



Designer supramolecular polymers with specific molecular recognitions

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Received: 19 July 2018 / Revised: 22 August 2018 / Accepted: 22 August 2018 / Published online: 21 September 2018
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Abstract

Supramolecular polymers are members of an emergent class of polymer materials that exhibit designability and flexibility. This article describes how supramolecular polymers can be synthesized by taking advantage of our host–guest structures based on a calix[5]arene, a bisporphyrin, and a self-assembled capsule. Linear and two-dimensional fullerene nanostructures can be fabricated using the designed monomer structures. The porphyrin donor–acceptor interaction directs the supramolecular polymerization, resulting in linear porphyrin polymers that behave similarly to a conventional polymer chain in solution, even though their structures are dynamic and time-averaged. The fragile supramolecular polymer chains are cross-linked to fabricate a robust self-standing film. The sequence reorganization of the supramolecular homopolymer is established by competitive ditopic guest complexation. The sequence-controlled terpolymer is fabricated via self-sorting behavior. The postmodifications of the supramolecular polymer chains, as well as the polymer chains themselves, are achieved by grafting and non-covalent cross-linking to regulate the macroscopic properties and structures of the polymer main chains. These uniquely organized polymers are fabricated on a nanoscale.

Introduction

Background

Charles Pedersen's discovery of metal ion-crown ether complexes in 1967 was the beginning of supramolecular chemistry [1]. Supramolecular chemistry is a field based upon intermolecular interactions and multiple molecular associations [2]. A supramolecular structure includes a group of molecular components. During the supramolecular organization process, a molecular component precisely recognizes its counterpart based on the intermolecular complementarity in their structural and electronic shapes. This molecular recognition is governed by various non-covalent interactions, such as hydrogen bonding, aromatic stacking, and CH/π interactions as well as coulombic, ion-dipole, van der Waals forces, etc. A supramolecular

structure is therefore in thermodynamic equilibrium and behaves as a single molecule. Even advanced and elaborate supramolecular structures can reach thermodynamic minima through supramolecular organization [3]. Such supramolecular structures on the nanoscale are common in nature. DNA and proteins are typical examples in living entities, and they participate in various levels of information transfer via molecular recognition [4, 5]. Biomolecular building blocks are also manipulated in a precise manner to generate functional supramolecular structures that rely on multiple non-covalent interactions. In the long history of supramolecular chemistry, much work has been devoted to bridging the gap between artificial and natural supramolecular structures and develop synthetic strategies that can be used to generate novel structures and materials with a specific set of functions. Today, supramolecular chemistry has enabled a bottom-up approach to create artificial nano-objects from simple building blocks and is now being applied in nanotechnology and nanoscience.

The study of supramolecular chemistry is related to the polymer chemistry, and their overlap has allowed the generation of supramolecular polymers [6, 7]. A complementary host–guest pair is built into a monomer (Fig. 1), and spontaneous self-assembly of the monomer leads to a polymeric structure through the molecular recognition of

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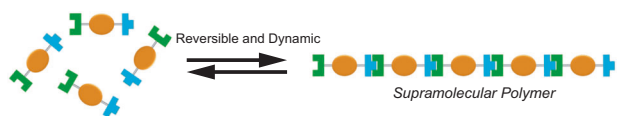


Fig. 1 Schematic representation of supramolecular polymerization

the complementary host–guest pair. The polymeric structure equilibrates between association and dissociation on the experimental timescale. This dynamic nature is characteristic of a supramolecular polymer; therefore, its size and dimensions are sensitive to external conditions. Supramolecular polymers are a unique class of polymer materials in terms of both their structure and their properties [8].

Designability of supramolecular polymers

The molecular recognition of a host and a guest can be engineered by arranging a number of interaction sites. Various sets of complementary host–guest pairs have been developed thus far. Therefore, a monomer structure for supramolecular polymerization is designable and versatile because a variety of host–guest pairs are available. Supramolecular polymer structures, such as linear polymers, networked polymers, block copolymers, and graft polymers, can be engineered by using a monomer structure with a specific host–guest pair. The most exploited host–guest pairs are hydrogen-bonding donor–acceptor (D–A) pairs. Initially, hydrogen bonding was employed to modify the side chain structures of liquid crystalline polymers [9–11]. The mesophase of a mesogenic polymer can be enhanced by introducing grafted side chains involving a hydrogen-bonded complex. Hydrogen-bonding host–guest pairs can be easily engineered to improve their directionality and versatility, as already realized in nucleobases. Multiple hydrogen-bonding host–guest pairs have been used as the primary building blocks of supramolecular polymers by Lehn et al. (Fig. 2a) [12]. Linear-chain polymeric structures were prepared with multiple hydrogen-bonding interactions [13]. The flexible designability of hydrogen-bonded host–guest pairs has inspired the development of hydrogen-bonded supramolecular polymers. Quadruple hydrogen-bonded pairs in a ureidopyrimidone (Upy) derivative were designed by Meijer et al. [14]. A self-complementary hydrogen-bonding array (DDAA–AADD) results in an extremely strong dimerization constant of $>10^7$ L mol⁻¹. A monomer possessing two Upy units polymerizes to produce linear chain polymers (Fig. 2b) [15]. Another example of a hydrogen-bonded supramolecular polymer was reported by Rebek Jr. et al. (Fig. 2c). A calix[4]arene, possessing four urea units at its upper rim, self-assembles to form a hydrogen-bonded dimer with eight head-to-tail hydrogen bonds [16]. This hydrogen-bonded

dimer can be used to build hydrogen-bonded supramolecular polymers [17].

Host–guest motifs that use interactions other than hydrogen bonding have also been developed. A crown ether was first employed for the construction of supramolecular polymers due to its tunable designability in the binding of cationic species through cation–dipole interactions. The ring sizes of crown ethers control their guest selectivity. A desired cationic guest is selectively captured within the cavity of a crown ether of a certain size. Gibson et al. reported that a monomer possessing a crown ether and a paraquat moiety self-assembled to form a supramolecular polymer in solution [18]. An extensive study undertaken by Huang et al. demonstrated that this high selectivity allowed alternating copolymerization when using two kinds of crown ether complexes (Fig. 3) [19]. Bis(*p*-phenylene)-34-crown-10 (BPP34C10) and dibenzo-24-crown-8 (DB24C8) selectively bind with paraquat derivatives and dibenzylammonium salts, respectively, in a ratio of 1:1. The monomers possessing the mismatched host–guest pairs exhibit self-sorting supramolecular polymerization, resulting in an alternating copolymer sequence.

Complementary sets of host–guest pairs have been frequently employed in supramolecular polymers. Cyclodextrins [20, 21], pillar[5]arenes [22–25], cucurbiturils [26–28], and calixarenes [29–32] are adaptable host molecules that can be flexibly used for supramolecular polymerizations. The designability of these host molecules offers a way to construct novel polymer materials with fascinating functions such as self-healing, stimuli-responsiveness, shear-thinning, and thermoplasticity, and such materials have become attractive alternatives to conventional synthetic polymers.

We have applied our host–guest complexes to the construction of supramolecular polymers [33]. The “ball-and-socket” calix[5]arene–fullerene complex, the donor–acceptor bisporphyrin–guest complex, the complementary bisporphyrin dimeric complex, and the host–guest complex of the coordination capsule are crucial intermolecular interactions that enable supramolecular polymerization. In this article, our latest developments in supramolecular polymers are described.

