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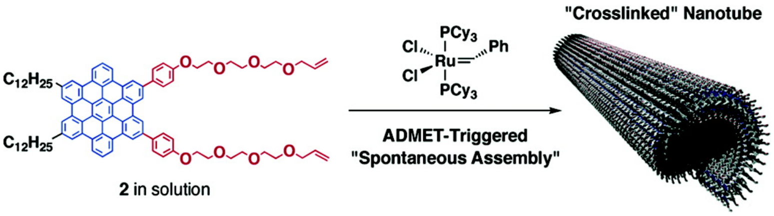

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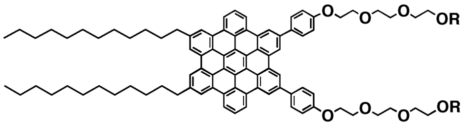
Controlled Self-Assembly Triggered by Olefin Metathesis: Cross-Linked Graphitic Nanotubes from an Amphiphilic Hexa-*peri*-hexabenzocoronene

Wusong Jin,[†] Takanori Fukushima,*[,†] Atsuko Kosaka,[†] Makiko Niki,[†] Noriyuki Ishii,[‡] and Takuzo Aida*[,†,§]

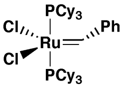
Aida Nanospace Project, Exploratory Research for Advanced Technology (ERATO), Japan Science and Technology Agency (JST), National Museum of Emerging Science and Innovation, 2-41 Aomi, Koto-ku, Tokyo 135-0064, Japan, Biological Information Research Center, National Institute of Advanced Industrial Science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

Received March 23, 2005; E-mail: fukushima@nanospace.miraikan.jst.go.jp; aida@macro.t.u-tokyo.ac.jp

Physical stabilization of self-assembled nano-objects through chemical cross-linking is an important subject for practical applications of supramolecular chemistry.[1] We recently reported that a Gemini-shaped hexa-*peri*-hexabenzocoronene[2] (HBC) amphiphile **1**, bearing two paraffinic long alkyl chains on one side and two triethylene glycol (TEG) chains on the other, self-assembles to give graphitic nanotubes.[3] The nanotubes are formed by helical rolling-up of a bilayer tape consisting of bilaterally coupled columns of π-stacked HBC units, where the paraffinic side chains are located within the wall, while the hydrophilic TEG chains cover both the inner and outer surfaces of the nanotubes (Figure 1). To enhance the structural robustness of the noncovalently assembled *graphitic* nanoarchitecture, we newly designed HBC amphiphile **2** bearing cross-linkable allylic functionalities at the termini of the TEG chains. Here, we report a serendipitous finding that acyclic diene metathesis (ADMET)[4] of **2**, assembled only dynamically in solution, results in the spontaneous formation of graphitic nanotubes with a cross-linked surface.



1: R = Me
2: R = $CH_2CH{=}CH_2$



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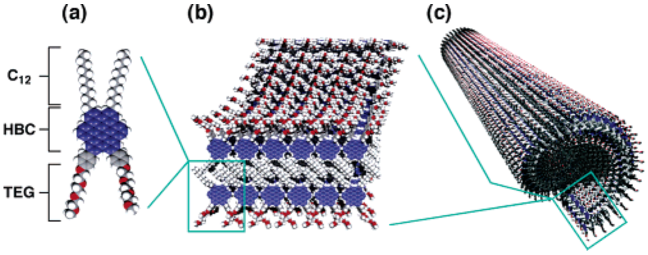

Figure 1. Schematic illustrations of the structures of (a) HBC amphiphile (C_{12}; dodecyl group), (b) self-assembled bilayer tape, and (c) graphitic nanotube.

