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Supramolecular Cross-Linking

Supramolecular Cross-Linking of [60]Fullerene-Tagged Polyphenylacetylene by the Host–Guest Interaction of Calix[5]arene and [60]Fullerene[**]

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The cross-linking of polymeric chains is one of the most important topics in polymer science. The cross-linking of linear polymers creates three-dimensional networks and reduces structural flexibility, leading to dramatic changes in macroscopic morphologies and properties.[1] These are irreversible because the three-dimensional networks are constructed with covalent bonds. The introduction of a reversible nature into polymer cross-linkage should generate a new class of intelligent polymer materials; their macroscopic properties might be turned "on" and "off" by external stimuli.

The reversible nature of the cross-linkages can be realized by employing noncovalent bonds. Grafting of supramolecular entities onto conventional polymeric scaffolds can produce a cross-linked three-dimensional polymer network with noncovalent bonds. Complementary hydrogen bonding,[2] salt bridges,[3] and metal–ligand interactions[4] produced stably cross-linked polymers, which displayed unusual behaviors and properties. Development of a new supramolecular cross-linkage offers an alternative way to control the three-dimensional structures of cross-linked polymer networks. The cross-linkages driven by host-guest interactions are limited to date.[5] Thus, much work remains to be done to develop a new class of supramolecular cross-linkages with specific host–guest interactions.

Fullerene and its analogues are an intriguing class of molecules owing to their unique physical and chemical properties. Fullerene-containing supramolecular polymers that self-assemble through host–guest interactions have been occasionally reported.[6] Our group has been developing fullerene hosts based on a calix[5]arene. During the course of these studies, we found that covalently linked double calix[5]arenes encapsulate fullerenes in their cavities to form 1:1 host–guest complexes.[7] The molecular association between a C_{60} molecule and a double-calix[5]arene is strong enough to create a supramolecular polymeric array of [60]fullerenes.[8] We set out to make use of this unique host–guest motif as a new class of supramolecular cross-linkage between polymer chains. Homoditopic host **2**[8a] has two double-calix[5]arene units, each of which can encapsulate a C_{60} moiety grafted onto an adjacent polymer chain to create a stable noncovalent cross-linkage. Herein, we present the supramolecular cross-linking of [60]fullerene-tagged polyphenylacetylene poly-**1a**, which is established by the host–guest complexation of **2** in an interchain manner (Figure 1); this process alters the molecular weight and solid-phase morphology of the original polymer.

A rhodium catalyst, $[\{Rh(nbd)Cl\}_2]$ (nbd = norbornadiene), is known to effectively polymerize phenylacetylenes to give high-molecular weight, stereoregular polyphenylacetylenes.[9] The copolymerization of phenylacetylenes **3** and **4** at a feed ratio of $[\mathbf{3}]/([\mathbf{3}]+[\mathbf{4}])=0.9$ proceeded smoothly under rhodium catalysis in chlorobenzene to give poly-**1a** in 51% yield.[10] Poly-**1a** was composed of **3** and **4** in a ratio of 93:7, as determined by ^{1}H NMR spectroscopy. Increasing the fraction of **4** incorporated into the polymer caused a serious decrease in product solubility and yield. The polymerization of **3** was carried out under rhodium catalysis in toluene to give poly-**1b** in 78% yield.

^{1}H NMR spectroscopy provides evidence for the supramolecular complexation of C_{60} by the double calix[5]arene unit of **2**. Calix[5]arenes are typically subject to a ring-flipping process that occurs rapidly at room temperature, resulting in a broad signal of the bridge methylene group. Upon complexation of a C_{60} molecule to the calix[5]arene cavity, the signal of the bridge methylene appears as an AB quartet owing to the increased energetic cost of the ring-flipping process. This result reflects the attractive van der Waals interactions that arise from the effective face-to-face contacts of the calix[5]arene aromatic rings with the molecular surface of C_{60}.[7b] Figure 2 shows how the bridge methylene signals of **2** change upon the addition of poly-**1a**. The methylene signal at approximately $\delta = 3.8$ ppm gradually broadened, and eventually split the two broad signals at approximately $\delta = 3.4$ and 4.0 ppm, whereas the addition of poly-**1b** did not induce any change to the spectrum. These observations suggest that the two cavities of **2** selectively encapsulate the C_{60} moieties of poly-**1a** to link the polymer chains.