Supramolecular polymers formed via unique molecular recognition modes

Supramolecular fullerene polymers and networks

Fullerenes have received a great deal of attention as new carbon materials due to their unusual electronic properties as well as their globular shape [34, 35]. Fabricating fullerenes into nano-organizations results in materials

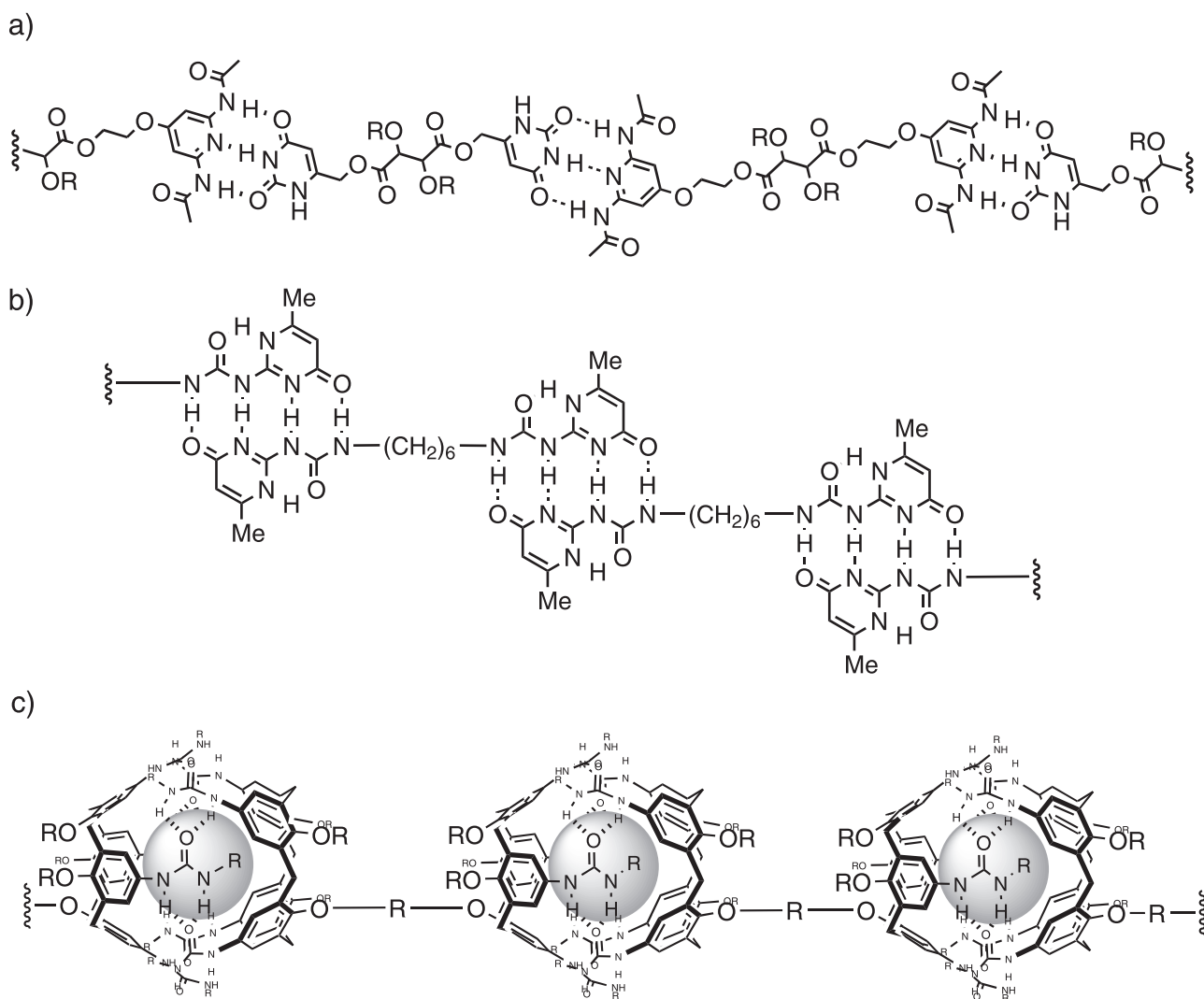
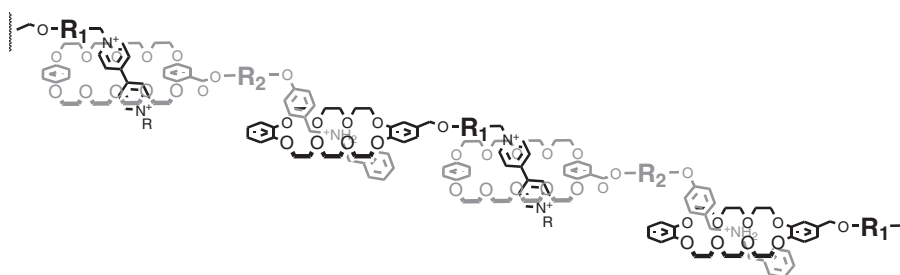


Fig. 2 Supramolecular polymers with unique hydrogen-bonding motifs

Fig. 3 Supramolecular alternating polymerization directed by molecular recognition of DB24C8 and BPP34C10



with electroconductivity, superconductivity, and photoconductivity [36–38]. Efficient photoelectronic conversion can be achieved in fullerene-based organic solar cells [39]. A great deal of effort has been devoted to directing the molecular organization of fullerenes at the nanoscale to refine device performance. Polymer chemistry can offer an alternative method for controlling fullerene organization at the molecular level. Therefore, direct polymerization

through the cycloaddition reactions of fullerenes was originally studied to provide fullerene-containing polymeric materials [40]. However, the one-, two-, and three-dimensional polymeric fullerene architectures were not prepared in stereo- and regio-regular fashions due to the equal reactivity of the fullerene double bonds. Supramolecular polymer chemistry offers an alternative method of controlling fullerene organization. Hummelen et al. reported

an interesting hydrogen-bonded supramolecular fullerene polymer [41]. β -CD-fullerene 2:1 host-guest complexation directs supramolecular fullerene polymerization. Liu et al. demonstrated that a ditopic host possessing two β -CD units can complex a fullerene molecule to form a supramolecular fullerene polymer in which the fullerenes are located in the main chain [42]. Recently, Martin et al. developed a π -extended analogue of the tetrathiafulvalene (exTTF)- C_{60} host-guest complex, which has been utilized in fabricating supramolecular fullerene polymers and dendrimers [43, 44].

A calix[5]arene is a cyclic pentamer derived from phenol derivatives. Five phenolic hydroxyl groups form a ring of hydrogen bonds that generates a cone-shaped cavity surrounded by the five phenolic rings. Various guest molecules can be encapsulated within the cavity; therefore, a calix[5]arene is a potential host molecule [45–48]. During the course of our studies, we discovered that the interior of calix[5]arene is complementary to the exterior of C_{60} . This shape complementarity results in an attractive stacking interaction that is responsible for a strong binding constant ($\log K_a$) of 3.2 in organic solvents [49]. Two calix[5]arene units can be connected with certain linkers to give rise to biscalix[5]arene derivatives. The cavity generated by the two calix[5]arene units is wider than that of a calix[5]arene, and biscalix[5]arenes can wrap around fullerenes. In fact, biscalix[5]arene binds to C_{60} with a vastly improved binding constant ($\log K_a$) of 4.8, which is due to the complementarity between the interior of the biscalix[5]arene and the exterior surface of C_{60} , causing increased aromatic stacking with concomitant substantial attractive energy gains (Fig. 4) [50–54]. In addition, biscalix[5]arenes can strongly encapsulate higher fullerenes than C_{60} due to the wide cavity between the two calix[5]arene units. Considering that the binding constant of C_{60} is on the order of 10^5 , this complementary “ball-and-socket” interaction can be strong enough to produce a supramolecular fullerene polymer.

A linear supramolecular fullerene polymer and a 2D supramolecular fullerene network were fabricated using ball-and-socket interactions [55, 56]. The multitopic host molecules were designed for the construction of supramolecular fullerene polymers (Fig. 5). Homoditopic monomer **1** possesses two guest binding sites, and each of the binding sites encapsulates one C_{60} molecule. The linear fullerene array can be established with the ball-and-socket interactions by a combination of dumbbell fullerenes and homoditopic monomer **1**. Tritopic host **2** can bind with the dumbbell fullerene to form the 2D network organization.

The intermolecular association of multitopic hosts **1** and **2** and dumbbell fullerene **3** forms the supramolecular fullerene polymer and the network. The size and dimension of the aggregates are determined using diffusion-ordered NMR techniques (DOSY). A degree of polymerization (DP) of 83 was estimated based on the diffusion coefficients in a 1:1

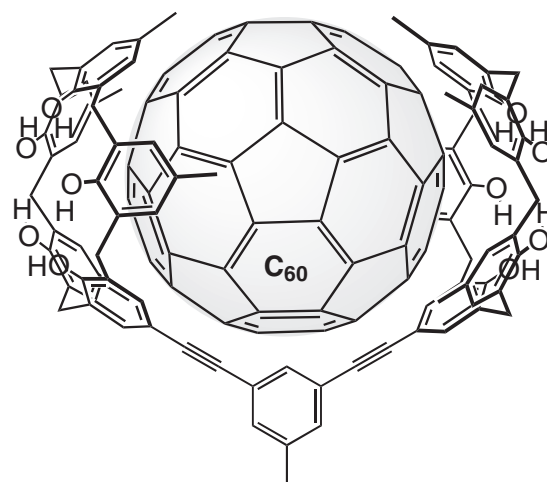


Fig. 4 Host-guest complex of biscalix[5]arene and fullerene

mixture of **1** and **3** at a millimolar concentration. A 2:3 mixture of **2** and **3** resulted in a higher DP of 151 at the same concentration. The association and dissociation of *poly-1•3* and *poly-2•3* are completely reversible. Supramolecular polymers *poly-1•3* and *poly-2•3* were disrupted by diluting their solutions to concentrations below millimolar levels. The supramolecular polymer solutions of *poly-1•3* and *poly-2•3* show meaningful changes in viscosity as a function of their concentrations. A viscous drag is produced by the overlap among the supramolecular polymer chains of *poly-1•3* in the semidilute regime. The intermolecular association of **2** and **3** produces cross-linked supramolecular polymer networks; thus, the supramolecular polymer solution of *poly-2•3* shows an increase in viscous drag.

