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Supramolecular Fullerene Polymers and Networks Directed by Molecular Recognition between Calix[5]arene and C_{60}

Takehiro Hirao,[a] Masatoshi Tosaka,[b] Shigeru Yamago,[b] and Takeharu Haino*[a]

Dedicated to Professor Dr. Julius Rebek, Jr. on the occasion of his 70th birthday

Abstract: A biscalix[5]arene–C_{60} supramolecular structure was utilized for the development of supramolecular fullerene polymers. Di- and tritopic hosts were developed to generate the linear and network supramolecular polymers through the complexation of a dumbbell-shaped fullerene. The molecular association between the hosts and the fullerene were carefully studied by using ^{1}H NMR, UV/Vis absorption, and fluorescence spectroscopy. The formation of the supramolecular fullerene polymers and networks was confirmed by diffusion-ordered ^{1}H NMR spectroscopy (DOSY) and solution viscometry. Upon concentrating the mixtures of di- or tritopic hosts and dumbbell-shaped fullerene in the range of 1.0–10 mmol L^{-1}, the diffusion coefficients of the complexes decreased, and the solution viscosities increased, suggesting that large polymeric assemblies were formed in solution. Scanning electron microscopy (SEM) was used to image the supramolecular fullerene polymers and networks. Atomic force microscopy (AFM) provided insight into the morphology of the supramolecular polymers. A mixture of the homoditopic host and the fullerene resulted in fibers with a height of (1.4 ± 0.1) nm and a width of (5.0 ± 0.8) nm. Interdigitation of the alkyl side chains provided secondary interchain interactions that facilitated supramolecular organization. The homotritopic host generated the supramolecular networks with the dumbbell-shaped fullerene. Honeycomb sheet-like structures with many voids were found. The growth of the supramolecular polymers is evidently governed by the shape, dimension, and directionality of the monomers.

Introduction

Supramolecular polymers consist of repeating units that are held together by reversible noncovalent interactions.[1] The sizes and dimensions of these supramolecular polymers depend on the directionalities and stabilities of intermolecular interaction connecting the repeating units. Recent efforts have devoted to the construction of advanced supramolecular polymer materials, providing innovative features such as stimuli-responsiveness,[2] self-healing,[3] and easy fabrication.[4] A great majority of the supramolecular polymers developed to date involve hydrogen-bonding motifs[5] or metal coordination.[6] Supramolecular polymerization reactions driven by host–guest interactions have been employed to a lesser extent, although a vast number of host–guest complexes are known to exist. Supramolecular polymerization requires host–guest interactions with very high affinities to obtain an appreciable degree of polymerization. This requirement restricts the number of possible variations of host–guest interactions that can be exploited for supramolecular polymerization. Crown ethers,[7] cyclodextrins,[8] cucurbit[*n*]urils,[9] calix[*n*]arenes,[10] and molecular clefts[11] are well recognized as host molecules with very high affinities for guest molecules and provide useful supramolecular structures for polymerization. Among calixarene families, calix[5]arenes are less employed as host molecules for supramolecular polymerization.[12] We have been developing calix[5]-arene-based host molecules,[13] and during the course of our studies, we discovered that they encapsulate fullerenes.[14] In one study, biscalix[5]arene structures were observed to be great host molecules for C_{60} as well as higher fullerenes.[15] Thus, we envisioned the development of supramolecular fullerene polymers and networks utilizing the host–guest interaction between a biscalix[5]arene and C_{60}.

The spherical shapes and unusual electronic properties exhibited by molecules of the fullerene family have attracted great interest for the construction of carbon-based materials that exhibit magnetic,[16] superconducting,[17] electrochemical,[18] and photophysical functions,[19] particularly n-type-directed fullerenes[20] for the development of organic solar cells. Nanofabrication of fullerene is a prerequisite for efficient photoelectronic conversion in fullerene-based organic solar cells.[21] Thus, recent endeavors have been dedicated to controlling the

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organization of fullerene nanoarrays at the molecular level, refining the performance of such devices. Supramolecular fullerene polymers can offer an effective way to organize fullerene nanoarrays. Hence, intensive research concerning the development of fullerene polymers in a noncovalent fashion is currently being conducted. Hummelen et al. reported the pioneering example of a hydrogen-bonded supramolecular polymer featuring a fullerene array.[22] Liu et al. demonstrated a metallo-bridged supramolecular fullerene assembly driven by a 1:2 complexation of C_{60} and β-cyclodextrin.[23] Recently, Martín et al. reported that exTTF–C_{60} complexation (exTTF = 9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene) is very useful for constructing supramolecular fullerene polymers and dendrimers.[24] However, placing fullerene molecules on polymer main chains is still challenging, because a limited number of fullerene host molecules have been used for supramolecular polymerization.

Preliminary results regarding supramolecular fullerene polymerization through molecular recognition between a calix[5]arene and C_{60} have been reported.[25] However, the macroscopic properties of the previous linear fullerene polymers in solution were not studied in detail due to the low solubility in common organic solvents. To improve the solubility of supramolecular fullerene polymers, long alkyl chains have been introduced into dumbbell-fullerenes. Herein, we describe the synthesis and the properties of a new class of linear and network fullerene polymers both in solution and in the solid state. Dumbbell-shaped fullerenes were newly designed to be sufficiently soluble in common organic solvents to study the formation of supramolecular fullerene polymers in solution (Figure 1). The supramolecular complexation between the calixarene hosts (**H1** and **H2**) and the guest fullerenes (**G 3a**,**b**) should give rise to linear supramolecular fullerene polymers and extended fullerene networks (Scheme 1), respectively.

