

Photochemical Stitching of a Tubularly Assembled Hexabenzocoronene Amphiphile by Dimerization of Coumarin Pendants

Jin Motoyanagi,[†] Takanori Fukushima,^{*,‡} Noriyuki Ishii,[‡] and Takuzo Aida^{*,†,‡}

Department of Chemistry and Biotechnology, School of Engineering, and Center for NanoBio Integration, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, ERATO-SORST Nanospace Project, Japan Science and Technology Agency (JST), National Museum of Emerging Science and Innovation, 2-41 Aomi, Koto-ku, Tokyo 135-0064, Japan, and Biological Information Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central-6, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8566, Japan

Received January 25, 2006; E-mail: fukushima@nanospace.miraikan.jst.go.jp; aida@macro.t.u-tokyo.ac.jp

Self-assembly of π -conjugated molecules has been recognized as a useful approach to the fabrication of electronic and optoelectronic soft materials with a nanometric structural precision.¹ Combination of this bottom-up supramolecular approach with top-down postprocessings would enable interesting applications of such functional nanostructures. To this end, π -electronic building blocks are required to possess a suitable functionality for processing, along with an implemented chemical program to trigger controlled self-assembly. Recently, we have found that Gemini-shaped amphiphilic hexa-*peri*-hexabenzocoronenes (HBCs) such as **2** (Figure 1a) self-assemble to form graphitic nanotubes,² which are electroconductive upon oxidation.^{2a,d} Under certain conditions, the nanotubes are aligned unidirectionally and exhibit an anisotropic electrical conduction.^{2d} Here we report novel coumarin-appended HBC amphiphile **1** (Figure 1a), which can be stitched in a self-assembled state by photochemical dimerization of the coumarin pendants (Figure 1b).³ In the present communication, we highlight controlled self-assembly of **1** and a lithographic postprocessing of the resulting graphitic nanotubes by their photoinduced solubility change.

Coumarin-appended HBC amphiphile **1** was synthesized by oxidative cyclization of the corresponding hexaphenylbenzene derivative using FeCl₃ in CH₂Cl₂/MeNO₂.⁴ When an EtOH vapor was allowed to diffuse at 25 °C into a CHCl₃ solution of **1** (0.7 mM), a yellow suspension resulted. Scanning electron microscopy (SEM) of an air-dried sample of the suspension showed the presence of hollow fibers with a large aspect ratio (Figure 2a). By means of transmission electron microscopy (TEM), the nanotubes were found to possess a uniform diameter of 20 nm with a wall thickness of 3 nm (Figure 2a, inset). The observed size regime is identical to those of the nanotubes from precedent amphiphilic HBCs.² This result is quite interesting, considering the presence of the bulky coumarin end groups in **1** that might impair the nanotubular assembly.

We confirmed that photochemical dimerization of the coumarin pendants of tubularly assembled **1** takes place in the solid state. Upon exposure at 25 °C to a light from a 500-W high-pressure Hg–Xe lamp through a Pyrex filter ($\lambda > 300$ nm), a cast film of the nanotubes on a CaF₂ plate displayed the appearance of a new C=O stretching vibration (1757 cm⁻¹) due to the coumarin functionality, next to its original vibration (1730 cm⁻¹), and a decrease in intensity of the C=C stretching vibration (1612 cm⁻¹) (Figure 3a). The spectral change subsided in 10 min, where the integral value of the C=C vibration dropped to 80% of the initial one. The photodimerization also proceeded when an EtOH suspension of the self-assembled nanotubes (0.1 mg in 10 mL) was

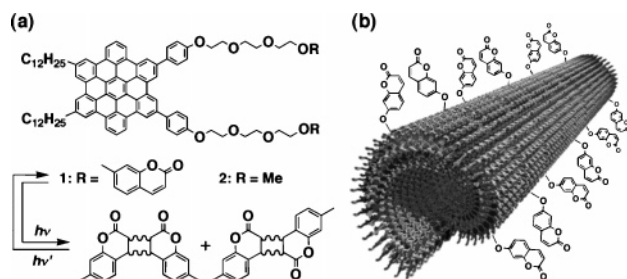


Figure 1. (a) Molecular structures of hexa-*peri*-hexabenzocoronene (HBC) amphiphiles and coumarin dimers formed by photoirradiation. (b) Schematic illustration of a graphitic nanotube formed from coumarin-appended HBC amphiphile **1**. The coumarin units located on the inner surface are omitted for clarity.