The morphologies of the supramolecular fullerene polymers are sensitive to the monomer structures in the solid-state. *Poly-1•3* formed entwined fibrillar networks (Fig. 6a), whereas *poly-2•3* formed a thick film (Fig. 6b). The structures of the supramolecular polymers can be modified by changing the monomer ratios. Terminating the chain growth by the addition of excess **1** resulted in separated thin fibers (Fig. 6c). Adding excess **2** transformed the thick film to fibers (Fig. 6d); therefore, two of the binding sites are occupied with the C_{60} moieties of **3**, and the rest of the binding sites do not participate in supramolecular polymerization. Accordingly, the ball-and-socket interactions control the macroscopic morphology and can be used to generate either fibers or films.

The highly oriented supramolecular polymeric chains of *poly-1•3* can be directly observed by atomic force microscopy (AFM) (Fig. 6e). In contrast, *poly-2•3* generates unique honeycomb-like networks with many voids (Fig. 6f). The diameters of the voids are close to the diameter of the macrocycle formed from **2** and **3** in a ratio of 6:6. The rationally designed monomer structures determine the resulting morphologies of the supramolecular polymers

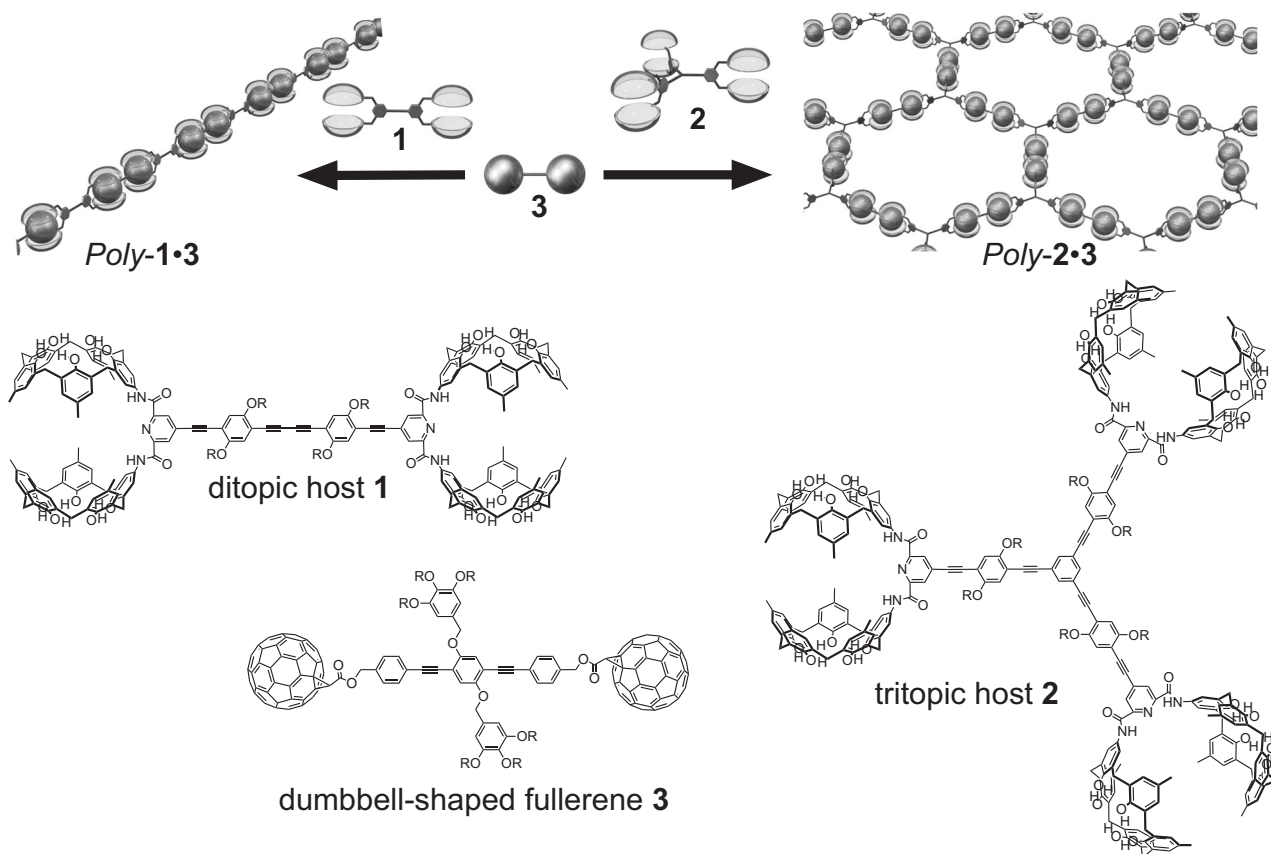


Fig. 5 Schematic representation of the supramolecular fullerene polymer and network and the structures of multitopic hosts **1** and **2** and dumbbell fullerene **3**. Adapted with permission from ref. [56]

through the ball-and-socket interaction. Finally, linear and two-dimensional honeycomb fullerene arrays can be constructed via supramolecular polymerization techniques.

Supramolecular porphyrin polymers

A donor–acceptor interaction is often used to control molecular organization on the nanoscale. A porphyrin is an electron-rich aromatic molecule, and it is a convenient donor unit for building supramolecular organization through a donor–acceptor interaction. Supramolecular porphyrin organizations have been constructed to achieve unique photophysical functions, such as photosynthetic centers and light-harvesting complexes [57, 58]. A substantial amount of effort has been devoted to integrating multiple porphyrin cores into elaborate architectures via self-assembly [59–61]. Supramolecular porphyrin polymers are attractive as functional supramolecular targets. To construct such nanometric porphyrin supramolecular arrays, coordination-driven self-assembly is often utilized [62, 63]. The coordination-driven supramolecular polymerization of porphyrin units was simultaneously and independently reported by Hunter [64] and Kobuke [65].

A bisporphyrin molecule has been used as an unique host molecule (Fig. 7) [66–68]. An interporphyrin distance of ~ 7 Å fits the thickness of an aromatic ring; thus, the electron-rich bisporphyrin cleft can capture a variety of electron-deficient aromatic guests through donor–acceptor interactions. Naphthalenediimide, pyromellitic dianhydride, and trinitrofluorenone are the best guests with association constants ($\log K_a$) of 5.0–5.6. The bisporphyrin molecule also demonstrates a unique head-to-head homodimeric association (Fig. 7). The pyridyl linkage connecting the two porphyrin rings is a complementary electron-deficient guest; therefore, a donor–acceptor interaction can drive dimerization. There are two supramolecular motifs that can be utilized for supramolecular porphyrin polymerization.

The donor–acceptor interaction can be exploited to construct supramolecular polymers (Fig. 8) [69]. Monomer **4** possesses the bisporphyrin cleft and the electron-deficient trinitrofluorenone (TNF) unit. The donor–acceptor host–guest interaction results in head-to-tail supramolecular porphyrin polymers. In dilute solutions, the monomeric form of **4** is dominant. Concentrating the solution of **4** resulted in a huge polymeric aggregate with a DP of ~ 600 , which was determined by DOSY experiments.