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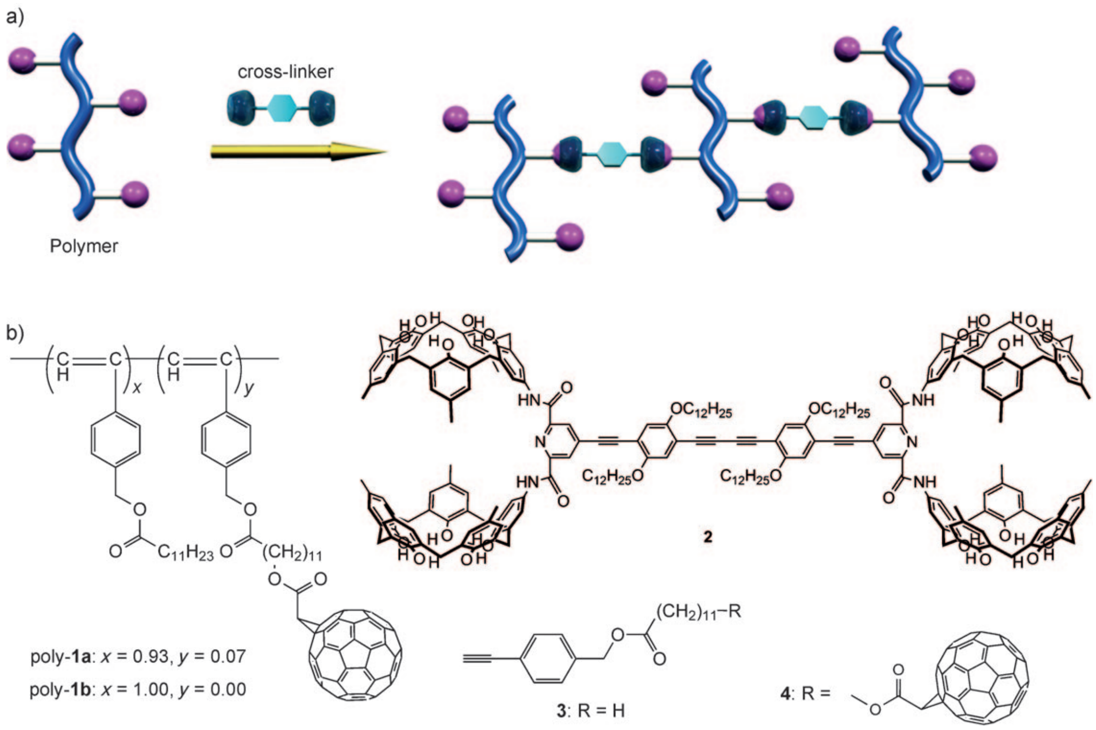

Figure 1. a) Representation of supramolecular cross-linking by a host–guest interaction between a C_{60} moiety (pink spheres) and the ditopic cross-linker. b) Polyphenylacetylenes poly-**1a**, **b**, ditopic cross-linker **2**, and phenylacetylenes **3** and **4**.

