

Supramolecular Nano Networks Formed by Molecular-Recognition-Directed Self-Assembly of Ditopic Calix[5]arene and Dumbbell [60]Fullerene

Takeharu Haino,* Youko Matsumoto, and Yoshimasa Fukazawa*

Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, 739-8526 Japan

Received April 14, 2005; E-mail: haino@sci.hiroshima-u.ac.jp

There has been considerable interest in the design and synthesis of supramolecular nano networks.¹ A novel class of self-assembling nano networks has recently emerged in which the molecular components are held together by reversible interactions, such as hydrogen bonds, metal–ligand interaction, CH/ π , and van der Waals forces.² One of the features of the self-assembling networks is to utilize complementary molecular affinities. Large and elaborate higher-order architectures can be constructed by using well-designed modules, capable of complementary interactions.

C₆₀ and its family represent an intriguing class of molecules due to their unique physical and chemical properties.³ The development of fullerene containing polymers has been actively studied;⁴ however, the polymer formation driven by the direct host–guest interaction of fullerene and its host is very limited.⁵

We now report the supramolecular polymeric nano networks by the molecular-recognition-directed self-assembly between a calix[5]arene and C₆₀.⁶ Covalently linked double-calix[5]arenes take up C₆₀ into their cavities.^{6c,e,f} This complementary interaction creates a strong noncovalent bonding; thus, the iterative self-assembly between dumbbell fullerene **1** and ditopic host **2** should produce the supramolecular polymer networks (Figure 1).

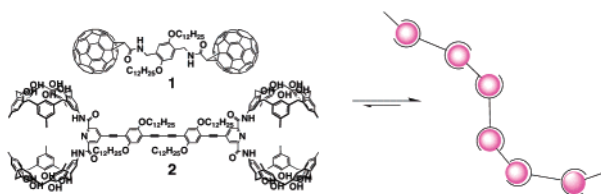
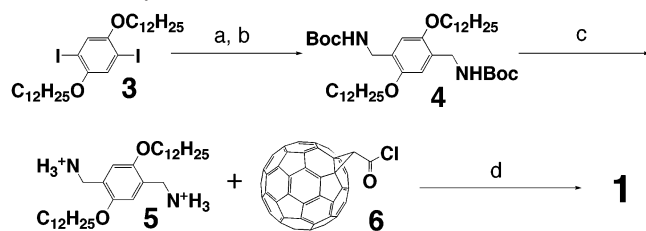


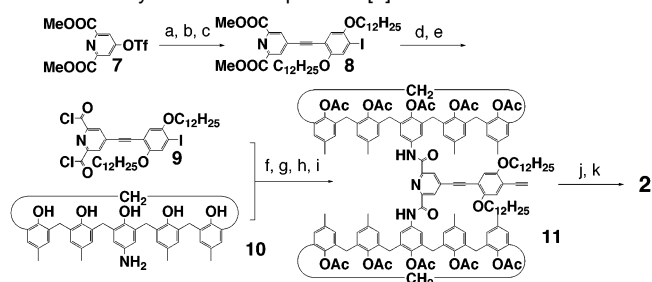
Figure 1. Schematic representation of self-assembling polymer formation by the iterative host–guest complexation between dumbbell fullerene **1** and ditopic calix[5]arene **2**.

Dumbbell fullerene **1** was prepared according to Scheme 1. Treatment of **3** with copper cyanide gave the dicyanobenzene derivative, which when reduced with lithium aluminumhydride, followed by protection of the resulting amino groups, afforded **4**. Deprotection of the Boc groups, and following coupling with fullerene derivative **6**,⁸ furnished desired dumbbell fullerene **1**.

Scheme 1. Synthesis of Dumbbell Fullerene **1**^a

^a Reagents and conditions: (a) CuCN, HMPA, 150 °C, 3 h, 83%; (b) LiAlH₄, THF, 12 h, and then Boc₂O, NaOH, 17%; (c) TFA, CH₂Cl₂, 3 h, 99%; (d) *i*-Pr₂NEt, C₆H₅Br, 12 h, 27%.

Ditopic calix[5]arene host **2** was synthesized from **7**⁹ (Scheme 2). Introduction of trimethylsilylacetylene to **7**, followed by removal of the trimethylsilyl group, and subsequent coupling with **3** afforded **8**, which was converted to acid chloride **9**. Two equivalents of amino calix[5]arene **10**¹⁰ smoothly reacted with diacid chloride **9**. Protection of 10 hydroxyl groups of the given double-calix[5]arene, followed by introduction of trimethylsilylacetylene and removal of the trimethylsilyl group, afforded fully protected double-calix[5]arene **11**. Oxidative homocoupling of **11** nicely proceeded under copper(II) catalysis. Deprotection of the 20 acetyl groups furnished desired ditopic host **2** in good yield.

Scheme 2. Synthesis of Ditopic Calix[5]arene Host **2**^a

^a Reagents and conditions: (a) TMSacetylene, CuI, *i*-Pr₂NEt, (Ph₃P)₂PdCl₂, THF, 2.5 h, 99%; (b) KF, MeOH, 15 min, 95%; (c) CuI, *i*-Pr₂NEt, (Ph₃P)₂PdCl₂, THF, 12 h, 63%; (d) NaOH, MeOH, 0 °C, 30 min, 98%; (e) (COCl)₂, THF, cat. DMF, 3 h, 99%; (f) THF, 3 h, 40%; (g) Ac₂O, pyridine, 3 h, 94%; (h) TMSacetylene, CuI, *i*-Pr₂NEt, (Ph₃P)₂PdCl₂, THF, 5 h, 87%; (i) TBAF, THF, 30 min, 99%; (j) Cu(OAc)₂, pyridine, 45 °C, 8 h, 99%; (k) LiOH, THF–MeOH, 40 °C, 2.5 h, 60%.