Fig. 6 SEM **a–d** and AFM **e, f** images of cast films of **a** a 1:1 mixture of **1** and **3**, **b** a 2:3 mixture of **2** and **3**, **c** a 2:1 mixture of **1** and **3**, **d** a 2:1 mixture of **2** and **3**, **e** a 1:1 mixture of **1** and **3** ($0.22\ \mu\text{m} \times 0.22\ \mu\text{m}$, phase), and **f** a 2:3 mixture of **2** and **3** ($0.18\ \mu\text{m} \times 0.18\ \mu\text{m}$, phase) prepared from their toluene solutions on mica. Adapted with permission from ref. [56]

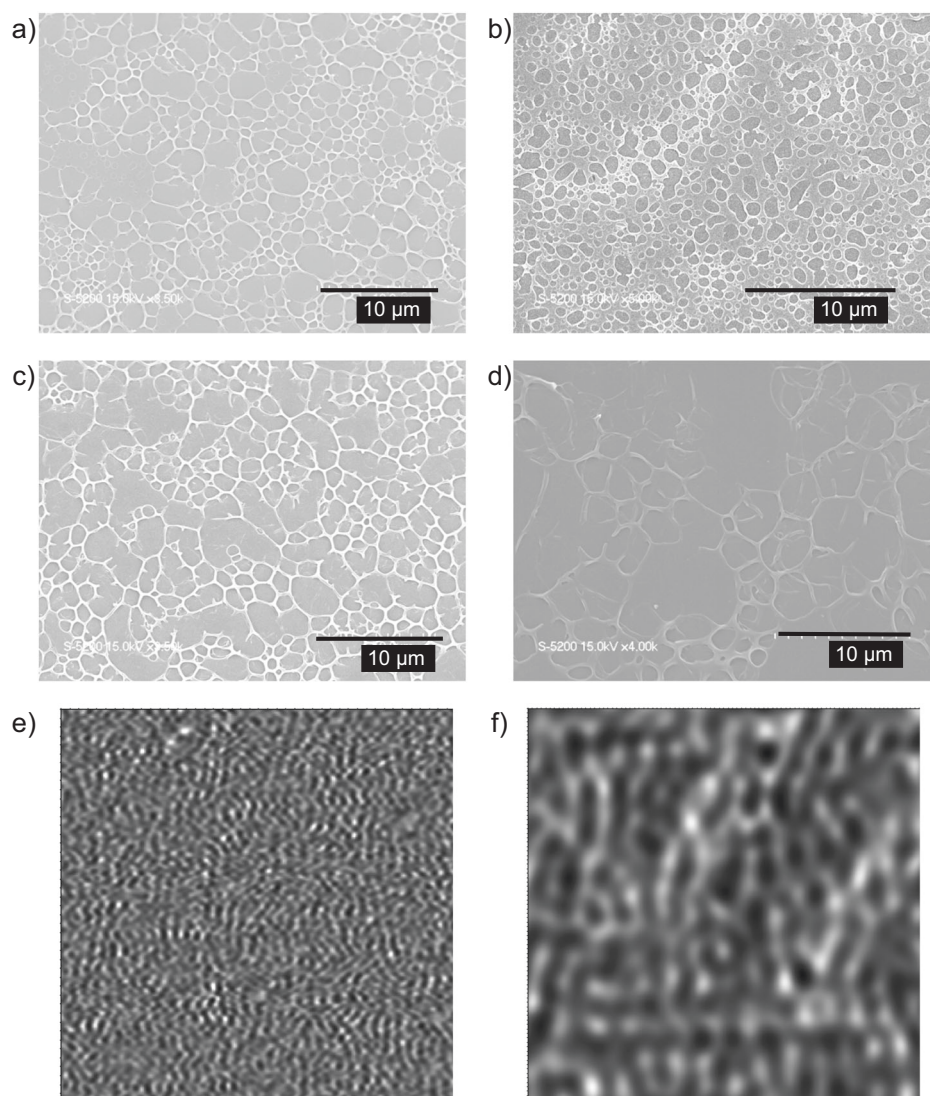
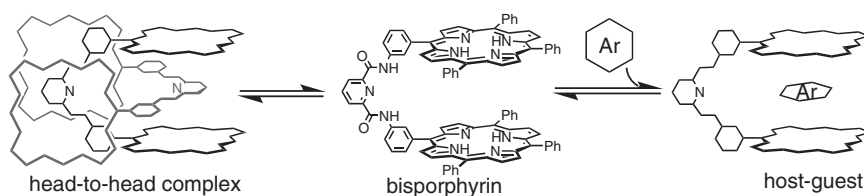


Fig. 7 Schematic representation of the bisporphyrin head-to-tail assembly and its dissociation by guest complexation



The supramolecular polymer chain of *poly-4* is composed of monomers held together by the host–guest association. The supramolecular polymer chain is therefore time-averaged due to the fast association and dissociation rate of the monomer. This feature of the chain results in unique behaviors in solution. The solution viscosity depends on its concentration, and a transition between the dilute concentration regime and the semidilute concentration regime can be seen. In the semidilute regime, the supramolecular polymer chains overlap, contributing to viscous drag; therefore, the

supramolecular chain behaves as a conventional polymer chain in solution. The dissociation and recombination of the host–guest pair is involved in the dominant relaxation process of the supramolecular polymer chain on the experimental timescale. Cates’s mixed reptation-breakage regime predicts that a scaling exponent of 3.0–3.4 is expected when the lifetime of the host–guest connection is sufficiently long [70]. An experimentally determined value of 3.07 in the semidilute regime is close to the value predicted by Cates. Accordingly, the supramolecular chain most likely relaxes via a reptation

Fig. 8 Supramolecular polymerization of the bisporphyrin cleft

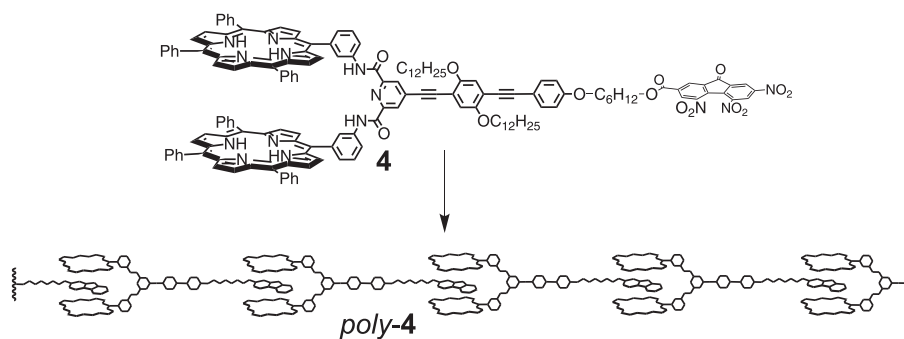
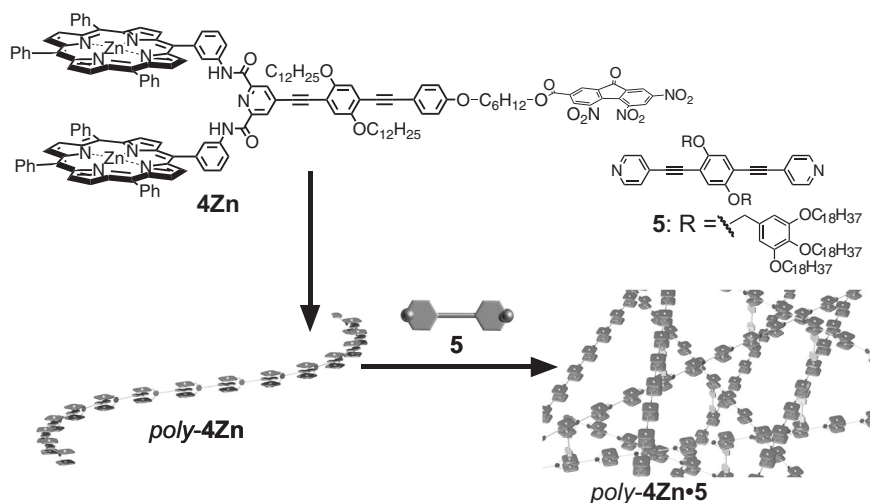


Fig. 9 Schematic representation of the cross-linking of supramolecular polymer *poly-4Zn* with bipyridine ligand **5**. Adapted with permission from ref. [72]



mechanism even though the monomers are connected via non-covalent host–guest interactions.

Supramolecular porphyrin networks

A supramolecular polymer generally gives rise to a fragile film in bulk because the supramolecular bonds holding the polymeric assembly together are weak enough to dissipate on relatively short timescales. Cross-linking supramolecular polymer chains is a reliable method of make supramolecular polymer materials robust in bulk. For example, Rebek's hydrogen-bonding calix[4]arene monomer, possessing multitopic binding sites, assembled to form supramolecular hydrogen-bonded polymer networks that exhibited measurable and meaningful mechanical integrity [71]. Chain cross-linking was extended to supramolecular porphyrin polymer *poly-4*. The extra coordination site of the porphyrin unit can be introduced by installation of a zinc ion in the porphyrin core, giving rise to monomer **4Zn** (Fig. 9) [72]. Bispyridine **5** is responsible for two coordination bonds that cross-link the supramolecular polymer chains.

