species were dominant. As the monomer concentrations gradually increase, signals of protons belonging to linear species become more and more evident, accompanied by leveling off of oligomeric peaks, suggesting that at high monomer concentration supramolecular alternating copolymers formed in solution. A double logarithmic representation of specific viscosity versus crown concentration demonstrated that at high concentration (concentration above CPC), the curve approached a slope of 2.05, higher than the slope of the curve at low concentration (1.02). The considerable slope change definitely supported the formation of alternating supramolecular copolymers. Theoretical calculations were also consistent with the results obtained from NMR and specific viscosity experiments.

We further utilized the orthogonal self-assembly protocol to control the topology of supramolecular polymers.[18,19,28] Briefly,
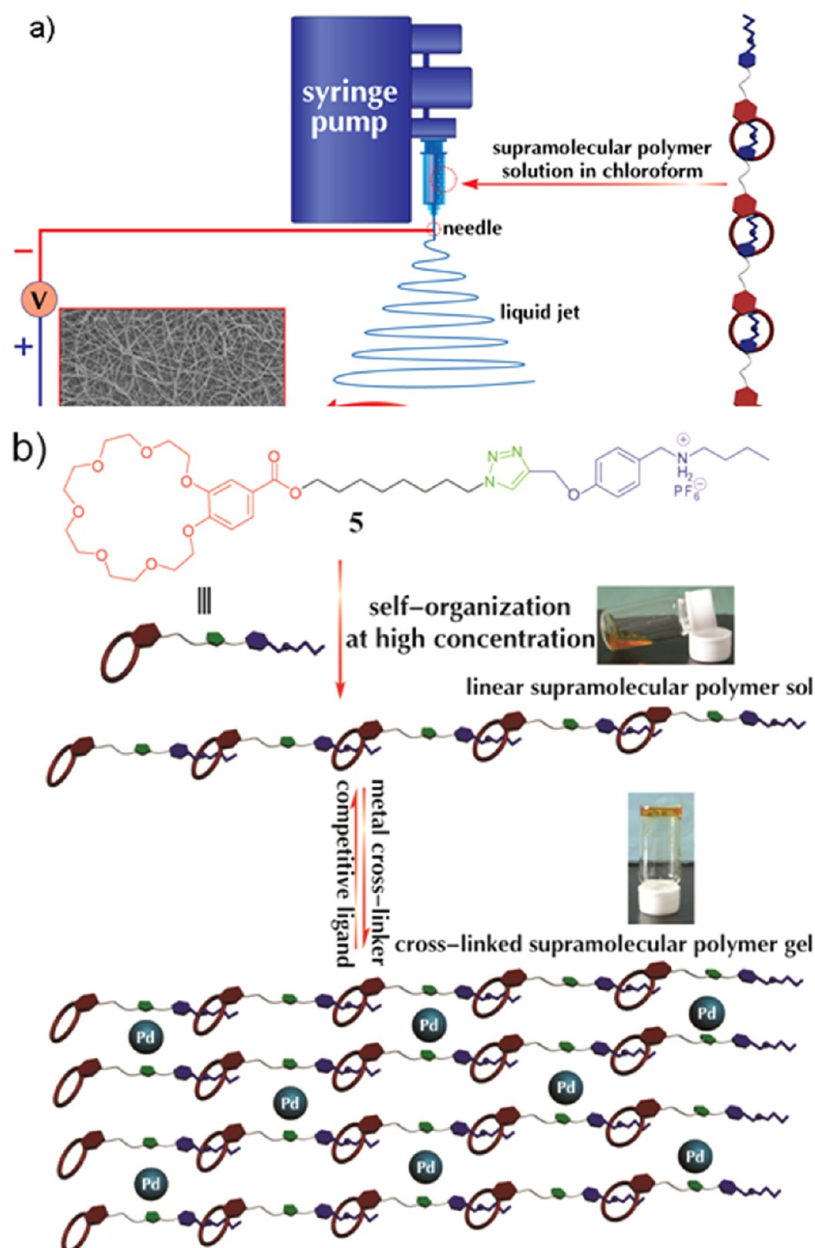
Figure 4. Electrospinning (a) and gelation properties (b) of an B21C7-based AB-type supramolecular polymer prepared from monomer **5**. Adapted with permission from refs 30 and 32. Copyright 2011 Royal Society of Chemistry and 2012 John Wiley and Sons, Inc., respectively.

our idea was to introduce metal coordination interactions to linear supramolecular polymers constructed via host–guest interactions.[18,19,28] Hence, we incorporated a 1,2,3-triazole unit into the structure of cryptand-paraquat-based monomer **3**, which served as the ligand for coordination with the transition metal Pd^{2+} (Figure 2).[28] Since a high association constant could be achieved for the cryptand and paraquat host–guest pair, monomer **3** formed a linear supramolecular polymer in acetonitrile. Furthermore, 1,2,3-triazole groups embedded in the linear polymeric species were coordinated with $PdCl_2(PhCN)_2$ to afford a cross-linked supramolecular polymer, which had relatively larger aggregation sizes compared with linear analogues, as evidenced by remarkable changes in viscosity and diffusion coefficient values. For example, when 0.5 equiv of $PdCl_2(PhCN)_2$ was added to a solution of monomer **3** at 100 mM, a decrease in the diffusion coefficient from 3.53×10^{-10} to 2.69×10^{-10} m^2 s^{-1} was observed. In view of that fact

that triphenylphosphine exhibits much stronger coordination ability than the 1,2,3-triazole group for Pd^{2+}, the cross-linked supramolecular polymers were converted back to the linear species via addition of this competitive ligand.