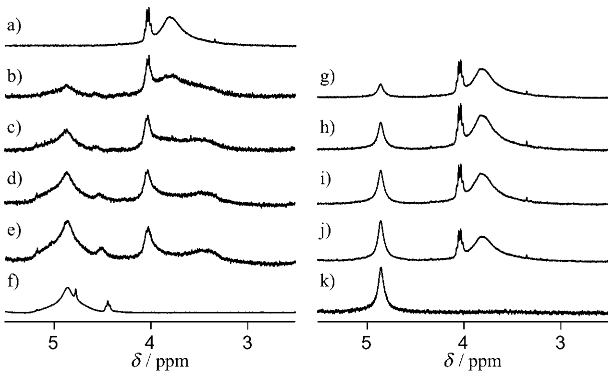

Figure 2. ^1H NMR spectra (300 MHz) of **2** (3.2×10^{-4} mol L^{-1}) in the presence of poly-**1a** (a–e: 0.00, 2.53, 5.06, 7.59, and 10.12 mg mL^{-1}) or poly-**1b** (g–j: 1.23, 2.46, 3.69, 4.92 mg mL^{-1}), and poly-**1a** (f) and poly-**1b** (k) at 298 K in [D]chloroform.

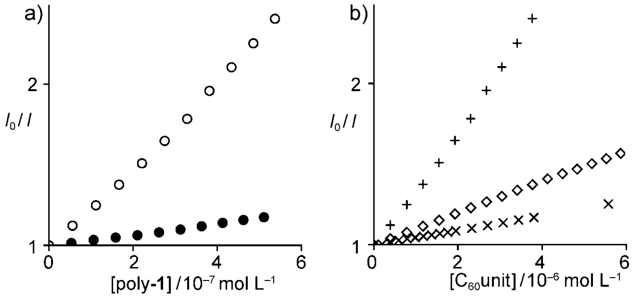

Figure 3. Stern–Volmer plots of **2** (1.0×10^{-6} mol L^{-1}) a) in the presence of poly-**1a** (○) and poly-**1b** (●) in toluene at 293 K, and b) in the presence of poly-**1a** in toluene (+), in chloroform (◇), and in *o*-dichlorobenzene (×).

Supramolecular complexation between the C_{60} moiety of poly-**1a** and host **2** was also detected by using fluorescence spectroscopy. Host **2** had an absorption band at about 420 nm owing to its highly conjugated nature, which is probably assignable to a π–π* transition. Excitation at the band wavelength gave rise to a strong emission at around 460 nm in toluene (see the Supporting Information). Fullerene is known to be a good energy acceptor;[11] thus, this emission can be quenched when a C_{60} moiety is encapsulated within the cavities of host **2**. The addition of poly-**1a** quenched the emission well, whereas poly-**1b** did not (Figure 3a). Stern–Volmer plots gave constants K_{sv} of $(34.9\pm1.5)\times10^5$ L mol^{-1} and $(3.4\pm6.9)\times10^5$ L mol^{-1} for the fluorescence quenching of poly-**1a** and poly-**1b**, respectively. The K_{sv} value of poly-**1a** is about ten times larger than that of poly-**1b**, indicating that host–guest complexation of the C_{60} moiety with **2** enhances the quenching effect.

To obtain the association constants for the two binding sites of host **2**, nonlinear regression analysis was carried out. Plotting the absolute intensities of the emission versus concentrations of the C_{60} moiety in toluene gave a hyperbolic curve. A 2:1 association model was applied to determine the association constants K_{11} and K_{21} ($(4.36\pm0.58)\times10^4$ and $(7.50\pm1.70)\times10^4$ L mol^{-1}, respectively). These values closely match the reference value obtained from *tert*-butyl fullerenoacetate **5** and double calix[5]arene **6** (see the Supporting Information).[12] Accordingly, the double-calix[5]arene units of **2** potently bind the C_{60} moieties even though they are connected to a large polymeric backbone.