The cross-linking by **5** is extremely effective for increasing the thermodynamic stability of the supramolecular networks

in solution. **4Zn** formed a head-to-tail supramolecular polymer with a DP of 17 at millimolar concentrations. Upon addition of **5** into a solution of **4Zn**, the coordination bonds cross-linked the supramolecular chains, resulting in supramolecular polymer networks that are thermodynamically stabilized with the cooperative assistance of the host–guest interaction and the coordination cross-links, leading to a very high DP of $>10^3$ at the same concentration.

The cross-linking of supramolecular polymer *poly-4Zn* significantly influences its chain dynamics in solution. At low concentrations, a solution of *poly-4Zn* acts as a Newtonian fluid. The viscosity of the solution gives rise to a critical polymerization concentration (CPC) at which the supramolecular polymer chains start overlapping in solution. The presence of cross-linker **5** reduces the CPC, and the magnitude of the reduction is correlated with the amount of **5** added; accordingly, the coordination of **5** to supramolecular polymer *poly-4Zn* facilitates polymer growth in solution. Eventually, the cross-linking of the supramolecular chains via coordination bonds promotes the formation of highly entangled polymer networks. The solution behavior follows the sticky reptation regime predicted based on the Rubinstein–Semenov model [73].

Fig. 10 A solution of **a 4Zn** (18 wt%) and a gel of **b 4Zn** with 1 eq. of **5** (18 wt%) in 1,1,2,2-tetrachloroethane. **c** A free-standing film prepared from a chloroform solution of **4Zn** with 1 eq. of **5**. Adapted with permission from ref. [72]

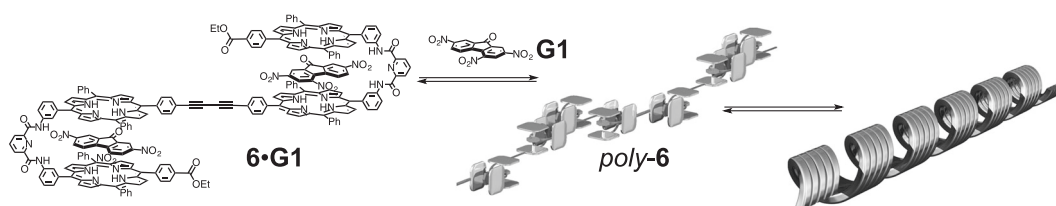
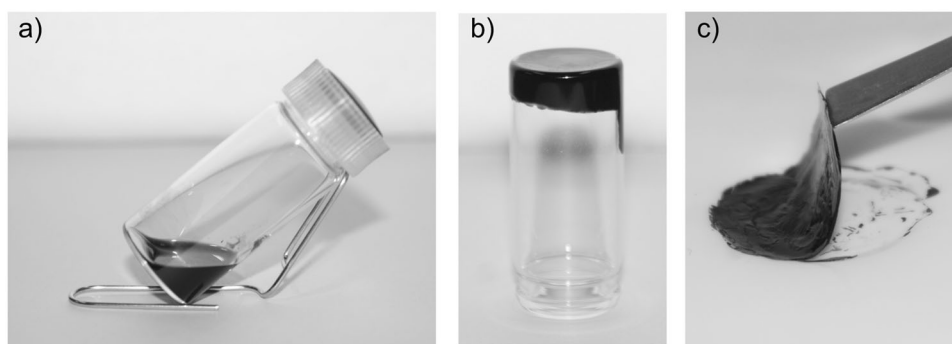


Fig. 11 Supramolecular polymerization via self-assembly of tetrakisporphyrin **6**. Adapted with permission from ref. [74]

The host–guest interactions and the coordination bond typically last for a shorter period than the chain terminal relaxation of the supramolecular polymer; therefore, the breaking and reforming of these non-covalent bonds determines the chain dynamics of the supramolecular polymer network of *poly-4Zn•5* in solution. The relaxation process of the supramolecular polymer network is dominated by a single terminal relaxation time. The breaking and reforming dynamics for the non-covalent bonds are similar to the lifetime of an equivalent unbreakable chain model in associating polymers. The chain relaxation process becomes faster than the breaking and reforming of the non-covalent bonds when high-frequency stress is applied. Accordingly, supramolecular polymer *poly-4Zn•5* gives rise to a solution consisting of an entangled associating polymer network for which the bond lifetime of the non-covalent connections and interactions between each monomer most likely become longer due to steric congestion.

Poly-4Zn in tetrachloroethane gives a purple solution (Fig. 10a). In contrast, a solution of *poly-4Zn•5* becomes sticky and forms a gel (Fig. 10b). The removal of the solvent from the gel results in a film of *poly-4Zn•5* that is stable in bulk, generating an elastic free-standing film (Fig. 10c). A Young's modulus of 1 GPa implies that the supramolecular network polymer, comprising the molecular units, is mechanically robust. The supramolecular network copolymer thus becomes a supramolecular material with a robustness that might be useful for self-healing applications.

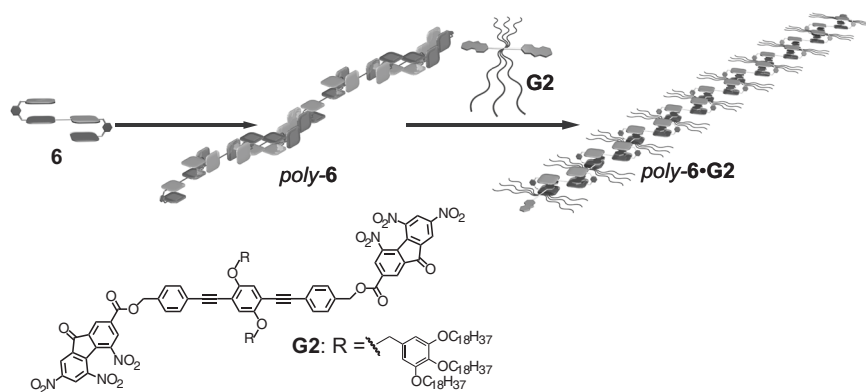
Porphyrin polymerization directed by complementary dimerization

The complementary head-to-head dimeric structure of the bisporphyrin cleft is controlled through donor–acceptor interactions and the stacking interactions (Fig. 7). A brand-new supramolecular polymer, *poly-6*, was fabricated by employing this unique supramolecular complex (Fig. 11) [74]. The two bisporphyrin units need to be connected with a butadiyne linker to give rise to homoditopic tetrakisporphyrin monomer **6**. The formation of the self-complementary dimeric bisporphyrin at each end results in supramolecular nanoscale polymer *poly-6*.

The self-association of **6** gave rise to an association constant ($\log K_a$) of 6.2. This extremely large association constant results in the formation of sizable supramolecular polymers in solution. The stimuli-responsive nature of supramolecular polymer *poly-6* was observed in solution. The competitive association of **G1** into the bisporphyrin cleft completely disrupts the supramolecular chain and forms host–guest complex **6•G1**₂.

Supramolecular polymer *poly-6* forms nanometer-scale, long, winding and fibrous fragments in the solid phase. A supercoiled structure with a pitch of 64 nm is seen in the AFM micrographs. Considering that the supramolecular chain structure has a diameter of ~2 nm, the oriented supercoiled structures are likely organized by the association of the supramolecular polymer chains of *poly-6*.

Fig. 12 Schematic representation of the structural reorganization of homopolymer *poly-6* into copolymer *poly-6•G2*. Adapted with permission from Ref. [75]



Approximately 30 polymer chains of *poly-6* compose each coiled fiber based on the magnitude of the pitch (Fig. 11).

Sequence regulation of supramolecular polymer chains

Sequence reorganization of homopolymers into copolymers

Copolymers are composed of two or more kinds of monomers that result in a variation to the polymer structures. The types of copolymer sequences are referred to as random, gradient, alternating, and block. The physical and chemical properties of the materials vary based on differences in the sequence structure. Determining these sequence structures is of great interest in polymer science. A conventional polymer chain is maintained with covalent bonds; thus, the copolymer structures are not generally interchangeable. It is challenging to reorganize these sequence structures through the postmodification of a polymer main chain.