We then turned to investigate supramolecular polymerization beyond the solution state. Therefore, by constructing cross-linked supramolecular polymeric architectures, we could further achieve soft materials such as gels and nanofibers, which are easier to process and regulate.[18,19,29−32] In 2011, we successfully obtained supramolecular organogels by the utilization of the DB24C8/DBA molecular recognition motif (Figure 3).[29] Specifically, monomer **4** self-assembled into a linear supramolecular polymer in acetonitrile. Under appropriate conditions, the linear polymer hierarchically assembled via weak van der Waals interactions into a three-dimensional network, which acted as the matrix to trap solvent molecules. Reversible transitions between gel and sol states were
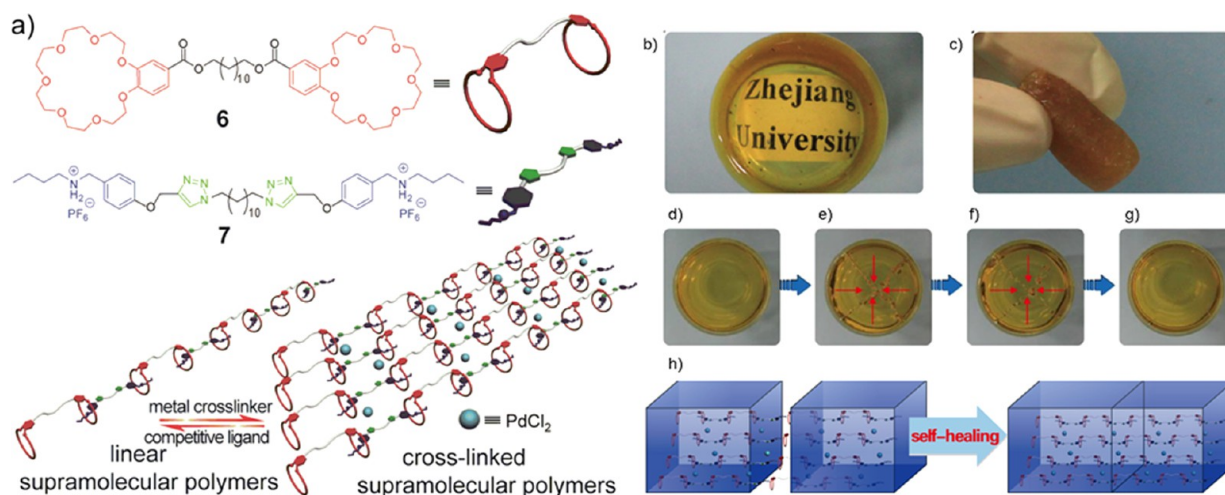
Figure 5. (a) Cartoon representation of controlling the topology of the supramolecular polymer from the self-assembly of AA-type monomer **6** and BB-type monomer **7**. (b) Transparent and (c) free-standing cross-linked supramolecular polymer gels. Photographs: (d) the supramolecular polymer gel, (e) after damage, (f) after free-standing for 1.5 min, (g) after free-standing for 3 min. (h) Cartoon illustration of the proposed mechanism of self-healing. Adapted with permission from ref 33. Copyright 2013 Royal Society of Chemistry.
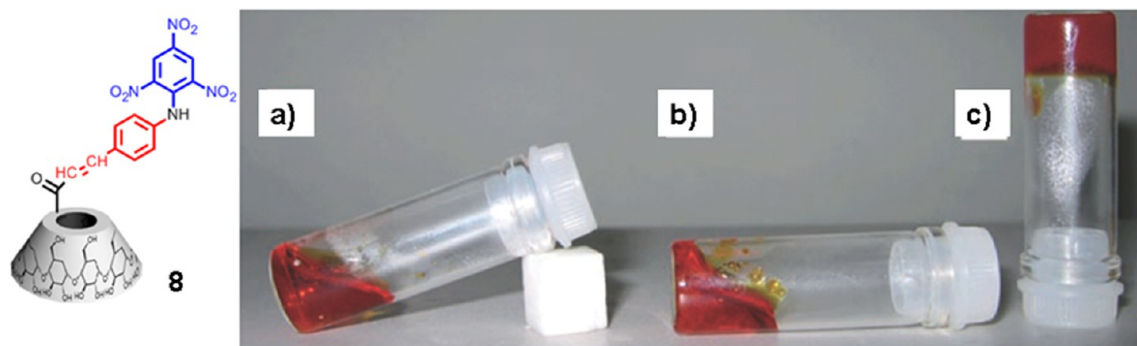
Figure 6. Formation of a supramolecular polymer gel from a CD-based AB-type monomer (samples a, b, and c display a concentration-dependent gelation process). Adapted with permission from ref 34. Copyright 2007 John Wiley and Sons, Inc.

successfully realized by different stimuli, due to the dynamic host−guest interactions between DB24C8 and DBA units. The potential application of this supramolecular gel as a controlled release system was also investigated. Hence, the fabrication of supramolecular organogels provides unique stimuli-responsive properties.

Supramolecular nanofibers and nanogels exhibit unique mechanical properties.[19] We designed and synthesized an AB-type monomer **5** containing a B21C7 group and a secondary ammonium salt moiety connected by a long alkyl chain (Figure 4).[30] This AB monomer self-assembled into a linear high molecular weight supramolecular polymer in solution, with low diffusion coefficient and high viscosity. Moreover, this linear supramolecular polymer formed smooth nanofibers via electrospinning technology,[19,30] which was quite rarely observed in the field of supramolecular polymers from low molecular weight monomers. This supramolecular polymer was also used to prepare intriguing film-type microstructures by the breath figure method, which showed concentration-dependent properties.[31] Later on, a supramolecular polymer network was successfully prepared by adding [PdCl$_2$(PhCN)$_2$] to a solution of monomer **5** using the design strategy of monomer **3** (Figure 2).[32] Based on self-assembly behavior in solution, we found that both host−guest and metal coordination interactions played important roles for the formation of the cross-linked supra-

molecular polymer, which led to a red supramolecular gel. Considering the existence of weak and reversible supramolecular interactions in the supramolecular gel, multiple external stimuli such as temperature, pH, and organic molecules were introduced into this system to realize reversible transitions between sol and gel phases. Unlike other crown ether-based supramolecular polymer gels, this gel showed prominent physical properties, such as self-standing, shape-persistence, and elasticity. From moving trajectory experiments and rheological characterizations, we proposed that the excellent mechanical and elastic properties were mainly attributable to the dynamic complexation properties between the B21C7 and secondary ammonium salt moieties.