Association studies between **1** and **2** were carried out by using ¹H NMR (Figure S1) and UV/vis absorption spectroscopies.¹¹ In free calix[5]arene host **2**, the ring flipping process of the calix[5]arene units rapidly occurs at room temperature to give a broad singlet of the bridge methylene resonance. The addition of **1** resulted in the AB-quartet-like resonance of the bridge methylene, indicating that the energetic barrier to the ring flipping is increased. This is commonly observed in calix[5]arene–fullerene complexation. Accordingly, the host–guest complexation between **1** and **2** occurred in solution.

The absorption spectra of a 1:1 mixture of **1** and **2** showed a band around 416 nm, which is characteristic for the formation of the C₆₀–calix[5]arene complex. The band decreased gradually with increasing of the temperature, and the isosbestic point appeared at 396 nm. These results obviously indicate that the association and the dissociation of **1** and **2** occur and suggest the formation of some supramolecular oligomers in the solution (Figure 2).

Diffusion coefficients *D* (4.09 ± 0.01 × 10^{−10} and 2.57 ± 0.04 × 10^{−10} m² s^{−1} for **2** and a 1:1 mixture of **1** and **2** at 296 K) at the concentration of 2 × 10^{−4} mol/L in chloroform were measured by pulsed field gradient NMR experiments using the BPPSTE pulse

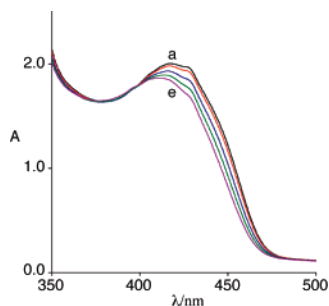


Figure 2. UV/vis absorption spectra of **1** (2.5×10^{-5} mol/L) and **2** (2.5×10^{-5} mol/L) in $\text{CHCl}_2\text{CHCl}_2$ at (a) 298, (b) 318, (c) 338, (d) 348, and (e) 368 K.

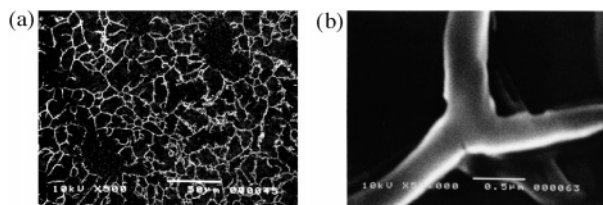


Figure 3. Scanning electron micrograph of the cast-film of the mixture of **1** and **2** on a glass plate.

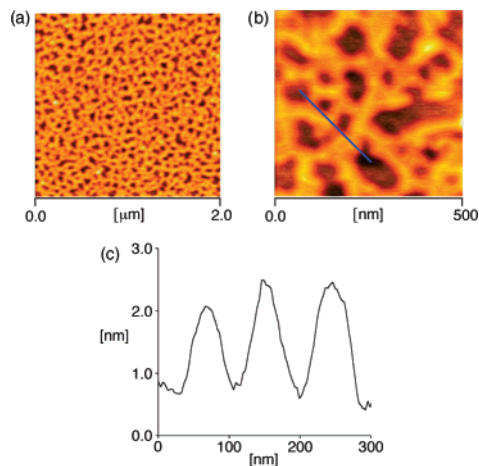


Figure 4. AFM images of drop-cast of the **1:2** solution in chloroform on mica: (a) $2.0 \times 2.0 \mu\text{m}^2$; (b) $500 \times 500 \text{ nm}^2$; (c) height profile of the fibrils on a cross-section of the blue line in the image b.

sequence. The resulting $D_{1:2}/D_2 = 0.63$ ratio is in reasonable agreement with the theoretical ratio of 0.59–0.60 expected for a linear trimer.¹² Judging from the ratio, a plausible structure of the main oligomer should be a trimeric supramolecular form composed of three units of **2** with a few of **1** at room temperature.

The size and morphology of the composite can be directly confirmed by scanning electron microscopy (SEM, Figure 3a,b). The film was prepared on a glass plate by casting the solution of the 1:1 mixture of **1** and **2**. Apparently, the thicker entwined fibers formed and had length of more than $100 \mu\text{m}$ and widths of 250–500 nm (Figure 3b), indicating that ditopic host **2** iteratively binds to dumbbell fullerene **1** to create a two-dimensional nano network.

More detailed information was given by atomic force microscopy. The cast film was prepared on a mica plate. The AFM images were measured by tapping-mode. Nano networks of fibrous assemblies

were seen in Figure 4a,b. They must be the aggregates of the linear polymers. The fibers formed on the mica plate have widths of 60–90 nm and heights of 1.2–1.9 nm (Figure 4c). Judging from the calculated structure of the oligomers (Figure S3), the alkyl side chains have length of about 3.5 nm, which is longer than the observed height. This suggests that the alkyl chains adopt parallel arrangement to the mica surface, and the nano assemblies are probably composed of a bundle of 40–60 polymer chains created by entangling the alkyl side chains with van der Waals interaction (Figure S4).

In summary, we succeeded showing the polymeric nano network by the fullerene–calix[5]arene interaction. At a low concentration, the supramolecular complexes mainly adopt the trimeric nature; however, the polymeric nature appeared in solid phase. The fibrous assemblies created the supramolecular nano network. The detailed studies are underway.

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Supporting Information Available: Synthetic procedures of compounds **1** and **2**, ^1H NMR spectra of the mixtures, Stejskal–Tanner plots of **2** and **1:2**, and the calculated structure of the oligomer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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