The chain modification of a supramolecular polymer requires that at least two competitive sets of host–guest interactions must be possible in a monomer: one set generates the supramolecular main chain, and the other allows the formation of the new supramolecular chain by simultaneously breaking the preformed supramolecular chain. The bisporphyrin cleft forms two supramolecular complexes of the self-complementary dimer and the donor–acceptor host–guest complex; thus, **6** fulfils this requirement. Guest **G1** is a strong competitor for disassembling supramolecular homopolymer chains *poly-6* (Fig. 11). Employing ditopic guest **G2** instead of **G1** allows the reorganization of homopolymer *poly-6* into supramolecular copolymer *poly-1•G2* with an alternating repeating host–guest sequence (Fig. 12) [75].

The complexation of **G2** to *poly-6* increases the average molecular weight of *poly-6*. A 1:1 ratio of **6** and **G2** leads to

the largest molecular weight of *poly-6* with **G2**, confirming the formation of the alternating repeating host–guest sequence of copolymer *poly-6•G2*. Excess **G2** relative to **6** disrupts supramolecular polymer *poly-6* to form **6•G2**₂. In contrast, a smaller amount of **G2** partially disrupts homopolymer *poly-6*. In this regime, the homopolymerization to form *poly-6* most likely competes with the copolymerization to form *poly-6•G2*, resulting in *poly-6*_m•*G2*_n random copolymers through the recombination between the homo- and copolymers.

The homo- and copolymer structures display distinct solution properties. Supramolecular polymers *poly-6* and *poly-6•G2* display a transition from the dilute to the semidilute concentration regimes due to the chain overlap, which contributes to the viscous drag. In the semidilute regime, Zimm-like behaviors are found in both types of supramolecular polymer chains, and they are described as unentangled semi-dilute polymer solutions. Supramolecular polymer *poly-6•G2* only shows a further transition in the semidilute regime where chain relaxation occurs, which is similar to that is seen with living polymer chains in the mixed reptation-breakage regime. Accordingly, the substantial supramolecular polymer comes in contact with itself, and the flexible supramolecular chain is entangled. In contrast, well-developed supramolecular chain *poly-6* is rod-like and thus cannot be entangled. The strong shear thinning behavior of *poly-6* is characteristic of a rigid rod-like polymer.

The competitive guest complexation perfectly reorganizes the main chain of homopolymer *poly-6* to copolymer *poly-6•G2* with a repeating host–guest sequence. The chain reorganization of the supramolecular polymer results in the postmodification of the chain in solution, altering its properties.

Sequence-controlled supramolecular terpolymer

Sequence regulation is one of the most challenging objectives in polymer science [76, 77]. Although a stepwise

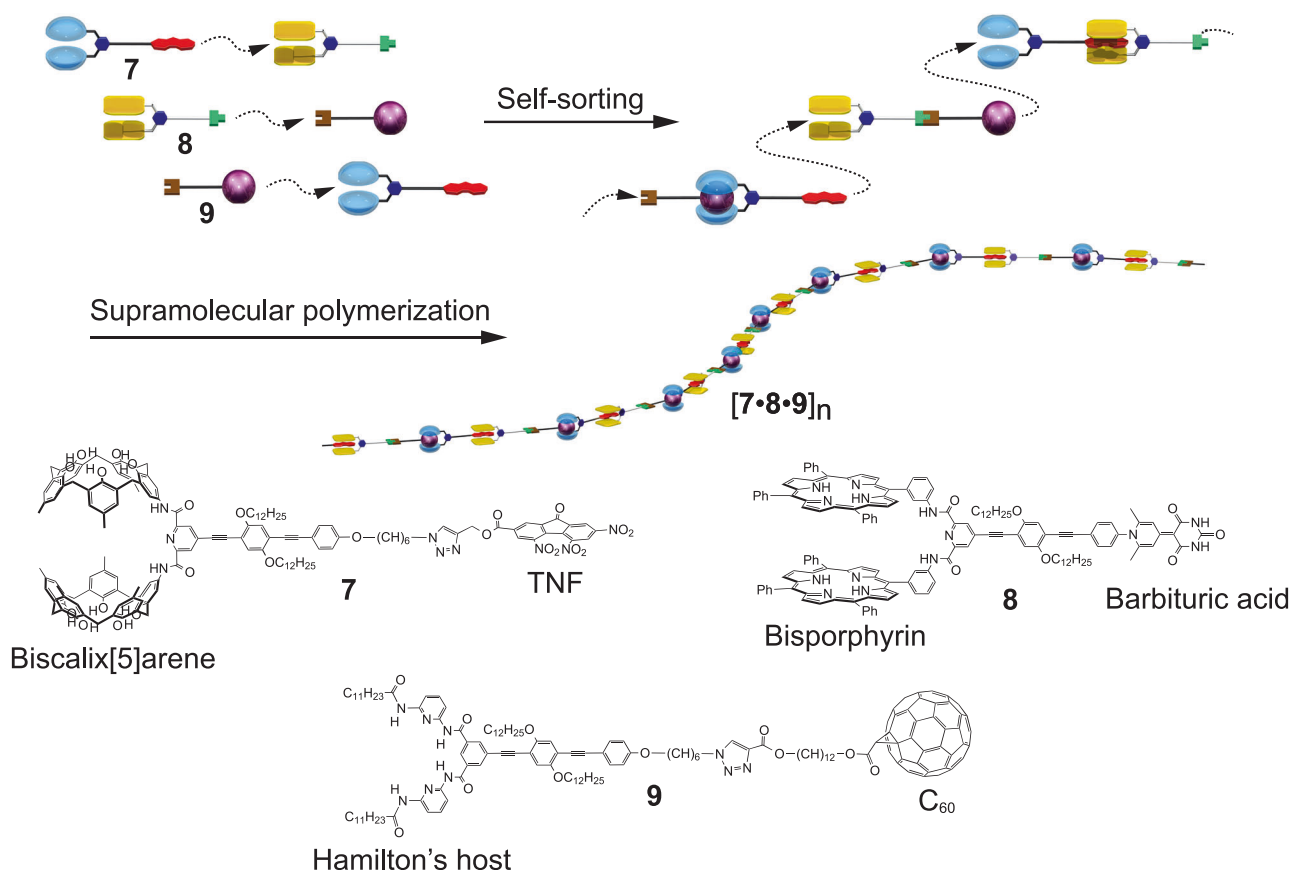


Fig. 13 Schematic representation of the supramolecular terpolymerization of three components, **7**, **8**, and **9**, via self-sorting assembly or random assembly. Structures of the three heteroditopic monomers, **7**, **8**, and **9**, possessing mismatched host–guest pairs. Adapted from ref. [84]

synthesis on a solid support guarantees the preparation of sequence-defined and monodisperse polymers, this method is not suitable for large-scale synthesis [78, 79]. Generating polymers with perfectly regulated microstructures using a straightforward, solution-phase polymerization process under controlled conditions is generally difficult [80–82]. Molecular recognition-directed self-sorting can be used to control the monomer sequence in a copolymerization. To synthesize an AB alternating repeating sequence of a supramolecular copolymer, only one set of host–guest structures is required because the AB sequence is established by the iterative host (H)–guest (G) association between homoditopic monomers H–H and G–G comprising two hosts or two guests. The supramolecular polymer is obtained in the sequence-defined form of $(H-H\cdot G-G)_n$. In contrast, ABC-sequence control requires three sets of host–guest structures that show extremely high specificities. A biscalix[5]arene- C_{60} complex and a bisporphyrin-TNF complex have been demonstrated for supramolecular polymerizations. The former is driven by stacking interactions, and the latter is stabilized by donor–acceptor interactions; thus, the different characteristics of the interactions result in high specificities in this host–guest complexation system.

ABC-sequence control must employ another host–guest motif that shows orthogonality to these host–guest complexes. A Hamilton-type hydrogen-bonding host–guest complex fulfils this requirement [83]. A biscalix[5]arene- C_{60} complex, a bisporphyrin-TNF complex, and a Hamilton-type hydrogen-bonding complex are capable of generating a supramolecular terpolymer with a controlled sequence through self-sorting behavior (Fig. 13) [84].

Designed monomers **7**, **8** and **9** possess a mismatched combination of host and guest units; therefore, the self-associations are not permitted, and the intermolecular associations are highly specific, and dimeric complexes **7•8**, **8•9**, and **9•7** can be formed. Eventually, a supramolecular terpolymer with the controlled sequence **7•8•9** is constructed via this self-sorting behavior.