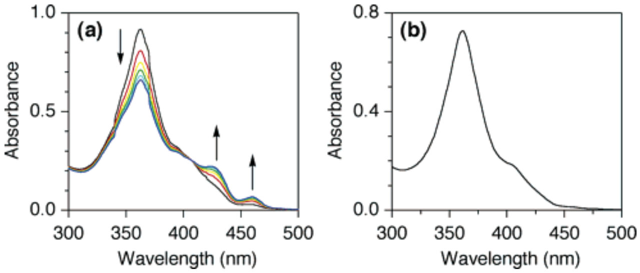

Figure 2. (a) Time-dependent electronic absorption spectral change of HBC amphiphile **2** in THF (0.7 mM) at 20 °C, on rapid cooling from 50 °C in a quartz cell of 0.1 mm path length. The spectra were taken with a 3 min interval. (b) Electronic absorption spectrum of **2** in CH_2Cl_2 (0.7 mM) at 20 °C in a quartz cell of 0.1 mm path length.

HBC amphiphile **2** was synthesized by oxidative cyclization of the corresponding hexaphenylbenzene using $FeCl_3$ in CH_2Cl_2/$MeNO_2$.[5] As observed for HBC amphiphile **1**,[3] a nanotubular assembly was formed when a THF suspension of **2** (1 mg/mL, 0.7 mM) was once heated at 50 °C, and then the resulting clear solution was allowed to cool to 20 °C. The absorption spectrum of the hot THF solution was typical of highly dispersed HBCs.[3,6] On rapid cooling, new absorption bands, characteristic of π-stacked HBC units, appeared at 426 and 460 nm with an isosbestic point at 407 nm (Figure 2a). Transmission electron micrograph (TEM) of an air-dried THF suspension showed that the nanotubes possess a uniform diameter of 20 nm with a wall thickness of 3 nm (Figure 3a). This size regime is identical to that of the nanotubes formed from **1**. On the other hand, **2** was highly soluble in halogenated solvents, such as CH_2Cl_2, where no tubular assemblies were formed even on slow evaporation (TEM, Figure 3b). Although the ^1H NMR spectrum in CD_2Cl_2 at 20 °C displayed a broadening of the aromatic signals,[5] the electronic absorption spectrum in CH_2Cl_2 (Figure 2b; 1 mg/mL, 0.7 mM) was substantially identical to that of the hot THF solution. Thus, HBC amphiphile **2** aggregates in CH_2Cl_2 but only dynamically.

To our surprise, attempted cross-linking of **2** in CH_2Cl_2 by means of ADMET resulted in the spontaneous formation of covalently stabilized graphitic nanotubes. For example,[5] when Grubbs catalyst **3**[4a] was added at 25 °C to a CH_2Cl_2 solution of **2**, the resulting mixture ([**2**] = 0.1 mmol, [**2**]/[**3**] = 1/0.5, CH_2Cl_2; 40 mL) gradually became turbid with an evolution of ethylene bubbles. MALDI-TOF MS spectrometry of the reaction mixture initially displayed molecular ion peaks due to the monomer up to tetrameric oligomers, which however disappeared after 3 days.[7] An insoluble fraction (71% yield), isolated by filtration from the reaction mixture, showed the absence of vibrational bands due to IR-active $H_2C{=}C$ ($C{=}C$; 1646, $H{-}C$; 996, 924 cm^{-1}) at the TEG termini,[5] indicating nearly a quantitative conversion of the allylic functionalities into internal olefins. Scanning electron microscopy (SEM) of the ADMET product showed the presence of bundles of a great number of nanotubes (Figure 3c). By means of TEM microscopy, we found

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[†] ERATO.
[‡] AIST.
[§] The University of Tokyo.

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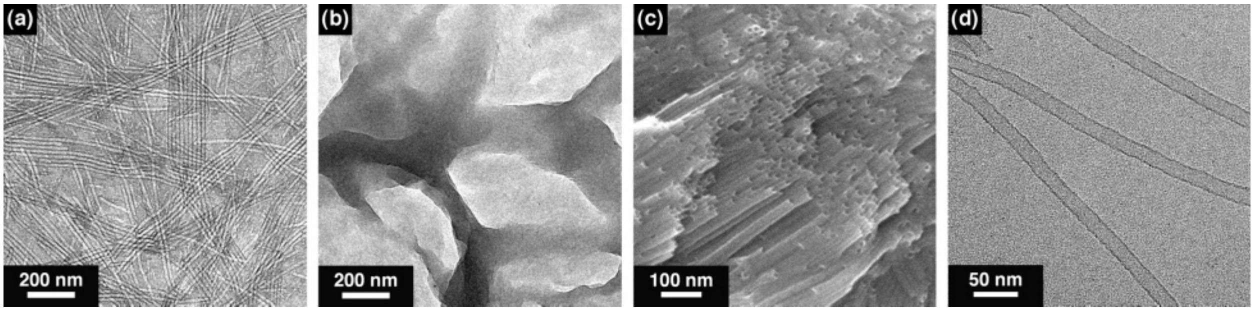