Results and Discussion

The syntheses of tetrakis- and hexakiscalix[5]arene hosts **H1** and **H2** are outlined in Scheme 2. The reaction of the 4-carboxybenzenediazonium chloride (**4**)[26] with calix[5]arene **5**,[14c] followed by the reduction of the azobenzene moiety produced aminocalix[5]arene **6**. 4-Ethynyldimetyl chelidamate (**7**) was used in the synthesis of aromatic linker **8**.[25] Sonogashira reaction of **7** with 1,4-bis(dodecyloxy)-2,5-diiodobenzene[27] and the subsequent hydrolysis of ester moieties yielded the corresponding diacid, which was converted to diacid chloride **8**. The acylation reaction of **6** with **8** smoothly proceeded in THF to afford biscalix[5]arene **9** in good yield. To avoid the tedious

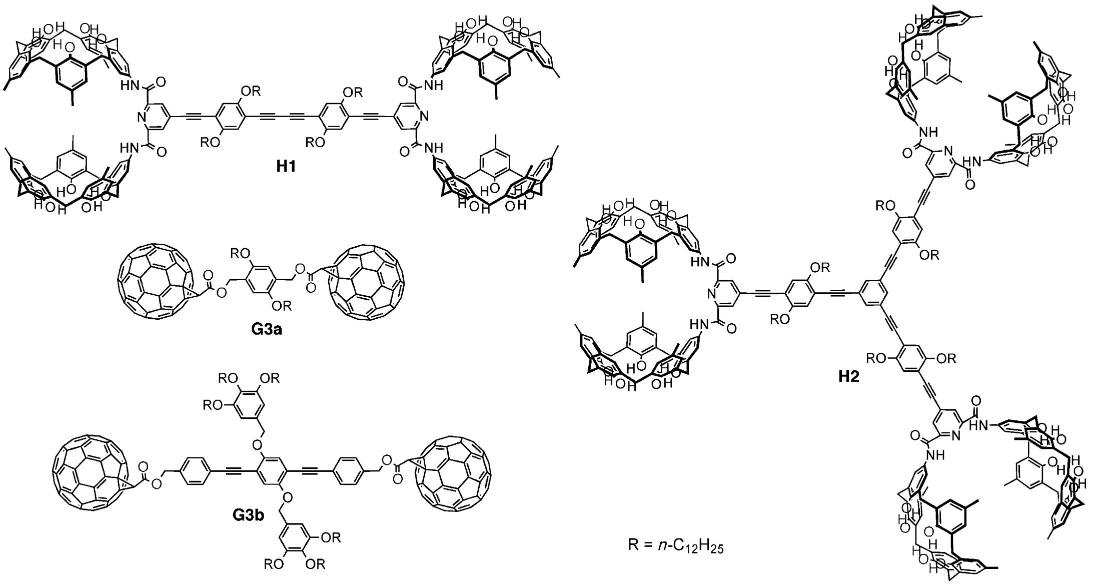
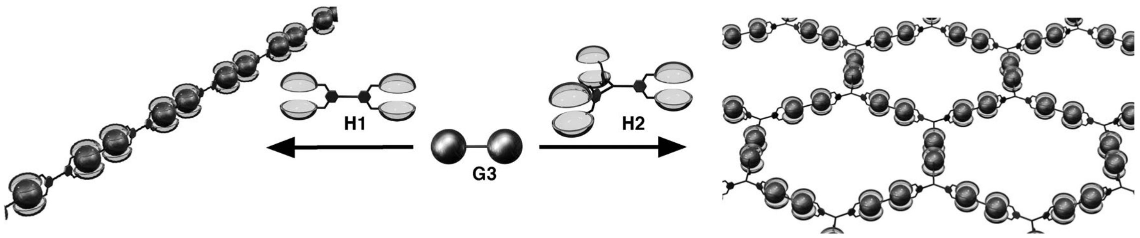
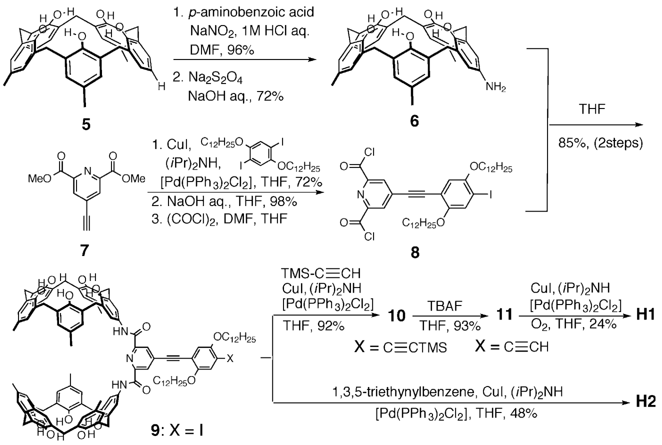


Figure 1. Molecular structures of calix[5]arene-based hosts **H1** and **H2** and dumbbell-shaped fullerene **G3 a**,**b**.