To get more insight into the mechanical properties of supramolecular polymers, we applied a three-component self-assembly strategy to realize a supramolecular cross-linked polymer (Figure 5).[33] Mixing the homoditopic crown ether monomer **6** and secondary ammonium salt monomer **7** led to the formation of a linear supramolecular polymer. Addition of PdCl$_2$(PhCN)$_2$ facilitated the formation of a supramolecular polymer gel. The resulting supramolecular gel not only exhibited quadruple-stimuli induced reversible gel−sol transitions but also demonstrated good viscoelastic properties. It was processed to free-standing and shape-persistent objects. Moreover, the supramolecular gel showed self-healing proper-

ties: it healed itself *in situ* within a short time, and the healing cycles were repeated many times, as confirmed by rheological experiments. The above examples suggest that the combination of multicomponent self-assembly and supramolecular gels will show great advantages in constructing supramolecular materials with desired properties.

■ SUPRAMOLECULAR POLYMERS CONSTRUCTED FROM CYCLODEXTRIN-BASED HOST−GUEST MOLECULAR RECOGNITION MOTIFS

Macrocyclic cylcodextrin molecules are a kind of water-soluble macrocyclic molecule with different numbers of glucopyranoside units (6−12 units) and show prominent host−guest interactions with various organic compounds and thereby form stable host−guest complexes in water, which serve as the basic building blocks to fabricate various kinds of supramolecular architectures.[8,9]

By utilizing the host−guest interactions between β-CD and 6-aminocinnamoyl derivatives, Harada and co-workers produced supramolecular gels, which showed stimuli-responsive behavior.[34] As shown in Figure 6, they designed and synthesized a β-CD-based AB-type monomer **8**. The monomer contained a β-CD unit, a cinnamic group, and a trinitrophenyl part. In solution, the cinnamic and trinitrophenyl parts were located in the CD cavities. At a monomer concentration of 5 mM, the molecular weight of the corresponding supramolecular polymer was about 16 kDa. More importantly, under appropriate conditions, monomer **8** further assembled into a red supramolecular polymer gel. They found that this supramolecular gel turned to a solution state upon addition of 1-adamantane carbonyl acid or urea, which acted as a competitive guest or denaturing reagent, respectively. Azobenzene-based traditional polymers were also applied to fabricate supramolecular polymer gels, which showed photoswitchable properties with cyclodextrins.[35]

By the successful combination of host−guest and metal−ligand interactions, Tian and co-workers elegantly developed a convenient "one-pot" method to construct linear supramolecular polymers from a multicomponent system. They designed and synthesized a guest molecule with two viologen groups and two azo-benzene units, as well as a β-cyclodextrin-based host molecule with a rigid 4,4′-bipyridine moiety.[36] Mixing the host and guest moieties led to the formation of [3]pseudorotaxanes. By adding ethylene diamine palladium chloride to the resulting [3]pseudorotaxanes, they found that these [3]pseudorotaxanes were noncovalently connected together to form a linear supramolecular polymer via metal−ligand coordination. Moreover, the host−guest interactions between the azobenzene moiety and cyclodextrin also aided the reversible transition between different polymerization degrees. Based on a similar design strategy, Tian and co-workers further constructed an interesting light-driven chiral supramolecular polymer in water (Figure 7).[37] First, the combination of monomer **9** and α-CD led to the formation of a pseudorotaxane, which was then connected by bis(p-sulfonatocalix[4]arene) to form a linear supramolecular polymer. This unique supramolecular polymerization process was monitored by NMR and DLS. They also utilized various characterization methods such as UV−vis spectroscopy, SEM, AFM, and TEM, to probe the resulting supramolecular polymers. Based on the TEM investigation, they directly observed that the supramolecular polymer exhibited different lengths, affording solid evidence for the formation of high
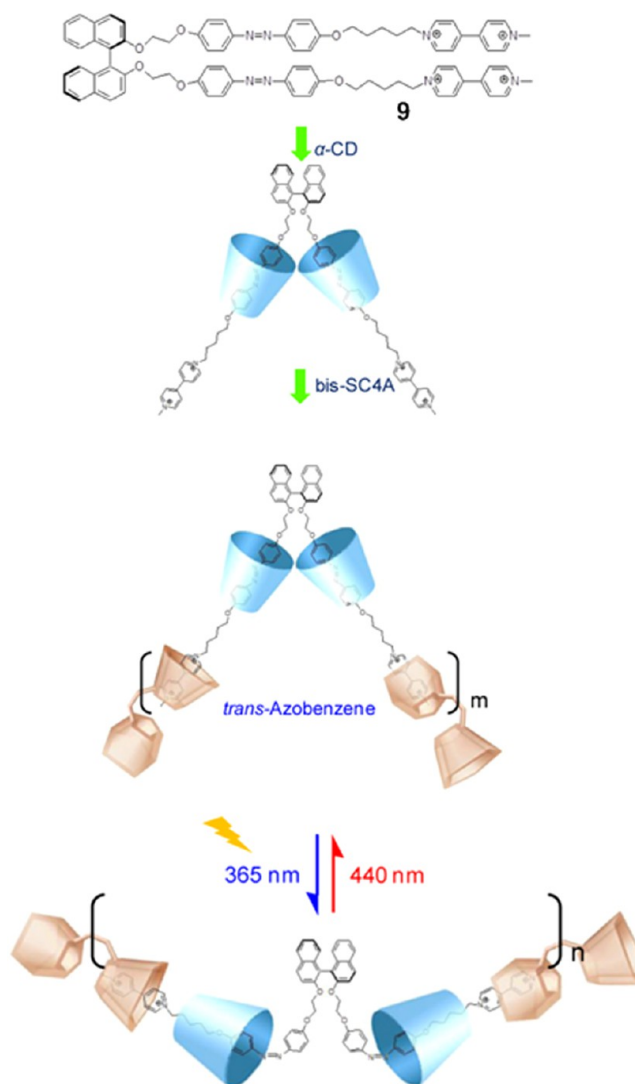

Figure 7. Formation of a photoresponsive linear supramolecular polymer. Adapted with permission from ref 37. Copyright 2013 American Chemical Society.

molecular weight aggregates. Light-driven dynamic self-assembly of the resulting linear supramolecular polymers was also explored.

