

## Radially Diblock Nanotube: Site-Selective Functionalization of a Tubularly Assembled Hexabenzocoronene

Justin L. Mynar,<sup>†</sup> Takuya Yamamoto,<sup>†</sup> Atsuko Kosaka,<sup>†</sup> Takanori Fukushima,<sup>\*,†,‡</sup> Noriyuki Ishii,<sup>§</sup> and Takuzo Aida<sup>\*,†,‡</sup>

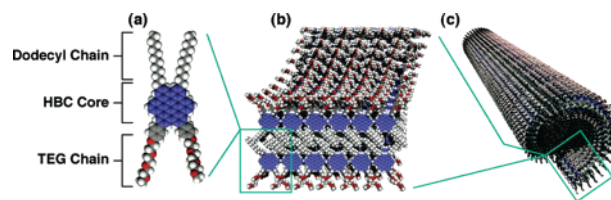
ERATO–SORST Nanospace Project, Japan Science and Technology Agency (JST), National Museum of Emerging Science and Innovation, 2-41 Aomi, Koto-ku, Tokyo 135-0064, Japan, Department of Chemistry and Biotechnology, School of Engineering, and Center for NanoBio Integration, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, 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 August 3, 2007; E-mail: fukushima@nanospace.miraikan.jst.go.jp; aida@macro.t.u-tokyo.ac.jp

Nanoscale tubular objects with functional surface groups have a variety of potential applications.<sup>1–3</sup> If the interior and exterior functionalities are individually designed, the expediency of the nanotubes could be greatly enhanced. However, such radially diblock nanotubes are very rare.<sup>4</sup> Recently, we have reported that Gemini-shaped amphiphilic hexa-*peri*-hexabenzocoronenes (HBCs) bearing triethylene glycol (TEG) chains self-assemble into graphitic nanotubes, which consist of helically rolled bilayer tapes composed of bilaterally coupled columns of  $\pi$ -stacked HBC units (Figure 1).<sup>5</sup> By self-assembly of HBCs with certain functionalities attached to the TEG termini, surface-functionalized graphitic nanotubes with applications including electronics, optoelectronics, and chirotechnology have been fabricated.<sup>6,7</sup> However, in principle, this design strategy never gives radially diblock nanotubes with different interior and exterior functionalities. Here we report the successful formation of such a new type of graphitic nanotube by site-selective post modification of a nanotubular precursor bearing reactive surface groups. Assuming that the interior reactive groups of the nanotube have a lower accessibility than the exterior ones, we expected that large molecules such as dendrons should graft on selectively to the exterior surface.<sup>8</sup>

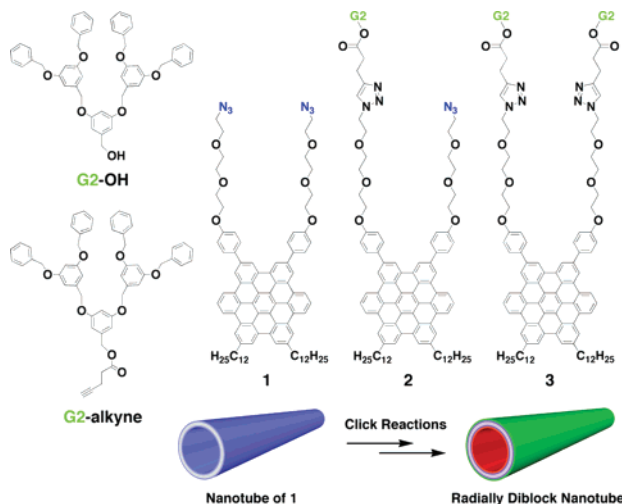
We have chosen to use the [3 + 2] cycloaddition of azides and alkynes as a means of chemically modifying the graphitic nanotubes. This reaction has been touted as a high-yielding reaction that not only is insensitive to oxygen and water but also is tolerant to many functional groups.<sup>9</sup> Most importantly for self-assembled materials,<sup>10</sup> the reaction can proceed under mild conditions, allowing for the functionalization of the nanotubes without destroying their structural integrity. Thus, a second generation Fréchet-type dendron with an alkyne focal core (G2-alkyne) was synthesized by carbodiimide coupling of G2-OH with pentynoic acid (Chart 1).<sup>11</sup> Meanwhile, the HBC amphiphile was modified by reacting its tosylated TEG-appended precursor with NaN<sub>3</sub> to yield diazido-HBC (**1**, Chart 1).<sup>11</sup> When a hexane vapor was allowed to diffuse at 25 °C into a THF solution of **1**, a yellow precipitate formed. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of an air-dried sample showed the presence of bundled nanotubes (Figure 2a), which were roughly 18 nm in diameter, as confirmed by atomic force microscopy (AFM).<sup>11</sup>