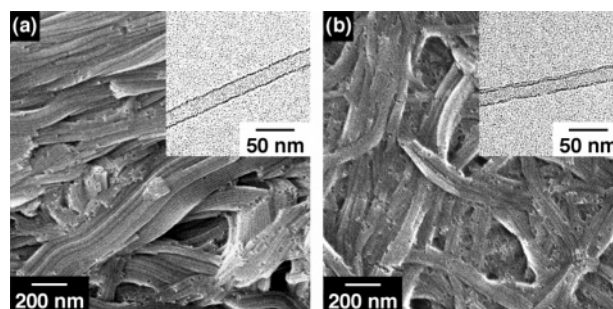


Figure 2. SEM and TEM (inset) micrographs of a thin film cast from a suspension of tubularly assembled **1** (a) before and (b) after irradiation at $\lambda > 300$ nm at 25 °C, followed by rinsing with CHCl₃.

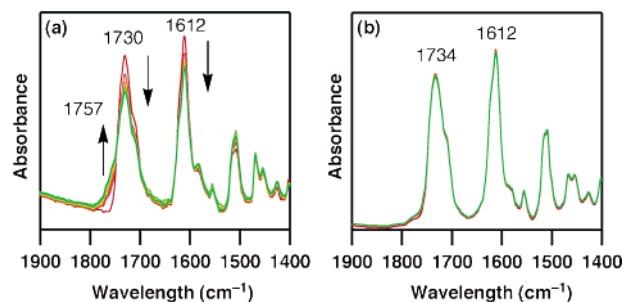


Figure 3. IR spectra of thin films cast from (a) a suspension of tubularly assembled **1** and (b) a homogeneous CHCl₃ solution of **1**, upon irradiation at $\lambda > 300$ nm (0–10 min) at 25 °C.

irradiated under conditions similar to the above, where an absorption band due to the coumarin units at 280–350 nm gradually decreased in intensity, while those due to the π -stacked HBC at 424 and 460 nm remained intact.⁴ In sharp contrast with the coumarin units in the nanotubes, those in a cast film from a homogeneous CHCl₃

[†] The University of Tokyo.

[‡] ERATO-SORST Nanospace Project (JST).

[‡] Biological Information Research Center (AIST).

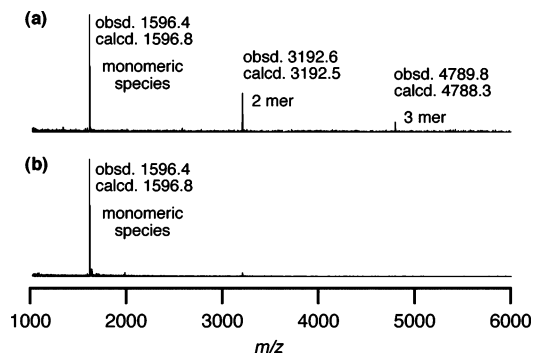


Figure 4. MALDI-TOF mass spectra (matrix; 9-nitroanthracene) of an EtOH suspension of tubularly assembled **1** after (a) irradiation at $\lambda > 300$ nm and (b) further irradiation at $\lambda = 250\text{--}350$ nm at 25 °C.

solution of **1** did not undergo photodimerization (Figure 3b). This contrasting result clearly demonstrates that the tubular assembly of **1** gives rise to a dense packing of the coumarin pendants, essential for the photodimerization.