In order to obtain supramolecular polymers with different topological structures, Tato and co-workers synthesized an A₂-type homoditopic monomer and two host monomers (B₂-type and B₃-type, respectively). The mixing of different hosts and guests led to the formation of supramoleucular polymers with different topological structures, from linear supramolecular polymers to dendritic supramolecular polymers.[38,39]

■ SUPRAMOLECULAR POLYMERS CONSTRUCTED FROM CALIXARENE-BASED HOST−GUEST MOLECULAR RECOGNITION MOTIFS

Calixarenes and their derivatives are cyclic oligomers which are prepared by the hydroxyalkylation of phenols and aldehydes.[2] Due to their hydrophobic cavities and the ability to be easily functionalized, calixarenes have been widely used in the field of the preparation of supramolecular polymers and the investigation of the polymerization mechanism.[2]
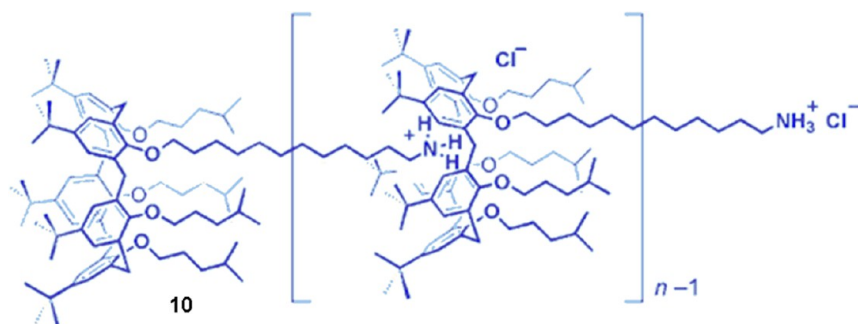
Figure 8. Calixarene-based supramolecular polymers. Adapted with permission from ref 40. Copyright 2007 John Wiley and Sons, Inc.

Considering the different binding capacities between alkylammonium/calix[5]arene and neutral alkylamino unit/calix[5]arene, Parisi and co-workers introduced a long alkylammonium group onto the lower rim of a calix[5]arene and synthesized AB-type monomer **10** (Figure 8).[40] After protonation, **10** showed the tendency to form linear supramolecular polymers. They found that the polymerization process was dependent on both the concentrations of monomers and the types of anions.

By utilizing host−guest interactions between calix[4]arenes and viologen derivatives, Liu and co-workers prepared linear supramolecular polymers with fantastic structures and responsiveness (Figure 9).[41] They designed and synthesized monomer **11** possessing two calix[4]arene units and monomer **12** containing two viologen groups. Simple mixing of the two monomers **11** and **12** led to the formation of a high molecular
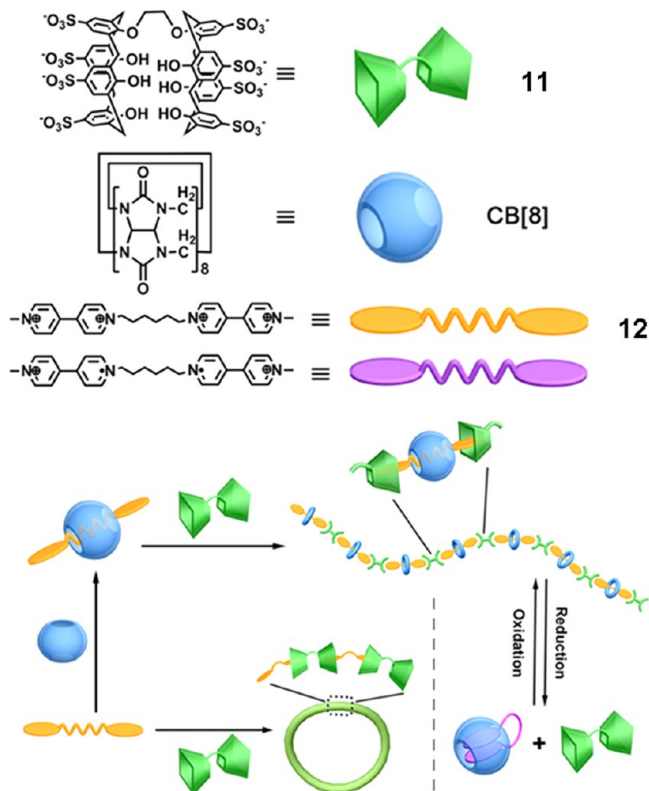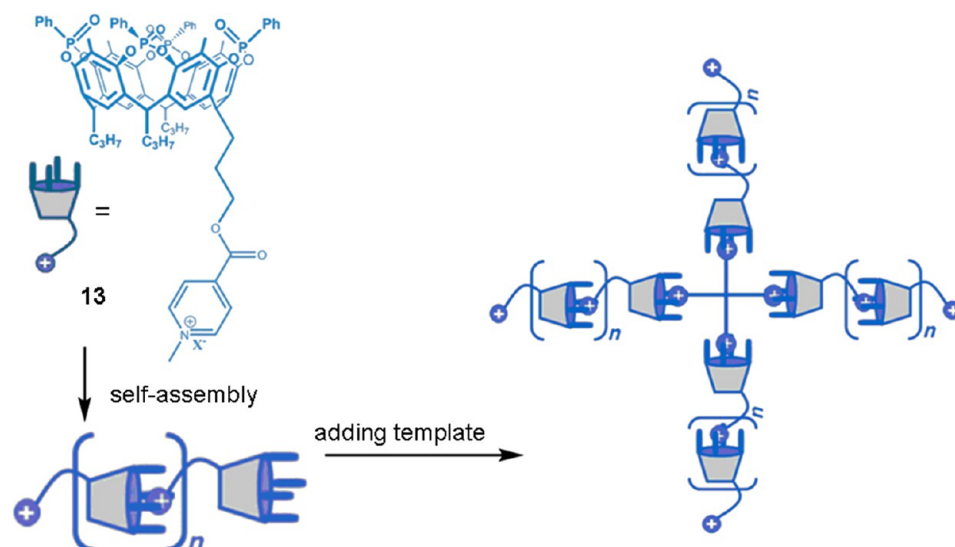
weight cyclic supramolecular polymer. They found that different bis(viologen) guests showed considerable effects on the topology of the resulting assemblies. The introduction of a long and flexible spacer into the bis(viologen) led to the formation of a cyclic oligomer instead of a linear polymer, which was quite different from the case encountered for the above-mentioned crown ether-based supramolecular polymers. They also incorporated cucurbit[n]uril (CB[n]) units into the host−guest binary system and thereby fabricated a ternary linear polymer with reduction/oxidation responsiveness. In a similar system, they further investigated the stimuli-responsive behavior and realized reversible assembly/disassembly processes by electrochemical or chemical stimuli.[42]