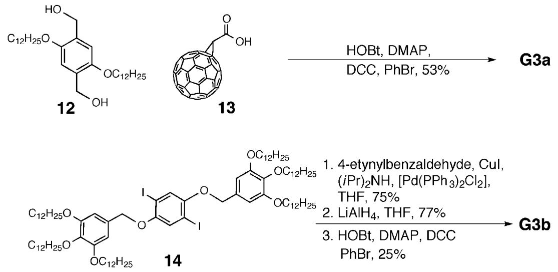
Scheme 1. Schematic illustration of the formation of supramolecular fullerene polymers.



Scheme 2. Synthesis of host molecules. DMF = dimethylformamide, THF = tetrahydrofuran, TMS = trimethylsilyl.

protection-deprotection procedures of the hydroxyl groups, an ethynyl group was directly introduced into **9**. Although oxidative coupling of **9** under Eglinton conditions was unsuccessful, modified Sonogashira conditions worked nicely to furnish ditopic host **H1** via compounds **10** and **11**. Sonogashira reaction of **9** with 1,3,5-triethynylbenzene proceeded smoothly to afford host **H2**.

The synthesis of dumbbell-shaped fullerenes **G3 a**,**b** is outlined in Scheme 3. Condensation reaction of **12**[28] and **13**[29] yielded **G3 a**. The synthesis of **G3 b** began with compound **14**.[30] Sonogashira reaction of **14** with 4-etynylbenzaldehyde followed by the reduction of the aldehyde groups and then a condensation reaction with **13** afforded **G3 b**.



Scheme 3. Synthesis of guest molecules. HOBt = 1-hydroxybenzotriazole, DMAP = *N*,*N*-dimethyl-4-aminopyridine, DCC = *N*,*N*′-dicyclohexylcarbodiimide.

Intermolecular associations between the homotopic hosts and dumbbell-shaped fullerenes in solution were studied using ^{1}H NMR, fluorescence, and UV/Vis absorption spectroscopy. Figure 2 shows the ^{1}H NMR spectra of **H1** and **H2** before and after the addition of **G3 a** in [D$_1$]-chloroform. A calix[5]arene adopts a cone conformation due to the cyclic hydrogen bonds of the five phenolic hydroxyl groups. When the ring flipping of a calix[5]arene is very slow on the NMR timescale, the bridge methylene protons are magnetically non-equivalent, resulting in an AB-type resonance. The bridge methylene protons commonly appear as a broad resonance at room temperature due to the rapid ring flipping. When C_{60} is encapsulated within a calix[5]arene cavity, it increases the ring-flipping activation energy. As a result, the bridge methylenes appear as an AB-like resonance.[14c] Thus, the proton resonance is a probe for the detection of the intermolecular association between a calix[5]arene and a C_{60} molecule.

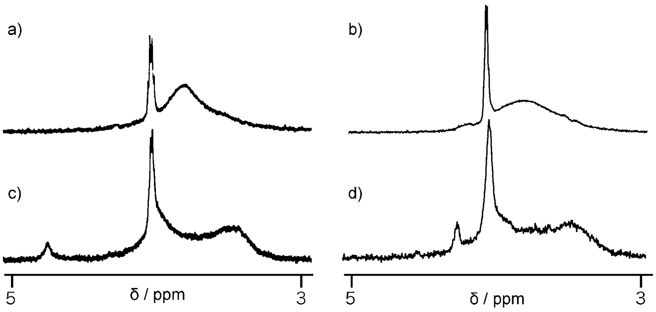


Figure 2. ^{1}H NMR spectra of a) **H1**, b) **H2**, c) a 1:1 mixture of **H1** and **G3 a**, and d) a 2:3 mixture of **H2** and **G3 a** at 293 K in [D$_1$]-chloroform.

Calix[5]arene hosts **H1** and **H2** displayed broad resonances of the bridge methylene protons at approximately 3.8 ppm, indicating that the ring-inversion process occurred rapidly even though the calix[5]arene moieties were close to their neighbors. Upon the addition of dumbbell-shaped fullerene **G3 a** in solutions of hosts **H1** and **H2**, the broad methylene resonances split roughly into two broad resonances, suggesting that the ring inversion of the calix[5]arene moieties became slower due to the complexation of the C_{60} moieties within the calix[5]arene cavity.