MALDI-TOF mass spectrometry of an EtOH suspension of the nanotubes of **1**, after a 10 min irradiation at $\lambda > 300$ nm, displayed molecular ion peaks due to short-chain oligomers such as dimer and trimer together with monomeric species (Figure 4a). Although the photodimerization can take place both in intra- and intermolecular manners, the above result indicates the occurrence of an intermolecular process, favorable for the solubility change of the nanotubes. In fact, entangled fibers in the irradiated suspension, upon dilution with CHCl_3 , hardly disappeared, as observed by fluorescence microscopy,⁴ while a nonirradiated sample after a similar treatment gave a homogeneous solution. By means of SEM and TEM (Figure 2b), we confirmed that the size regime of the irradiated nanotubes remains substantially unchanged upon immersion in CHCl_3 . Hence, such photochemical stitching of the noncovalently assembled HBC monomers endows the nanotubes with an enhanced shape stability against solvents.⁵

Cyclobutane derivatives, formed upon dimerization of coumarins, are known to undergo photochemical cleavage upon irradiation with UV light, to regenerate parent coumarins.³ When an EtOH suspension of the stitched nanotubes (0.1 mg/10 mL) at 25 °C was irradiated at $\lambda = 250\text{--}350$ nm through a filter (1.1 M aqueous $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), an absorption band at 280–350 nm due to the coumarin functionality was enhanced.⁴ Furthermore, MALDI-TOF mass spectrometry of the reaction mixture only showed a single molecular ion peak due to monomeric species (Figure 4b). Dilution of the resultant EtOH suspension with CHCl_3 , as observed by fluorescence microscopy,⁴ gave a homogeneous solution without any fibrous aggregates. Thus, the photochemical stitching process in the nanotubes is reversible (Figure 1a).

By taking advantage of this reversible solubility change, we could develop both negative and positive patterns of the nanotubes by a lithographic postprocessing. An EtOH suspension of the nanotubes was cast on a silicon substrate, and the resulting thin film, after being air-dried, was covered by a 400 mesh Cu grid with hole and bar dimensions of 30 and 33 μm , respectively. Then, the masked surface of the film was exposed perpendicularly to a light with $\lambda > 300$ nm for 15 min. Subsequent rinsing with CHCl_3 resulted in the development of a negative grid pattern with a dimension identical to that of the photomask (Figure 5a). On the other hand, for the positive patterning, a cast film of the nanotubes, once stitched

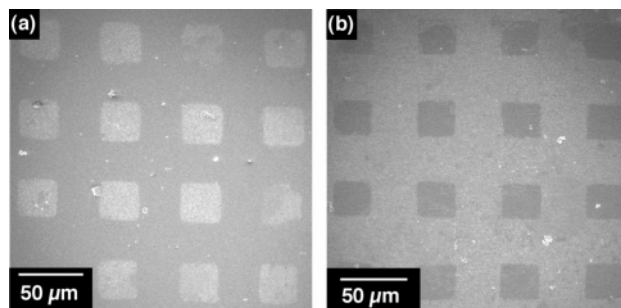


Figure 5. SEM micrographs of (a) negative and (b) positive patterns of the graphitic nanotubes of **1** on a silicon substrate, developed by rinsing with CHCl_3 after irradiation at $\lambda > 300$ and $= 250\text{--}350$ nm, respectively, through a 400 mesh Cu grid with hole and bar dimensions of 30 and 33 μm .

photochemically, was exposed to a UV light ($\lambda = 250\text{--}350$ nm) through the same photomask from an orthogonal direction to the substrate surface. Then, unmasked domains were rinsed off from the film with CHCl_3 (Figure 5b).

Self-assembled conductive nanotubes eligible for photolithographic applications are unprecedented. We have developed a novel coumarin-appended amphiphilic hexa-*peri*-hexabenzocoronene (**1**) that self-assembles to form graphitic nanotubes with a photostitching capability. The tubular assembly of **1** enabled dense packing of the coumarin pendants essential for the photochemical dimerization. The stitched nanotubes were hardly disrupted in good solvents for **1** and preserved their tubular morphology. Owing to the reversible nature of the photostitching process, both negative and positive patterns of the graphitic nanotubes were developed by a lithographic postprocessing. This achievement may not only lead to the fabrication of hexabenzocoronene-based electronic devices^{1b} but also suggests an interesting possibility of clipping off aligned nanotubes with desired lengths.

Supporting Information Available: Details of synthesis and characterization of **1**, absorption spectra, fluorescence and TEM micrographs of self-assembled **1** upon irradiation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (4) See Supporting Information.
- (5) Considering the large solubility change despite a rather small IR spectral change upon irradiation (Figure 3a), we assume that better-exposed coumarin pendants located on the outer surface of the nanotubes might be dimerized predominantly and stabilize the entire nanotubes.

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