In addition to linear supramolecular polymers, other types of calix[4]arene-based supramolecular polymers with different topological structures were also studied. Dalcanale and co-workers synthesized a heteroditopic monomer **13** containing a tetraphosphonate calix[4]arene unit and a methylpyridium group (Figure 10).[43] In chloroform, this AB-type monomer formed a linear supramolecular polymer with a high degree of polymerization via host−guest interactions between calixarene and methylpyridium groups. For example, at a monomer concentration of 15.0 g L^{-1}, a linear supramolecular polymer with the molecular weight of 26.3 kDa was achieved, indicating that the average degree of polymerization was about 18. Furthermore, they synthesized a four arm template, which showed a strong tendency to complex with monomer **13**. They found that the addition of small amounts of the template to the linear supramolecular polymer led to the fabrication of star-branched polymers. When 2.0% template was added to a monomer **13** solution (4.10 g L^{-1}), from static light scattering measurements, an increase of the average molecular weight from 15.9 to 49.7 kDa was observed. Further adding butylmethylammonium iodide or 1,8-diazobicyclo[5.4.0]-undec-7-ene caused a reversible transition between monomeric and polymeric structures.

SUPRAMOLECULAR POLYMERS CONSTRUCTED FROM CUCURBITURIL-BASED HOST−GUEST MOLECULAR RECOGNITION MOTIFS

Cucurbit[n]urils are composed of different numbers of glycoluril units.[10,11] Although the reaction to yield cucurbit[n]urils is easy, the isolation and purification of pure products is difficult work. Considering that it is difficult to functionalize cucurbit[n]urils, much attention has been paid to the derivatization and functionalization of different guest molecules for them.[10,11]

Kim and co-workers elegantly realized supramolecular polymerization on a gold surface (Figure 11). Specifically, the

Figure 9. Formation of calixarene-based supramolecular polymers with different topological structures controlled by the addition of CB[8]. Adapted with permission from ref 41. Copyright 2012 John Wiley and Sons, Inc.

Figure 10. Self-assembly of calixarene-based linear and star supramolecular polymers. Adapted with permission from ref 43. Copyright 2008 John Wiley and Sons, Inc.
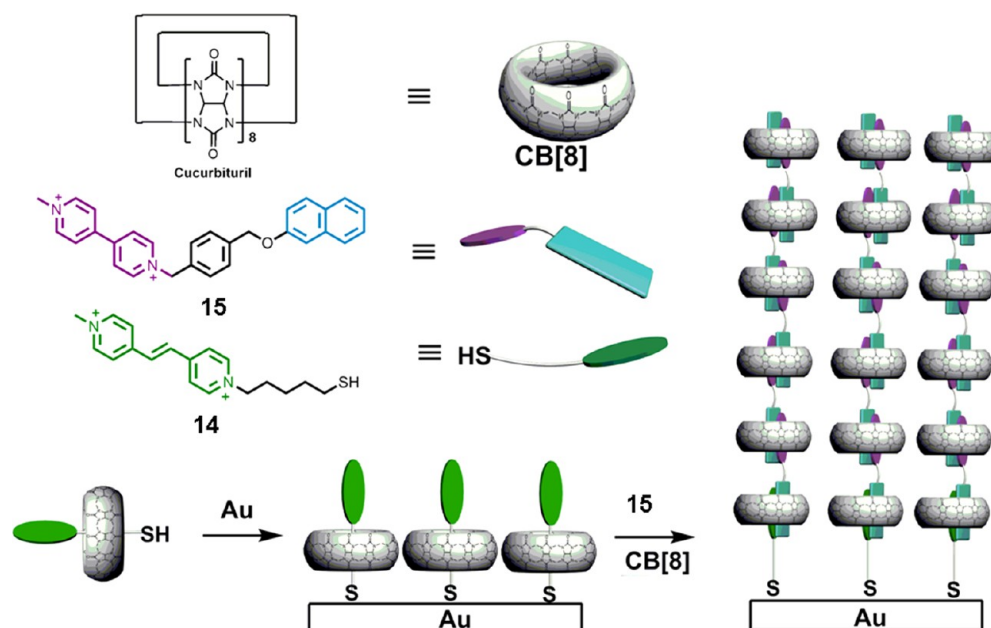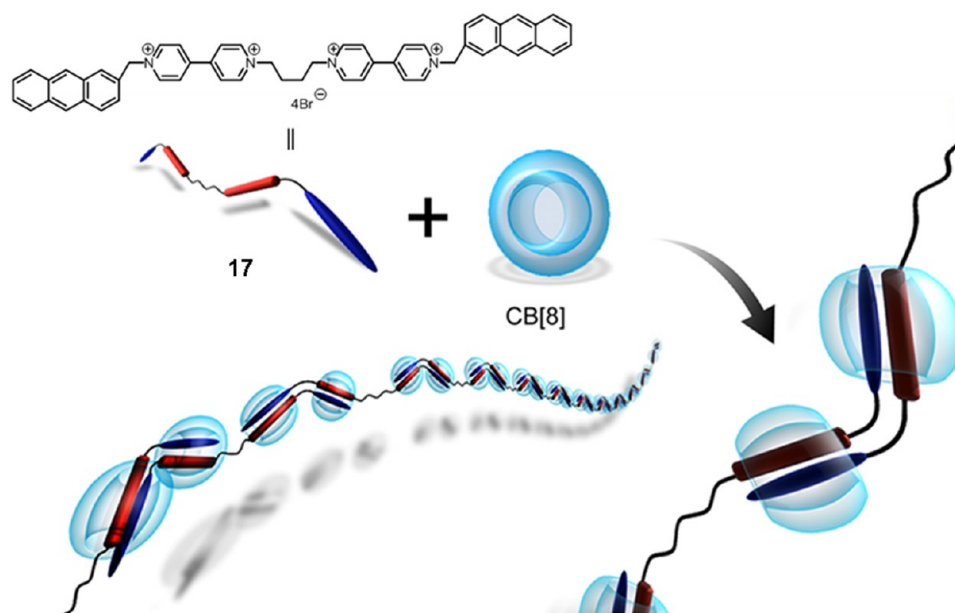