It is accepted that the stability of the host–guest complex between a calix[5]arene and fullerene is solvent dependent.[13] To evaluate the effect of various solvents on the supramolecular association of poly-**1a** and host **2**, Stern–Volmer constants (K_{sv}) were determined to be $(38.0 \pm 0.7) \times 10^4$, $(9.60 \pm 0.02) \times 10^4$, and $(5.60 \pm 0.09) \times 10^4\,\mathrm{L\,mol^{-1}}$ in toluene, chloroform, and *o*-dichlorobenzene, respectively, on the basis of concentrations of the C_{60} moiety (Figure 3b). The K_{sv} values are obviously solvent-dependent and proportional to the association constants between **5** and **6** in these solvents. Accordingly, the values indicate that the binding affinities of host **2** and the C_{60} moieties of poly-**1a** are diminished in solvents in the order toluene, chloroform, and *o*-dichlorobenzene.

Size-exclusion chromatography (SEC) is a powerful technique for determining the molecular weight distribution of polymeric materials. SEC of poly-**1a** in toluene gave an elution peak and an estimation of its average molecular weight ($M_n = 13\,000$, $M_w = 18\,000$, PDI = 1.38). Upon addition of **2** to a solution of poly-**1a**, the elution peak maximum shifted, and free host **2** did not elute until a molar ratio of the binding site of **2** and the C_{60} moiety reached 1:1 (Figure 4a). Further addition of **2** brought about only an additional peak assignable to free host **2**. The M_n value and PDI (polydispersity index) of poly-**1a** in the presence of 0.25 and 0.5 equivalents of **2** were determined to be $M_n = 25\,000$ and $32\,000$, and PDI = 2.80 and 2.81, respectively. The complexation of **2** increased its molecular weight to over twice that of free poly-**1a**. Surprisingly, excess **2** did not break previously formed cross-linkages in toluene, even though the host–guest complexation of a calix[5]arene and C_{60} is driven by noncovalent interactions. From these results, it is evident that homoditopic host **2** finds its complements on the polymer chains to create remarkably stable cross-linkages by host–guest interactions in toluene (Figure 4a). However, chromatograms obtained in chloroform and in *o*-dichlorobenzene contrasted sharply to that in toluene. The peak maximum of poly-**1a** did not show a significant shift in the presence of host **2**, and poly-**1a** and free host **2** eluted separately. These results are quite consistent with the trend of binding affinities between the C_{60} moiety and the double-calix[5]arene unit in these three solvent systems. The more competitive solvation of chloroform and *o*-dichlorobenzene weakens the host–guest interaction, and host **2** was unable to create stable cross-linkages between the polymer chains.

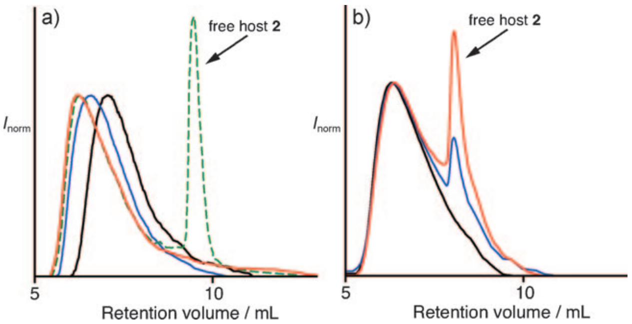

Figure 4. Size-exclusion chromatograms of poly-**1a** in the presence of **2** in a) toluene and b) *o*-dichlorobenzene. The molar ratios of [**2**]/[C_{60} unit] are: 0.0 (black), 0.25 (blue), 0.5 (red), and 1.0 (green).

Morphologies of the films prepared by casting solutions of poly-**1a** in the presence and absence of **2** were investigated by field emission scanning electron microscopy (FESEM). Poly-**1a** formed agglomerated nanostructures consisting of particle-like aggregates in the range of 10–30 nm (Figure 5a,b). It has been noted that π–π interactions and the immiscible nature of fullerenes often induce their self-assembly, giving rise to spherical particles.[14] The polymer has long alkyl chains as well as C_{60} moieties; the immiscible nature of the C_{60} moiety can account for their microphase separation. This presumably leads to further aggregation to form the particle-like nanostructures. By contrast, the addition of ditopic host **2** to poly-**1a** brought about a dramatic morphological change in which the particle-like nanostructures completely disappeared, and a wide-spread fibrous network formed (Figure 5c,d).