The formation of the desired sequences of terpolymer $[7\cdot 8\cdot 9]_n$ was assessed in the gas phase. Three sets of pentamers, $[7\cdot 8\cdot 9\cdot 7\cdot 8]$, $[8\cdot 9\cdot 7\cdot 8\cdot 9]$, and $[9\cdot 7\cdot 8\cdot 9\cdot 7]$, three sets of tetramers, $[8\cdot 9\cdot 7\cdot 8]$, $[7\cdot 8\cdot 9\cdot 7]$, and $[9\cdot 7\cdot 8\cdot 9]$, and one set of trimers, $[7\cdot 8\cdot 9]$ were found in the gas phase, consistent with the fragments expected from the designed repeating sequence of supramolecular terpolymer $[7\cdot 8\cdot 9]_n$. Site-specific chain termination by end-capping experiments

with C₆₀, 2,4,6-TNF, and barbituric acid ruled out scrambled repeating sequences. Thus, the repeating sequence **7-8-9** in the supramolecular terpolymer was established in the gas phase.

The DP of supramolecular polymers relies on their concentrations. A 1:1:1 mixture of **7**, **8**, and **9** showed a concentration-dependent DP in solution. At high concentrations, a DP of 200 was found, whereas only monomers were observed at low concentrations. The solution viscosity displayed an even more obvious concentration dependence. A 1:1:1 mixture of **7**, **8**, and **9** resulted in a viscous solution at high concentrations; whereas, the monomers did not affect the solution viscosity. The supramolecular terpolymer chain is well-developed at high concentrations, which contributes to viscous drag.

SEM measurements showed well-developed polymeric fibers with sheet-like bundles generated from a 1:1:1 ratio of **7**, **8** and **9**. Accordingly, the formation of long, fibrous polymer chains occurs through the iterative molecular recognition of **7**, **8**, and **9** in a self-sorting manner.

An ABC-sequence-controlled supramolecular terpolymer is constructed by using ball-and-socket, donor-acceptor, and hydrogen-bonding interactions. The high-fidelity self-sorting of these molecular recognition moieties determines the directionality and specificity that directs the supramolecular terpolymerization and forms the controlled ABC-sequence. Many host-guest structures with controllable structural and electronic properties are available. Thus, extensive application of our synthetic methodology may allow the construction of synthetic polymers with tailored sequences and structural variations.

Postmodification of polymer chains by molecular recognition

Supramolecular graft copolymerization via molecular recognition of a self-assembled capsule

A branched copolymer possessing one or more polymeric side chains may be introduced into a polymer backbone, and this is known as a graft polymer. The steric interactions of dense side chains can significantly reduce the conformational flexibility of a polymer main-chain. A difference in conformation is associated with changes in physical properties, leading to potential applications of graft polymerization for practical uses. Graft polymer synthesis has become an active technique in polymer science. “Graft through,” “graft onto,” and “graft from” are methods for fabricating graft structures in conventional polymers [85, 86]. However, synthetic methods that allow access to graft polymer structures are complicated.

Supramolecular chemistry can offer an approach to producing graft polymer structures in a facile manner. Guests repeatedly located in a polymer chain are recognized by a host to direct the formation of a graft polymer structure. Our resorcinarene-based coordination capsule **10** was employed to fabricate a graft copolymer. Guest **G3** is encapsulated and is located along the principal axis within capsule **10** (Fig. 14) [87–90]. The dynamic interconversion between the (*P*)- and (*M*)-enantiomeric forms of capsule **10** is biased by the encapsulation of chiral guest (*R*)-**G3**, resulting in (*R*)-**G3** ⊂ (*M*)-**10** with an extremely high diastereoselectivity of 98%. This host-guest structure exploited, resulting in a supramolecular graft polymer. The synthetic strategy for preparing the supramolecular graft polymer is shown in Fig. 15. Multiple guest units are incorporated into the polyester main chain. Site-selective molecular recognition of the capsule results in the supramolecular graft copolymer (Fig. 15) [91].

The repeating guest sites in *poly-11* are recognized by capsule **10**. The hydrodynamic volumes of the polymer chains are substantially increased upon complexation with the capsule. When 50% of the guest units are encapsulated with the capsules, the hydrodynamic volume of the graft polymer is 15 times higher than that of the polymer without the capsule. Therefore, the capsules are successfully located on the polymer main chain, changing its solution properties.

In the solid-state, the flexible chain of *poly-11a* forms random aggregates, which are visibly converted into the completely extended polymer chain by the complexation of capsule **10**. The substantial steric interactions most likely occur among the bulky capsules located on the polymer chain; these interactions decrease the conformational flexibility of the polymer chain and lead to chain extension. The average length of the fibers (DP = 23) given based on the AFM image nicely matches the DP of 19 determined by GPC analysis. The shorter interguest distance in *poly-11a* results in a different morphology. *Poly-11b* gives rise to agglomerates due to non-specific aggregation. The guest encapsulation with the capsule causes a shift from an agglomerate morphology to helical organization. The (*M*)-helical configuration of the capsule determines the (*M*)-helical morphology of the polymer.

The molecular recognition of a molecular guest by the capsule is completely independent in solution. In contrast, the chirality of the grafted capsule is not linearly correlated with the enantiopurity of the stereo-random copolymers upon encapsulation of the guests on the random copolymers. The dominant enantiomer of the guest units is observed to have a disproportionate effect on the chirality of the grafted capsules. This uncommon chiral amplification in the supramolecular grafting polymer is known as a

Fig. 14 Structure of supramolecular capsule **10** and encapsulation of chiral guest **G3**

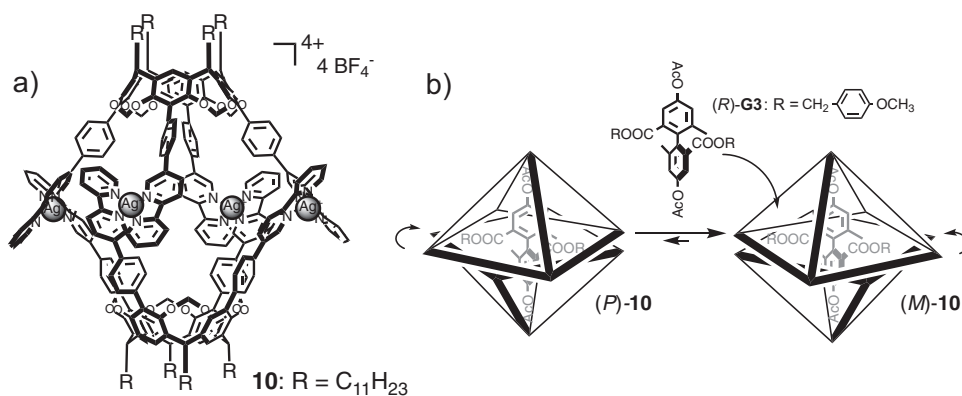


Fig. 15 Schematic representation of supramolecular graft polymerization. Adapted with permission from ref. [91]