Figure 11. Growth of a linear supramolecular polymer via CB[8]-enhanced charge-transfer interactions.[44]
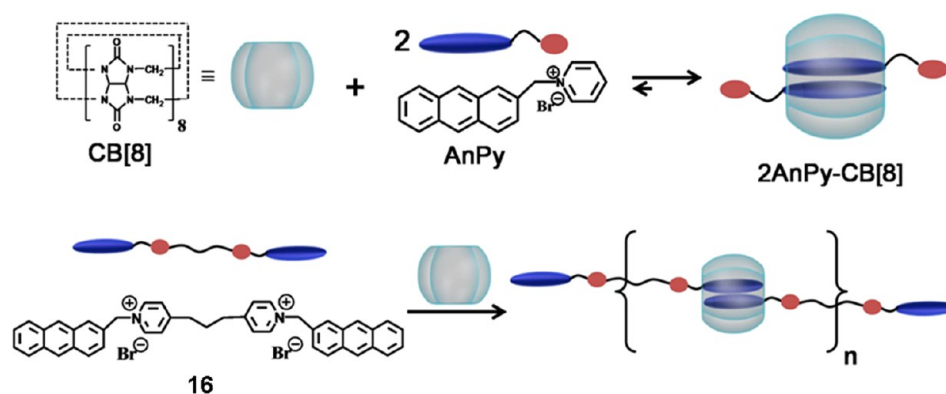
Figure 12. Supramolecular polymerization of DAP and CB[8] driven by host-enhanced $\pi-\pi$ interaction. Adapted with permission from ref 45. Copyright 2011 John Wiley and Sons, Inc.

Figure 13. Formation of a linear supramolecular polymer via CB[8]-enhanced charge-transfer interactions. Adapted with permission from ref 46. Copyright 2010 John Wiley and Sons, Inc.

gold surface was first modified to attach a dipyridinium-methylene−CB[8]-based host−guest complex (**14** and CB[8]).[44] The gold surface was then soaked in a solution of bisfunctional monomer **15** and CB[8] to form the corresponding supramolecular polymer. A variety of characterization methods such as IR, SPR, and AFM proved the formation of supramolecular polymeric assemblies. The successful introduction of CB-based supramolecular assemblies on gold surfaces could significantly expand the applications of supramolecular polymers.

By utilizing the strategy of host-enhanced $\pi-\pi$ interaction, Zhang and co-workers successfully fabricated an interesting cucurbituril-based supramolecular polymer in water (Figure 12).[45] They synthesized a bisfunctional monomer **16**, which contained two AnPy units. Due to the 2:1 stoichiometry and the high binding constant between AnPy and cucurbit[8]uril moieties, the mixture of monomer **16** and cucurbit[8]uril led to the formation of a linear supramolecular polymer. Based on the AFM data, they calculated that the length of the resulting supramolecular polymer was at least 23.9 nm. DLS and other optical measurements also provided reliable evidence for the formation of high molecular weight supramolecular polymeric structures.

Furthermore, with the same strategy, Zhang and co-workers designed and synthesized a unique multifunctional guest monomer **17** (Figure 13), which contained two anthracene units and two viologen parts, and successfully realized its supramolecular polymerization.[46] In aqueous solution, a pair of anthracene and viologen units were located in the cavity of CB[8] to form a tenary host−guest complex. Furthermore, these complexes assembled into a linear supramolecular polymer, which was confirmed by single-molecule force spectroscopy (SMFS), DLS, and NMR. Notably, with increasing monomer concentration, the linear supramolecular polymer further assembled into a dark purple supramolecular gel.