H1 and **H2** displayed absorption bands at 419 and 397 nm, attributable to the π–π* transition of the di(pyridylethynylphenyl)butadieyne and tri(pyridylethynylphynylethynyl)benzene moieties. Upon the addition of dumbbell-shaped fullerenes **G3 b** to the solutions of **H1** and **H2**, new bands emerged at approximately 420 and 400 nm, which are characteristic of the formation of a C_{60}•calix[5]arene complex (Figure S1 in the Supporting Information).[14c] When cooling the solution from 343 to 303 K, the absorption bands gradually increased in intensity. This finding implied that the host–guest complexations of **H1** and **H2** with **G3 b** were enhanced, resulting in the supramolecular aggregates. However, the overlap of the absorption bands of **H1**, **H2**, **G3 b**, and their complexes restricted the precise analytical treatments required to determine the intermolecular association. The highly conjugated aromatic linker moieties of **H1** and **H2** generated intense fluorescence at 451 and 464 nm, most likely corresponding to π–π* transitions (Figure 3 a,b). Fullerene is known to be a good energy acceptor;[15b] thus, these emissions can be quenched when a C_{60} moiety is encapsulated within the cavities of the hosts. The addition of **G3 b** quenched the emissions of **H1**. The emission of **H2** was more efficiently quenched than that of **H1** in the presence of **G3 b**; **H1** possesses two fullerene-binding cavities, each of which is composed of two calix[5]arenes, whereas three fullerene-binding cavies are implemented in **H2**. Accordingly, the concentration of the fullerene moieties closer to the fluorophores resulted in the effective quenching of **H2**.

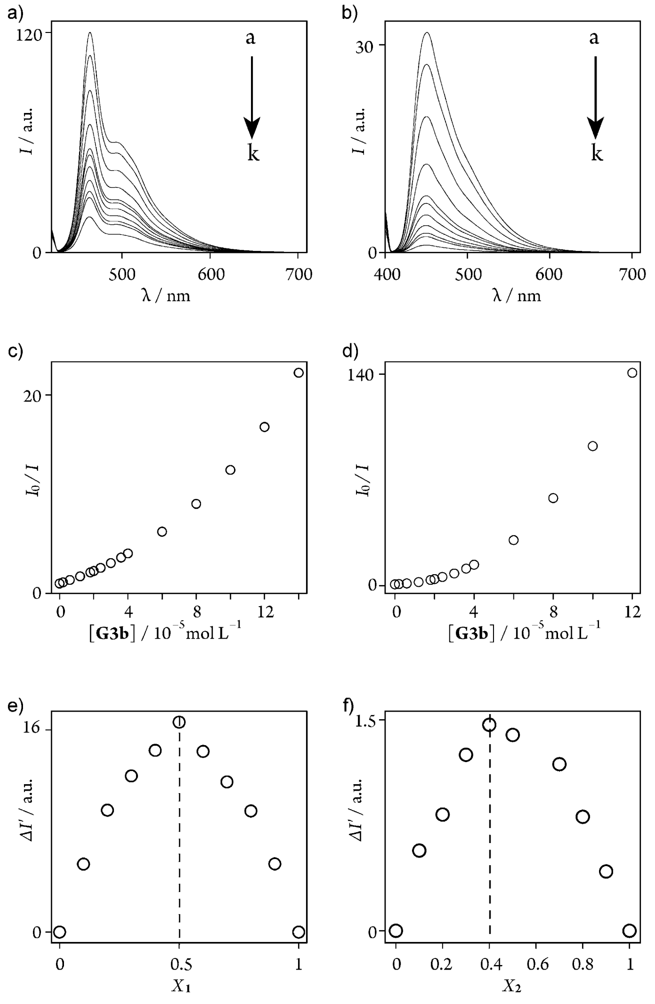


Figure 3. Fluorescence changes in a) **1** (2.0×10^{-5} mol L^{-1}, $\lambda_{ex}=420$ nm) and b) **H2** (2.0×10^{-5} mol L^{-1}, $\lambda_{ex}=400$ nm) in the presence of **G3 b** (a–k: 0.0, 0.1, 0.3, 0.6, 0.9, 1.0, 1.2, 1.5, 1.8, 2.0, 3.0×10^{-5} mol L^{-1}) at 298 K in toluene. Stern–Volmer plots for c) **H1** (2.0×10^{-5} mol L^{-1}, $\lambda_{ex}=420$ nm) and d) **H2** with **G3 b**. Job plots for e) **H1** with **G3 b** ([**H1**] + [**G3 b**] = 2.0×10^{-5} mol L^{-1}) and f) **H2** with **G3 b** ([**H2**] + [**G3 b**] = 2.0×10^{-5} mol L^{-1}). X_1 and X_2 indicate the molar fractions of **H1** and **H2**, respectively. $\Delta I'$ indicates $|I - I_0X|$.

Fluorescence quenching can occur by dynamic quenching (molecular collision), static quenching (complex formation), or by both dynamic and static quenching mechanisms simultaneously. In dynamic quenching, a quencher diffuses to a fluorophore during the lifetime of the excited state, and the fluorophore returns to the ground state without emission of a photon. In this case, the Stern–Volmer equation is expressed as $I_0/I = 1 + K_d[Q]$, in which K_d and [Q] are the Stern–Volmer constant for dynamic process and the concentrations of quencher, respectively. In common host–guest complexation, strong molecular association participates in the quenching process; thus, in combined dynamic quenching for partitioning molecules and static quenching for binding molecules, the Stern–Volmer equation is expressed as $I_0/I = (1 + K_d[Q])(1 + K_a[Q])$, in which K_a is the associate constant between quencher and fluorophore. In this case, the plot of I_0/I versus [Q] based on the equation should bend upward.[31] Figure 3 c,d shows the Stern–Volmer plots obtained from fluorescent intensity measurements upon the addition of **G3 b** in toluene. The plots of the relative fluorescence intensities I_0/I of **H1** and **H2** versus the concentrations of **G3 b** gave rise to a steeply upward curvature above a concentration of 4.0×10^{-5} mol L^{-1}. Static as well as dynamic quenching clearly participated in the overall quenching process. At low concentrations at which dynamic quenching was dominant, the distinct temperature dependence of the fluorescence quenching provided additional support for the static quenching mechanism that was involved in the host–guest complexation between fluorescent hosts **H1**, **H2**, and **G3 b** (Figure S4 in the Supporting Information). To gain stoichiometric insight into the intermolecular associations of hosts **H1**, **H2**, and **G3 b**, Job plots confirmed that **H1** bound **G3 b** in a ratio of 1:1, whereas the complexation of **H2** and **G3 b** resulted in host–guest complex in a ratio of 2:3 (Figure 3 e,f).