Figure 3. (a) TEM micrograph of an air-dried THF suspension of **2**. (b) TEM micrograph of an air-dried CH_2Cl_2 solution of **2**. (c) SEM micrograph of a solid product isolated from the reaction mixture of **2** and **3** in CH_2Cl_2 at 25 °C for 3 days. (d) TEM micrograph of an air-dried reaction mixture of **2** and **3** in CH_2Cl_2 at 25 °C for 3 days.

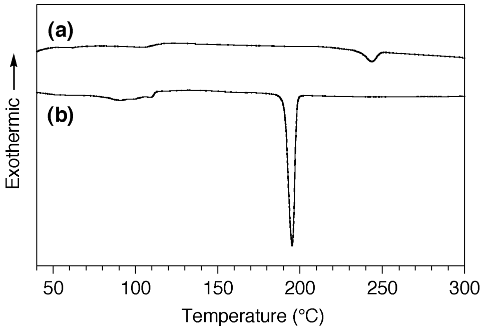

Figure 4. DSC thermographs (first heating) of the nanotubes of **2** cross-linked with **3** (a) and uncross-linked (b). Scan rate: 10 °C/min.

that the cross-linked nanotubes are uniform in diameter and have a size regime identical to that of the nanotubes obtained through self-assembly of **2** in THF (Figure 3d). Furthermore, X-ray diffraction (XRD) analysis of the cross-linked nanotubes indicated that the molecular graphene units are regularly stacked with a *d* spacing of 3.44 Å.[5]

The cross-linked nanotubes exhibited an enhanced thermal stability as well as a high resistivity to solvents. As observed by SEM,[5] heating, for example, at 175 °C of the uncross-linked nanotubes resulted in complete disruption of their hollow structure within 2 h. In sharp contrast, the cross-linked nanotubes, under identical heating conditions, survived to a large extent after 24 h, and even partly after 3 days. In differential scanning calorimetry (DSC),[5] the uncross-linked nanotubes, on first heating, displayed an endothermic peak at 195 °C due to a phase transition to a liquid crystalline mesophase. On the other hand, the cross-linked version showed only a small endothermic peak at a much higher temperature (244 °C) (Figure 4).

Initially, we attempted ADMET of the allylic surface groups of the preformed nanotubes through self-assembly of **2** in THF. However, catalyst **3** did not work properly in this solvent. Even after 4 days, the reaction mixture yet showed a major MALDI-TOF MS peak due to the monomer along with small peaks corresponding to short-chain oligomers. Thus, our finding of ADMET-triggered formation of cross-linked nanotubes is quite interesting, considering also a general understanding that cross-linking of dynamic assemblies usually gives rise to irregular aggregates. In CH_2Cl_2, HBC amphiphile **2** most likely forms such a dynamic assembly. However, cross-linking of **2** could reduce the dynamic property of the assembly and enhance the π-stacking ability of **2**. We also think that the cross-linking of the TEG termini could break the symmetry of the dynamic assembly to induce a large dipole moment, wherein the lipophilic long alkyl chains are forced to align on the other side of the cross-linked TEG chains in a way suitable for the formation of a bilayer tape, a precursor of the nanotube.

Although many examples[8,9] are known for the stabilization of self-assembled molecular objects by post cross-linking, controlled self-assembly triggered by bond-forming chemical reactions, demonstrated herein, is unprecedented. The cross-linked graphitic nanotubes have chemically accessible olefinic functionalities on the surface[5,10] and can, therefore, be hybridized with a variety of substances with different functions.

Supporting Information Available: Details for synthesis and characterization of **2**, experimental procedures for ADMET, spectral data, XRD pattern, and SEM micrographs, DSC thermographs, data of contact angle measurements (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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