Moreover, with the introduction of azobenzene units in the guests, a photocontrollable CB[8]-based supramolecular polymerization was realized.[47] Except for linear supramolecular polymers, a two-dimensional supramolecular polymer via the host−guest interaction between CB[8] and guest molecules was also prepared in water.[48] Many other types of dimeric guests were designed and synthesized. These guests also formed 2:1 host−guest complexes with CB[8] and assembled into supramolecular polymeric species.[49]

■ SUPRAMOLECULAR POLYMERS CONSTRUCTED FROM PILLARARENE-BASED HOST−GUEST MOLECULAR RECOGNITION MOTIFS

Pillar[n]arenes possess symmetrical, rigid, and pillar-shaped structures compared with other macrocyclic hosts.[12] Due to their unique molecular structures, various organic compounds, such as viologen derivatives, bis(imidazole) derivatives, ionic liquids, and ammonium salts, have been used in pillararene-based host−guest complexes.[12] Although pillararenes have been utilized to fabricate different kinds of supramolecular assemblies, their application in the field of supramolecular polymers has been still rarely explored.[12,50−56]

The first pillararene-based supramolecular polymer was reported by our group. Previous work demonstrated that pillar[5]arene binds n-hexane to form a 1:1 host−guest complex driven by C−H⋯π interactions.[15] Based on this observation, we designed and synthesized a novel pillar[5]arene derivative by the attachment of a long alkyl chain (Figure 14).[50] At high concentration, monomer **18** formed a linear supramolecular polymer in chloroform, as evidenced by the results of ^{1}H NMR, specific viscosity measurements, and DOSY. More importantly, we obtained the single crystal structure of monomer **18**, which proved the formation of the linear supramolecular polymer in the solid state. Based on the crystal structure, we obtained clear evidence that the driving force for the supramolecular polymerization was mainly derived from multiple C−H⋯π interactions.

Inspired by the first example of pillararene-based supramolecular polymers, we applied external stimuli to regulate the properties of pillar[5]arene-based supramolecular polymers.
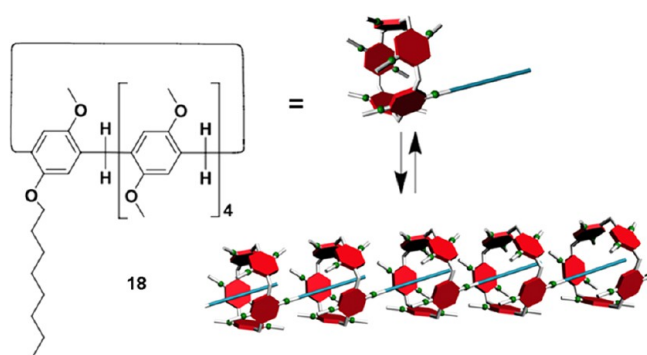
Figure 14. Formation of a linear supramolecular polymer from self-organization of monomer **18**. Adapted with permission from ref 50. Copyright 2011 John Wiley and Sons, Inc.

Hence, we prepared a pH-responsive supramolecular polymer based on the pillar[5]arene/imidazolium recognition motif (Figure 15).[51] In chloroform, monomer **19** self-assembled into a high molecular weight linear polymer, which was characterized by a variety of experiments. After acidification of the neutral monomer **19**, we found that the newly formed positively charged monomer **20** assembled into a linear supramolecular polymer with a relatively higher molecular weight. For example, at the same monomer concentration (200 mM), monomer **19** formed polymeric assemblies with a molecular weight of about 11.8 kDa, while for the cationic monomer **20** the corresponding value was 52.0 kDa. Hence, by changing the pH of the chloroform solution of monomer **19**, we realized the size control for the resulting supramolecular polymers.

By utilizing the different binding capacities between pillar[5]arene and pillar[6]arene, Ogoshi and co-workers prepared a novel alternating copolymer (Figure 16) based on the concept of self-sorting organization.[52] By mixing two monomers **21** and **22** together, they formed a high molecular weight copolymer.

With the combination of pillar[5]arene-based host–guest interactions and quadruple hydrogen bonding interactions, Wang and co-workers elegantly constructed orthogonal supramolecular polymers, which showed high molecular weights and high viscosities.[53,54] Yang and co-workers reported the first example of pillar[5]arene-based electrospun nanofibers from a highly concentrated supramolecular polymer solution, which was prepared via the polymerization of a pillar[5]arene-based AB-type monomer.[55] With the combination of a pillar[5]arene-based [c2]daisy chain and a dimer-type pillar[5]arene derivative, Li and co-workers demonstrated an effective and beautiful strategy to fabricate supramolecular alternating copolymers.[56]