The sizes and dimensions of supramolecular polymers in solution can be determined by diffusion-ordered ^{1}H NMR spectroscopy (DOSY). According to the Stokes–Einstein relation, $D = k_BT/6\pi\eta R$, the diffusion coefficient (D) of a molecular species is inversely proportional to the hydrodynamic radius (R). Therefore, the degree of polymerization (DP) can be estimated by the weighted diffusion coefficients of existing molecular species. Figure 4 a demonstrates that diffusion coefficients of **H1**, **H2**, and **G3 b** were concentration-independent. No aggregate was formed in solution. By contrast, the diffusion coeffi-

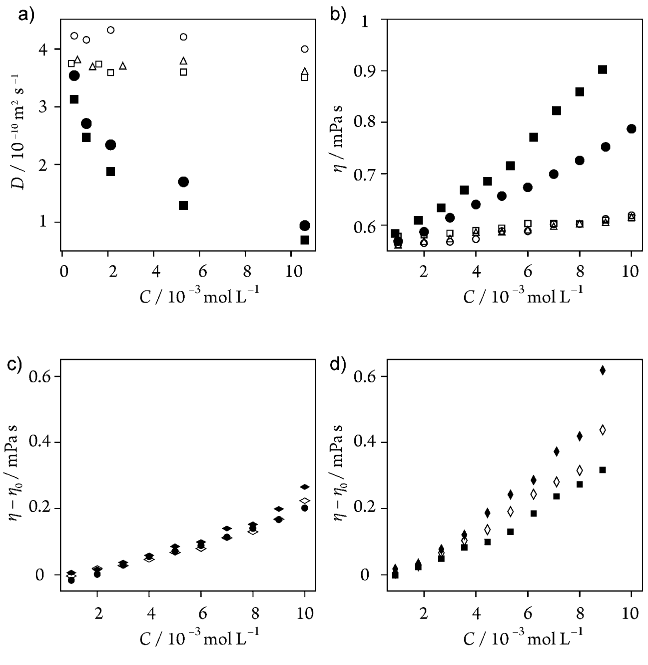


Figure 4. a) Diffusion coefficients (D) and b) viscosities (η) of **H1** (open circle), **H2** (open square), **G3 b** (open triangle), **H1** with one equivalent of **G3 b** (filled circle), and **H2** with 1.5 equivalents of **G3 b** (filled square) at 297 K in chloroform. Relative viscosities ($\eta - \eta_0$) of c) **H1** in the presence of one equivalent of **G3 b** at 297 (filled circle), 287 (open rhombus), and 277 K (filled rhombus), and d) **H2** in the presence of 1.5 equivalents of **G3 b** at 297 (filled square), 287 (open rhombus), and 277 K (filled rhombus) in chloroform. C denotes the weighted-average concentrations of **H1** or **H2** when **G3 b** is present.

cients of **H1** with **G3 b** and **H2** with **G3 b** depended on concentrations. In the low-concentration range, the diffusion coefficients for **H1** and **H2** in the presence of **G3 b** were similar to those for **H1** and **H2**. As the concentrations of the mixtures were increased, the diffusion coefficients of **H1** and **H2** decreased nonlinearly by approximately 80 %. These findings indicate that large polymeric aggregates are formed through the host–guest complexation between the biscalix[5]arene and the C_{60} moieties. Assuming the aggregates were hydrospherical,[32] the DPs for a 1:1 mixture of **H1** and **G3 b** and a 2:3 mixture of **H2** and **G3 b** were roughly estimated to be 83-mer and 151-mer, respectively, in the high-concentration range.

Viscometry provides useful information for determining the dimensions of supramolecular polymers and networks in solution. The viscosities of solutions of **H1** and **G3 b** and of **H2** and **G3 b** in chloroform were directly determined using a viscometer. Figure 4 b displays the concentration-dependent behavior of the solution viscosities. The solution viscosities were not affected when **H1**, **H2**, and **G3 b** were individually dissolved. The solutions of **H1** and **H2** became viscous when **G3 b** was added. The meaningful changes in the viscosities as a function of the concentration are indicative of the semidilute concentration regime in which overlap between chains contributes to viscous drag. The concentration dependence of the viscosity for the solution of **H2** is more distinct than that for **H1**, implying that the structures of the supramolecular aggregates formed from **H2** and **G3 b** are dimensionally extended, resulting in the supramolecular polymeric networks.