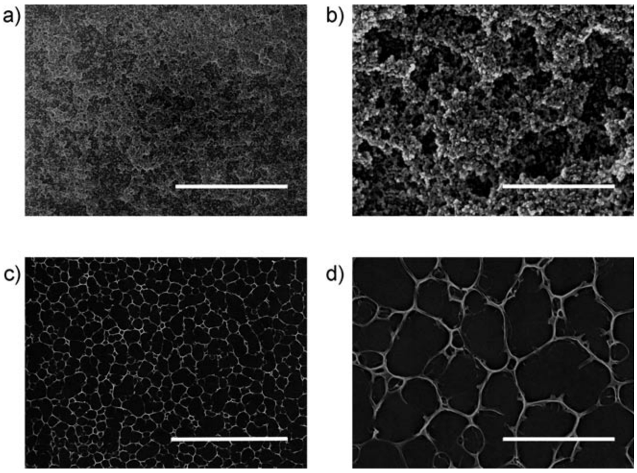

Figure 5. Field-emission scanning electron microscope images of thin films on glass plates prepared by casting benzene solutions of a,b) poly-**1a** ($6.93 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$), c,d) poly-**1a** ($6.93 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$) with **2** ($9.7 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$). Scale bars: a) 5 μm, b) 500 nm, c) 40 μm, d) 10 μm.

Atomic force microscopic (AFM) observation of the cast films of poly-**1a** in the absence and presence of **2** prepared on HOPG gave more detailed insights into the assembled state of poly-**1a** on the nanoscale (Figure 6). In the absence of **2**, nanoparticle-like agglomerates were observed in the film prepared from a solution of poly-**1a** as seen in the FESEM observation (Figure 6a). In contrast, supramolecular cross-linking of poly-**1a** by the complexation of **2** led to a dramatic change in morphology. Figure 6b shows a phase image of the well-oriented fibrils. This indicates that the highly ordered nanostructures are built from the self-assembly of these fibrils. The peak-to-peak profile of the phase gave a uniform pitch of (19.6 ± 1.6) nm, suggesting that the supramolecular assembly of poly-**1a** with **2** produced fibrils possessing a

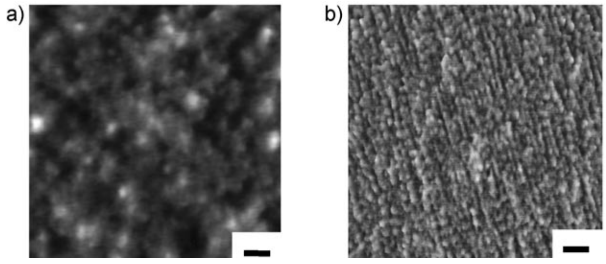

Figure 6. AFM images of assembled poly-**1a** on HOPG: a) without **2**, b) with **2** (left: height contrast; right: phase contrast). Scale bars: 100 nm.

uniform diameter. The addition of double calix[5]arene **6** instead of **2** gave rise to the randomly aligned fibrils, which are different from the morphologies of poly-**1a** observed in the absence and presence of **2**; these results imply that the supramolecular cross-linking plays a key role for the formation of the highly ordered nanostructures (see the Supporting Information).

In summary, we have demonstrated that homoditopic host **2** selectively encapsulates C_{60} moieties grafted onto a polymer chain. Furthermore, this process creates a remarkably stable cross-linkage, leading to an increase in molecular weight and unique morphological changes to the polymer in its solid state. The stability of the supramolecular cross-linkage directly depends upon the solvent; thus, the supramolecular cross-linkage of the polymer can be regulated by the solvent system. The macroscopic solid-state morphologies of poly-**1a** are highly influenced by the supramolecular cross-linking. Nanoparticle-like morphologies are probably favored by the immiscible nature of the C_{60} moiety, but the supramolecular cross-linking makes the polymer bundle together to form uniform fibrils. These, in turn, align into a well-oriented two-dimensional array on a HOPG surface.