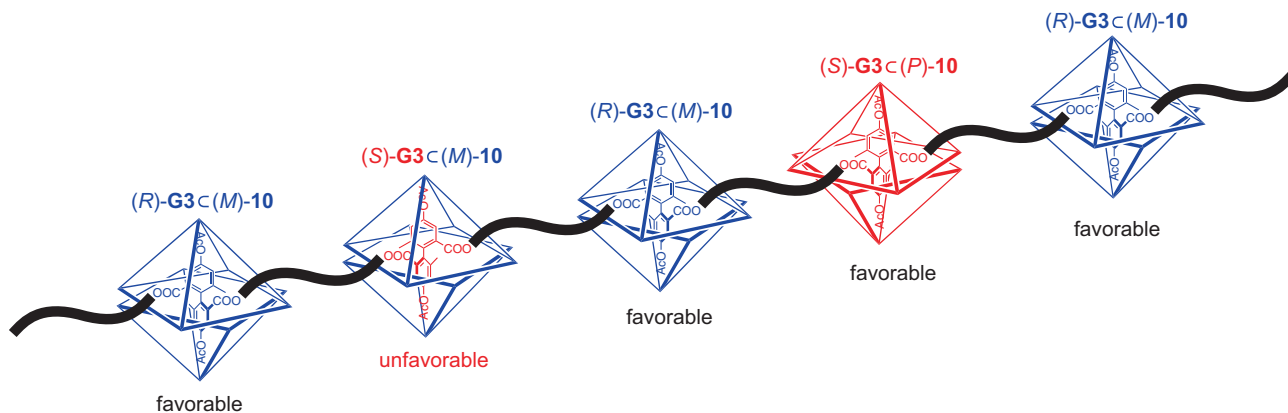
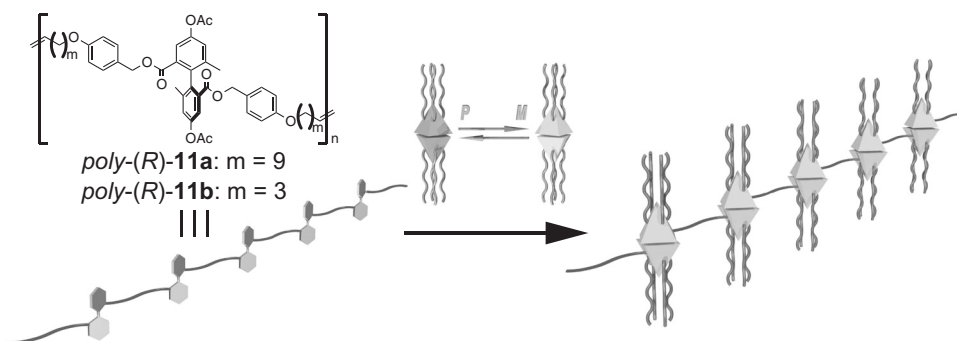


Fig. 16 Majority-rules effect in guest recognition on a polymer chain

majority-rules effect. The multiple guests binding to the polymer main chain causes the capsules to be closer to each other, most likely resulting in certain steric interactions among the exteriors of the bound capsules (Fig. 16). Then, the favorable interaction between a (*P*)-capsule and an (*S*)-guest is shifted to predominantly the unfavorable (*M*)-capsule with an (*S*)-guest interaction. The energetic penalty in the unfavorable diastereomeric complex is most likely compensated by the preferable steric interaction at the exteriors of the neighboring predominant diastereomeric complexes.

Supramolecular cross-linking of polymer chains to control polymer organization by ball-and-socket interactions

The cross-linking of a polymer chain results in a networked polymer with a significantly reduced structural flexibility, which has considerably different macroscopic morphologies and properties compared to the parent polymer. Covalent bonds are generally utilized for cross-linking; therefore, cross-linked networks are irreversible and stable. Introducing non-covalent bonds into a

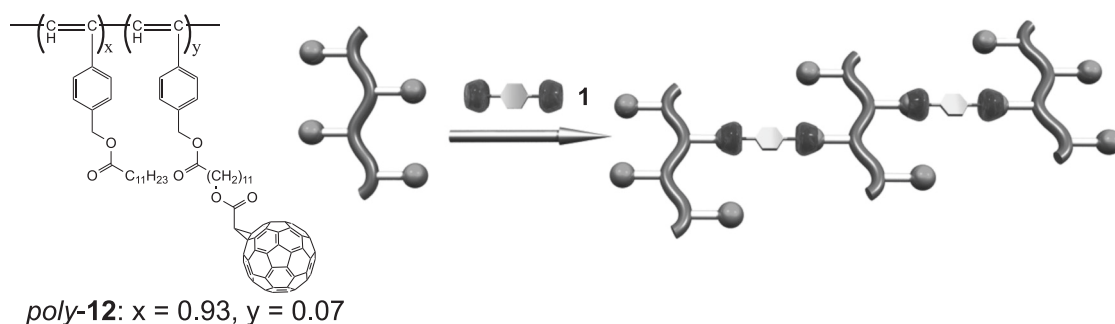
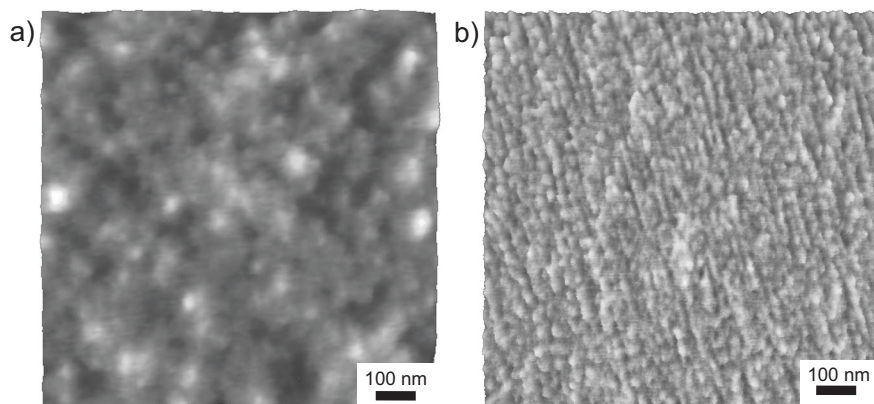


Fig. 17 Supramolecular cross-linking by ball-and-socket interactions. Adapted with permission from ref. [92]

Fig. 18 AFM images of *poly-12* **a** without **1** and **b** with **1**. Adapted with permission from ref. [92]



polymer chain cross-linkage produces reversible polymer networks that can serve as stimuli-responsive polymer materials.

The calix[5]arene–fullerene interaction can be employed for the cross-linking of polyacetylene polymer chains (Fig. 17) [92]. The fullerene units grafted on the polyacetylene chains are encapsulated with ditopic calix[5]arene host **1**. The multiple “ball-and-socket” interactions form stable cross-links to fullerene-containing polyacetylene *poly-12*. The formation of the cross-links via the “ball-and-socket” interaction increases the molecular weight of *poly-12* more than twofold. The formed cross-links are quite stable even in the presence of excess **1**. The intermolecular interaction of the calix[5]arene and the fullerene depends on the solvent. Halogenated solvents, such as chloroform and chlorobenzene, weaken the intermolecular interactions, completely disrupting the cross-links in *poly-12*.

The morphologies of *poly-12* are notably affected by cross-linking. The immiscibility and π – π interactions of the fullerene units are responsible for their cohesion, which results in random aggregation and leads to agglomerated particles of *poly-12* (Fig. 18a). When the fullerene is encapsulated by **1**, the interfullerene interactions are disrupted, resulting in the chain extension of *poly-12*. As a

result, the macroscopic morphologies of the particle-like agglomerates completely disappear, and they are transformed into widespread fibrillar networks. A highly organized two-dimensional polymer array can be produced by aligning the cross-linked polymer fibrils on a highly oriented pyrolytic graphite (Fig. 18b).

Conclusion

A supramolecular polymer can be considered a supramolecular assembly that is structurally similar to a conventional polymer. Currently, these polymers are classified as an emerging type of material in the field of polymer science. The structure and properties of a supramolecular polymer are primarily determined by the complementary molecular interactions that connect each monomer. The specificity and stability of the complementary molecular interactions are directly determined by non-covalent interactions. Therefore, the functionalities that will afford the desired selectivity and specificity can be incorporated into complementary host–guest structures. This flexibility in the host–guest structures allows substantial and adaptable designability of the structure of the supramolecular polymer chain. The rational design of a complementary host–guest structure

results in a designer supramolecular polymer with the desired functions.

Our recent progresses in developing designer supramolecular polymers using unique complementary host–guest interactions are described in this article. The supramolecular polymer chains are demonstrated to behave similar to conventional polymer chains, even though their structures are constitutionally dynamic and time-averaged. The limited robustness of the supramolecular polymers due to the weakness of the non-covalent bonds may impede the practical application of supramolecular polymer materials. However, the supramolecular networking of linear polymeric assemblies has been shown to generate self-standing films that possess a certain durability. This has been demonstrated as a strategy for overcoming the poor robustness. The high designability of the monomer structure is a great advantage of supramolecular polymer materials. The photochemical and electrochemical properties, as well as mechanical properties, are tunable; therefore, supramolecular polymer materials with fascinating functions can be prepared and might be coming into their own.

Acknowledgements This work was supported by Grants-in-Aid for Scientific Research, JSPS KAKENHI Grant Numbers JP15H03817 and JP15KT0145, and by Grants-in-Aid for Scientific Research on Innovative Areas, JSPS KAKENHI Grant Numbers JP15H00946 (Stimuli-responsive Chemical Species), JP15H00752 (New Polymeric Materials Based on Element-Blocks), JP17H05375 (Coordination Asymmetry), and JP17H05159 (π -Figuration). We also acknowledge the Futaba Electronics Memorial Foundation.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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