In general, a host–guest interaction is enhanced by cooling the host–guest solution. As a result, supramolecular polymers grow and shrink in response to temperature. Cooling the mixture solutions should facilitate the growth of the polymers. The solution viscosities of the mixtures were measured at three temperatures: 24, 14, and 4 °C. Although the intermolecular association between **H1** and **G3 b** must be promoted by cooling the solutions, the viscosities were not significantly affected (Figure 4 c), whereas the solution of **H2** and **G3 b** became more viscous upon cooling (Figure 4 d). These highly contrasting viscometric behaviors provided insight into the nature of the polymeric aggregates formed in solution.

Compounds **H1**, **H2**, and **G3 b** are rigid. Therefore, the linear polymers formed by the complexation of **H1** and **G3 b** can be rigid "rod-like" macromolecules that cannot entangle. Molecular collisions affect solution viscosity because the rods cannot pass through each other. In the dilute regime, the rods can be randomly oriented and rotate freely without being constrained by neighboring rods. In the semidilute regime, the solution viscosity are slightly affected, because molecular rotations are fairly impeded.[33] However, upon cooling, the newly grown termini can be randomly placed at the polymer ends with a negligible probability of the termini increasing the contact between other rods. The rod-like structures are characterized by a low-temperature sensitivity of the polymer solutions. In contrast, the supramolecular association between **H2** and **G3 b** can promote extended polymeric networks in solution upon cooling. The networks can be cross-linked, and each of the binding sites might participate in a cooperative fashion. As a result, dimensionally grown polymer network structures are formed, explaining the temperature-dependent viscosity of the solution.

Scanning electron microscopy (SEM) provided insight into the morphology of the supramolecular polymers in the solid state. Dumbbell-shaped fullerenes **G3 a**,**b** gave rise to particle-like morphologies due to their cohesive nature (Figure S6 in the Supporting Information). A 1:1 mixture of **H1** and **G3 a** gave rise to fibrillar morphologies with a diameter of (180 ± 50) nm (Figure 5 a), whereas a 2:3 mixture of **H2** and **G3 a** produced thin-film morphologies (Figure 5 b). The large morphological differences between **H1** and **H2** with **G3 a** most likely arise from the dimensions of the host molecules; the polymer formed from **H1** and **G3 a** grows in a linear fashion, whereas that formed from **H2** and **G3 a** results in widespread sheet-like growth. Although the supramolecular polymers were successfully obtained, the polymeric structures were thin, most likely due to the limited attractive interchain interactions of the alkyl side chains. More alkyl chains must be incorporated to gener-

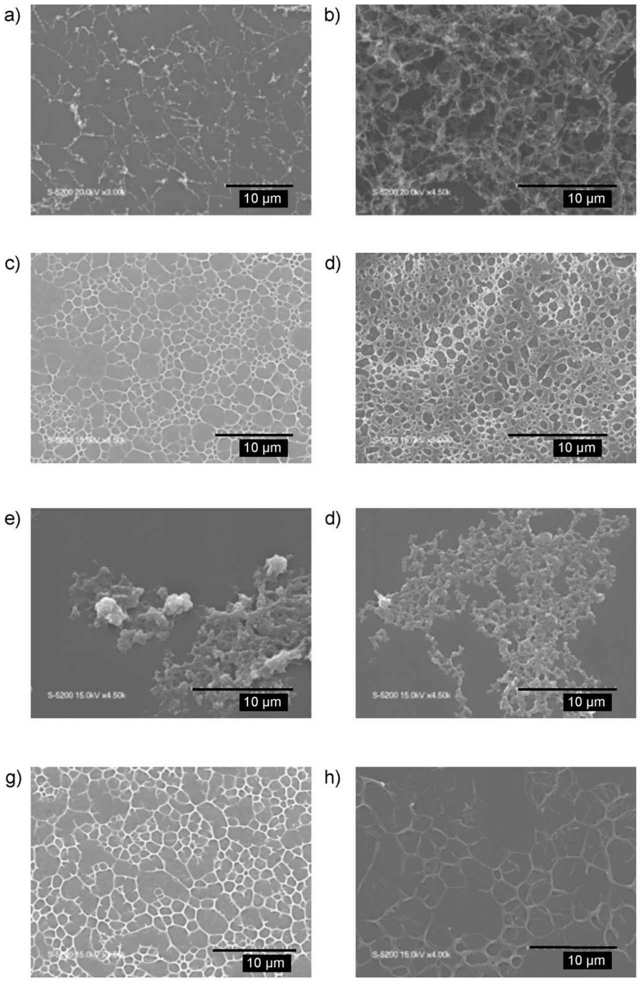


Figure 5. SEM images of cast films of a) a 1:1 mixture of **H1** and **G3 a**, b) a 2:3 mixture of **H2** and **G3 a**, c) a 1:1 mixture of **H1** and **G3 b**, d) a 2:3 mixture of **H2** and **G3 b**, e) a 1:2 mixture of **H1** and **G3 b**, f) a 2:5 mixture of **H2** and **G3 b**, g) a 2:1 mixture of **H1** and **G3 b**, and h) a 2:1 mixture of **H2** and **G3 b** prepared from their solutions in toluene on a glass plate.

ate the attractive interpolymer interactions required to facilitate the further growth of the supramolecular polymers. In fact, when **G3 b**, which possesses six long alkyl chains, was employed, **H1** produced thicker and entwined fibrillar networks with diameters of (250 ± 30) nm (Figure 5 c). Figure 5 d shows the thicker widespread film produced by the molecular association of **H2** and **G3 b**.