■ CONCLUSIONS AND PERSPECTIVES

Macrocyclic host–guest complexes are considered versatile building blocks to construct various types of supramolecular assemblies, from simple mechanically interlocked structures to functionalized and complicated supramolecular biomimetic
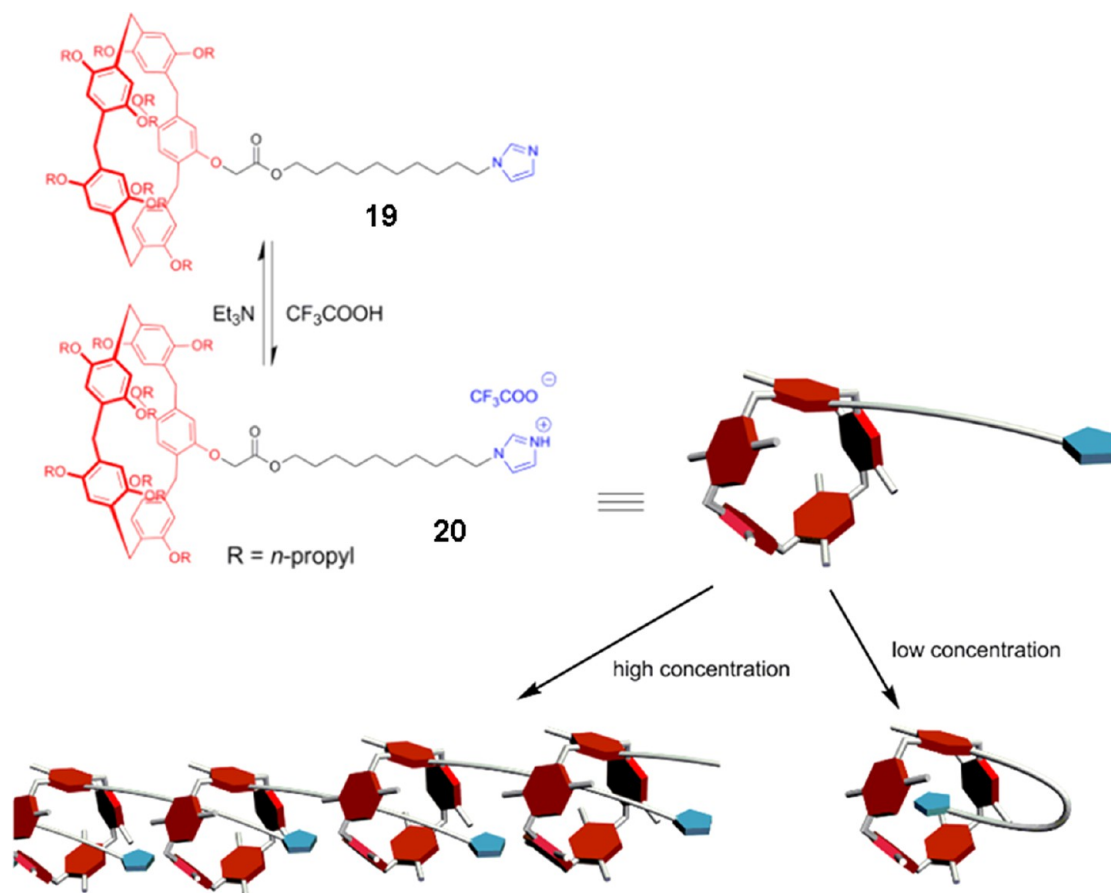
Figure 15. The formation of a linear supramolecular polymer from monomer **19** and its pH-responsiveness. Adapted with permission from ref 51. Copyright 2013 Royal Society of Chemistry.
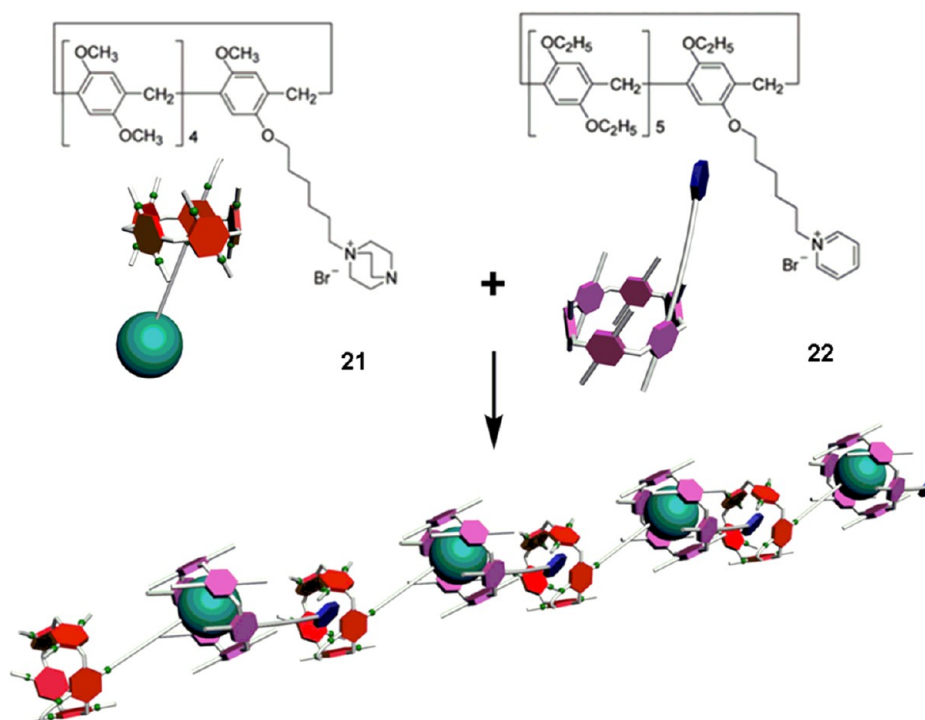
Figure 16. Formation of an alternating supramolecular polymer from a pillar[5]arene-based monomer **21** and a pillar[6]arene-based monomer **22**.[52]

systems.[2,18−20] For the formation of different kinds of macrocyclic host-based supramolecular polymers, host−guest interactions between macrocyclic hosts and complementary organic guests are the main driving forces and play a crucial role in controlling the structures and functions of the resulting supramolecular polymers.[18,19] The highly reversible and stimuli-responsive properties of host−guest interactions endow these supramolecular polymers with fascinating stimuli-responsive and self-adjusting properties.[19]

Supramolecular polymers constructed from different macrocycle-based molecular recognition motifs are different and diverse. Crown ether- and pillararene-based supramolecular polymers have mainly formed in organic solvents, such as chloroform and acetonitrile, while cyclodextrin- and cucurbituril-based supramolecular polymerization has been usually observed in aqueous solutions. For calixarenes, both organic solvents and water have been used as suitable media for supramolecular polymerization.

Although a large number of macrocyclic host-based supramolecular polymers have been constructed, there are still many uncharted terrains for chemists to explore. First, most supramolecular polymerization processes of macrocyclic host-based monomers, especially for crown ether-, calixarene-, and pillararene-based ones, occur in organic solvents, quite different from the aqueous environment adopted by natural assemblies. Hence, it is of primary importance to develop water-soluble supramolecular polymers based on these systems. Second, further studies concerning the mechanism of supramolecular polymerization, and deeper insights into kinetics and thermodynamics of supramolecular polymers are still needed. Third, in order to control polymerization processes more efficiently, new stimuli such as gas, magnetic field, and near-infrared radiation are urgently anticipated to regulate the properties of supramolecular polymers. Fourth, most of the macrocyclic host-based supramolecular polymers are studied in solution. From the perspective of functional material

applications, efforts should be devoted to developing supramolecular polymers in the bulk or in the gel state, which endows us the ability to develop functional materials and to discover their applications in various areas. Finally, much more attention should be focused on the improvement of the chemical, physical, and mechanical properties, as well as the establishment of structure−property relationships for the resulting supramolecular polymeric assemblies.[18,19]

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Notes

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