Experimental Section

Polymerization reactions were carried out in a dry Schlenk flask under a dry nitrogen atmosphere using [{Rh(nbd)Cl}$_2$] as the catalyst. Typical procedures are described below.

Poly-**1a**: Monomer **3** (56.6 mg, 180 μmol) and **4** (21.8 mg, 20.0 μmol) were placed in a Schlenk flask, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this procedure was repeated three times, chlorobenzene (3.0 mL) and triethylamine (28.0 μL, 202 μmol) were added by syringe. A solution of [{Rh(nbd)Cl}$_2$] (1.0 mg, 2.17 μmol) in chlorobenzene (1.0 mL) was added to this solution. After stirring at 30 °C for 24 h, the resulting mixture was diluted with a large amount of chloroform, and filtered through a Florisil column. The filtrate was concentrate in vacuo, and the resulting crude mixture was subjected to preparative GPC to remove the unreacted monomers. The desired fraction was collected, and concentrated in vacuo to give poly-**1a** (42.7 mg, 51 %). Weights were determined by SEC ($M_n = 1.3 \times 10^4$ and $M_w = 1.8 \times 10^4$). The content of the cis–transoidal structure was estimated to be more than 99 mol % based on the ^{1}H NMR spectrum. ^{1}H NMR (300 MHz, $CDCl_3$, 50 °C): $\delta = 6.30$–7.40 (m, aromatic, 4 H), 5.75 (s, C=C-H, 1 H), 4.60–5.20 (br, CH_2, 2 H), 4.78 (s, CH, 0.07 H), 4.46 (t, O-CH_2, 0.14 H, $J = 7.1$ Hz), 2.28 (br, C(O)CH_2, 2 H), 1.86 (quintet, CH_2, 0.14 H, $J = 7.2$ Hz), 1.20–17.0 (m, CH_2, 17.86 H), 0.88 ppm (t, CH_3, 2.79 H, $J = 6.6$ Hz).

Poly-**1b**: Monomer **3** (62.9 mg, 200 μmol) and triethylamine (28.0 μL, 202 μmol) were dissolved in toluene (2 mL). A solution of [{Rh(nbd)Cl}$_2$] (1.0 mg, 2.2 μmol) in toluene (2.0 mL) was added to this solution. After stirring at 30 °C for 24 h, the resulting mixture was diluted with methanol. The resulting precipitates were filtered off and dried under reduced pressure to give poly-**1b** (49 mg, 78 %). Weights were determined by SEC ($M_n = 4.1 \times 10^4$ and $M_w = 9.7 \times 10^4$). The content of the cis–transoidal structure was estimated to be about 97 mol % based on the ^{1}H NMR spectrum. ^{1}H NMR (300 MHz, $CDCl_3$, 50 °C): $\delta = 6.85$ (br, aromatic, 2 H), 6.54 (br, aromatic, 2 H), 5.73 (s, C=C-H, 1 H), 4.85 (br, CH_2, 2 H), 2.26 (m, C(O)CH_2, 2 H), 1.20–1.40 (m, CH_2, 18 H), and 0.86 ppm (t, CH_3, 3 H, $J = 6.8$ Hz).

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[12] The association constants K_a between *tert*-butyl fullerenoacetate **5** and double-calix[5]arene **6** were determined by standard titration experiments using absorption spectroscopy in toluene, chloroform, and *o*-dichlorobenzene: $K_a = (73\,300 \pm 2800)$, (8610 ± 920), and (378 ± 10) $\mathrm{L\,mol^{-1}}$. See the Supporting Information.

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