Binary supramolecular polymers are maintained by noncovalent intermolecular interactions, and the dimensions of the supramolecular polymers can be reorganized by stoichiometric regulation and the addition of a competitive guest molecule. An excess amount of guest **G3 b** filled most of the guest binding pockets, which completely collapsed the supramolecular polymeric fibers and sheets, giving rise to agglomerated morphologies due to the random aggregation of the uncomplexed C_{60} moieties (Figure 5 e,f). An excess of the hosts also affected the morphologies of the supramolecular polymers. End-capping of the polymeric fibers with **H1** terminated polymer growth, resulting in thinner fibers with dangling bonds (Figure 5 g). Surprisingly, in the presence of an excess amount of **H2**, the film transformed into fibers (Figure 5 h). This remarkable morphological transition can be rationalized by considering that two of the C_{60} moieties of **G3 b** were fully encapsulated by two of the binding sites of **H2**, the rest of which did not participate in supramolecular polymerization; as a result, supramolecular polymers developed linearly. The addition of C_{60} interfered with the growth of the supramolecular polymers and networks, which completely collapsed the fibers and films (Figure S6 in the Supporting Information). Accordingly, the formation of fibers, films, networks and agglomerates was driven by the intermolecular calix[5]arene–C_{60} interaction.

Information about the microstructure of the supramolecular polymers was obtained by solid-phase wide-angle X-ray diffraction (WAXD). As shown in Figure S7 in the Supporting Information, monomers **H1** and **H2** presented strong scattering in the small-angle region, indicating large-scale density fluctuation. The broad scattering peak of **H1** at $q \simeq 15\,\text{nm}^{-1}$ indicates the amorphous nature of the sample, whereas the small sharp peaks of **H2** at $q \simeq 3$, 11 and $16\,\text{nm}^{-1}$ suggest crystallinity. This difference in crystallinity is thought to derive from the different dimensional features between **H1** and **H2**; relative to **H1**, **H2** has a more planar (two-dimensional) structure that is advantageous for the formation of crystal nuclei by stacking upon evaporation of the solvent. Fullerene **G3 b** has two peaks at $q \simeq 2$ and $14\,\text{nm}^{-1}$, which were not as sharp as the crystalline peaks but not as broad as the amorphous halo. The intermediately ordered structure related to this type of WAXD spectrum is attributed to a so-called mesophase. The WAXD spectra of a 1:1 mixture of **H1** and **G3 b** and a 2:3 mixture of **H2** and **G3 b** showed features similar to those of **G3 b**, but with different peak q values. Furthermore, the WAXD spectra of the mixtures were not explained by a mathematical summation of those of the individual monomers **H1**, **H2**, and **G3 b**. These results indicate that different mesomorphic structures were generated in the mixtures as a result of host–guest complexation. It is noted that the above-mentioned results were obtained for the bulk solid (three-dimensional aggregates) of the samples. Molecular arrangements in different dimensions were further investigated as indicated below.

Atomic force microscopy (AFM) imaging provided detailed insights into the nanoscale molecular array of the polymers formed. Cast films of the supramolecular polymer and network were prepared on a mica surface. The linear polymers of **H1** and **G3 a** were aligned on a mica sheet (Figure 6 a), exhibiting a height of (1.4 ± 0.1) nm and a width of (40 ± 10) nm (Figure S8k in the Supporting Information). Judging from the calculated structure of the oligomers (Figure 7 a), the height matched the diameter of the C_{60}–biscalix[5]arene complex, and the alkyl side chains measured approximately 3.6 nm in length, which is larger than the observed height. These findings suggest that the alkyl chains were arranged parallel to the mica surface, and the polymer chains formed a bundle of approximately ten polymer chains created by the intertwining of alkyl side chains via van der Waals interactions. Figure 6 b shows that widespread sheet-like morphologies were obtained for the cast films of **H2** and **G3 a**. The uniform height of (1.2 ± 0.1) nm (Figure S8l in the Supporting Information) is consistent with the height of the diameter of the C_{60}-biscalix[5]arene complex, clearly indicating that two-dimensionally-grown, single-layered spread sheets were formed on a mica surface (Figure 6 b).

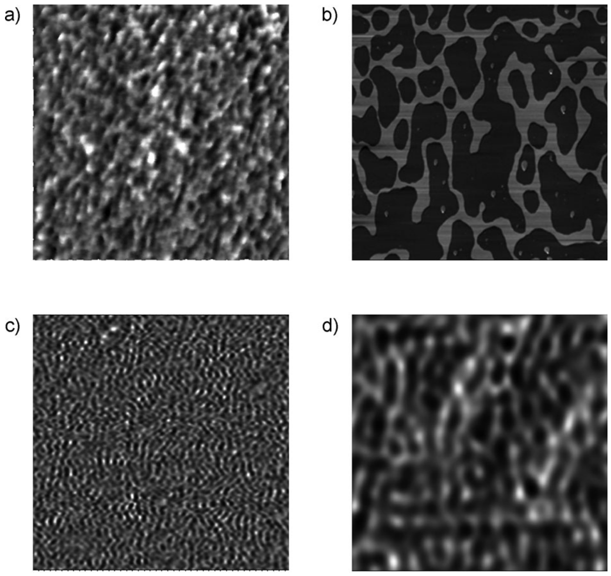


Figure 6. AFM images of cast films of a) a 1:1 mixture of **H1** and **G3 a** (5.0 μm × 5.0 μm, topography), b) a 2:3 mixture of **H2** and **G3 a** (10 μm × 10 μm, topography), c) a 1:1 mixture of **H1** and **G3 b** (0.22 μm × 0.22 μm, phase), and d) a 2:3 mixture of **H2** and **G3 b** (0.18 μm × 0.18 μm, phase) prepared from their solutions in toluene on mica.

To investigate the interchain interactions of the supramolecular polymers, **G3 b** was employed instead of **G3 a** for polymerization. AFM images of the cast films of **H1** and **H2** with **G3 b** provided more detailed information regarding the organization of the polymeric arrays. In Figure 6 c, highly oriented supramolecular polymeric chains of **H1** and **G3 b** with a rather uniform interchain distance of (5.0 ± 0.8) nm (Figure S9a in the

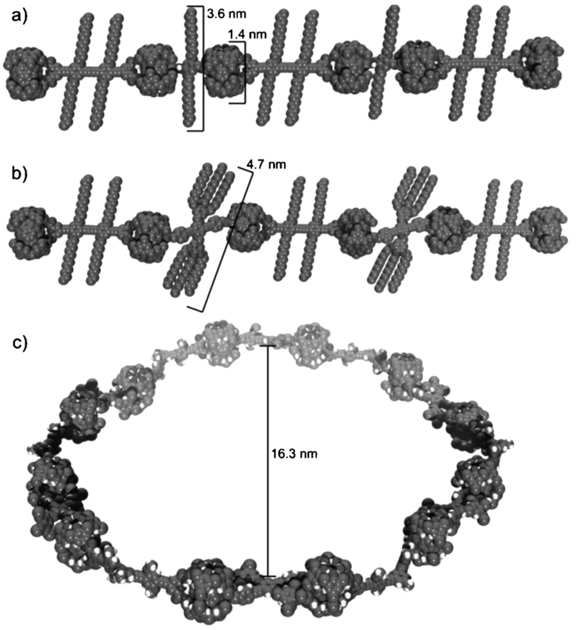


Figure 7. Calculated structures of the oligomeric assemblies of a) **H1** and **G3 a**, b) **H1** and **G3 b**, and c) **H2** and **G3 a** (one of the biscalix[5]arene moieties and the alkyl chains are omitted for clarity).

Supporting Information) can be observed, most likely due to the microphase separation between the C_{60}-containing polymer chains and the long flexible alkyl side chains; in fact, the interchain distance is fairly consistent with the width of 4.7 nm (Figure 7 b). The formation of two-dimensionally grown supramolecular polymeric networks of **H2** and **G3 b** is confirmed in Figure 6 d. The unique honeycomb-like network organization is composed many voids, the average diameter of which is (14 ± 3) nm (Figure S9b in the Supporting Information), consistent with the diameter of the macrocyclic aggregate composed of **H2** and **G3 b** in a ratio of 6:6 (Figure 7 c).

Conclusion

We described a facile process for fabricating fullerene polymers driven by host–guest interactions between calix[5]arene and C_{60}. The formation and structures of the supramolecular polymers and networks were carefully examined using a variety of spectroscopic techniques. During the experiments, the dimensions of the supramolecular polymers were controlled by the rational design of the monomer components. Although each of the monomers was connected via noncovalent interactions, supramolecular polymers belong to the class of polymers in terms of macroscopic properties. The designability of supramolecular polymers could open up new possibilities for molecular organization in nanospace.

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FULL PAPER

Supramolecular Chemistry

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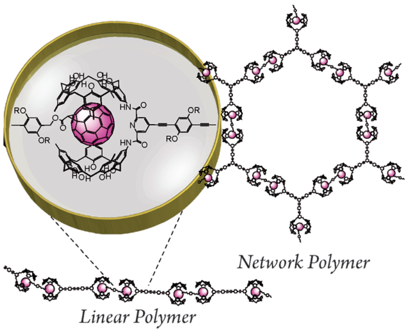
Supramolecular Fullerene Polymers and Networks Directed by Molecular Recognition between Calix[5]arene and C_{60}



Let's do some networking! A biscalix[5]arene-C_{60} supramolecular structure was utilized for the development of supramolecular fullerene polymers. Di- and tritopic hosts were developed to generate the linear and network supramolecular polymers (see figure) through the complexation of a dumbbell-shaped fullerene. The growth of the supramolecular polymers is governed by the shape, dimension, and directionality of the monomers.

New linear and networked…… fullerene polymeric organizations were synthesized through self-assembly directed by molecular recognition of a biscalix[5]arene and C_{60}. The cover represents the schematic representation of the supramolecular organization processes for the formation of the linear and network fullerene polymers. For more details see the Full Paper by T. Haino et al. on page ■■ ff.