Click chemistry was performed at 25 °C by adding CuSO<sub>4</sub>/sodium ascorbate to a THF/MeOH/hexane suspension of a mixture of G2-alkyne and tubularly assembled **1** ([G2-alkyne]/[**1**] = 2).<sup>11</sup> After 10 h without stirring, visualization by SEM and TEM microscopy confirmed that the tubular objects have survived under the mild click conditions (Figure 2b).<sup>11</sup> Noteworthy, images provided by AFM of the dendronized nanotubes showed a 4 nm



**Figure 1.** Schematic structures of (a) Gemini-shaped amphiphilic HBC, (b) self-assembled bilayer tape, and (c) graphitic nanotube.

**Chart 1.** Schematic Structures of Dendrons (G2-OH, G2-alkyne) and Hexabenzocoronenes (**1**–**3**), and Illustration of Two-Stage Site-Selective Functionalization of Tubularly Assembled **1** to Form a Radially Diblock Nanotube



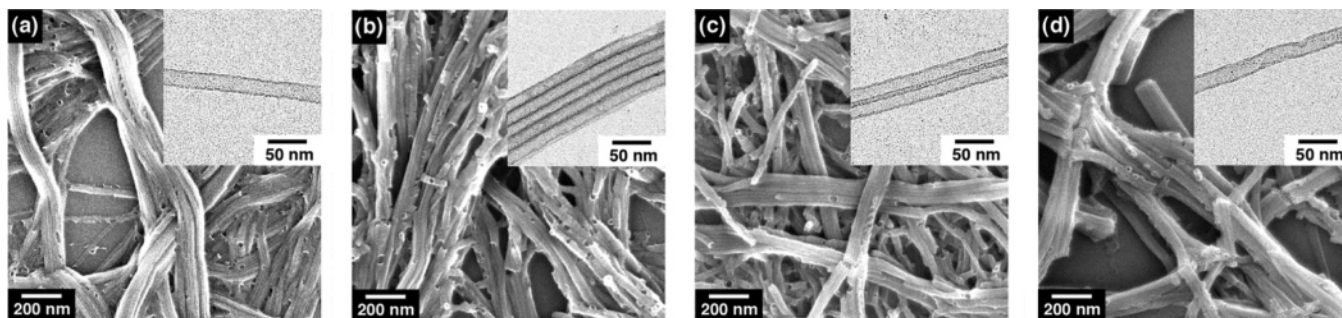
increase in diameter.<sup>11</sup> Since the dendron is roughly 2 nm in size, this observation indicates that the exterior surface of the nanotube has been fully modified. Meanwhile, attempted self-assembly of a dendronized-HBC (**3**), synthesized from **1** and G2-alkyne,<sup>11</sup> resulted in the formation of an irregular aggregate.

MALDI-TOF mass spectrometry of the reaction mixture showed the presence of single- and double-click products **2** and **3**, respectively, along with unreacted **1**.<sup>11</sup> We hypothesized that the steric bulk of the G2 dendron would prevent dendronization of the HBC molecules located on the inner layer of the graphitic bilayer wall. To determine the amount of the dendron grafted on, we utilized analytical size exclusion chromatography (SEC) monitored by absorption of the HBC moiety at 360 nm. In conformity with the result of MALDI-TOF mass spectrometry, the SEC trace of the reaction mixture in, for example, 6 h (Figure 3a) indicated the presence of unreacted **1** and double-click **3** as major fractions with

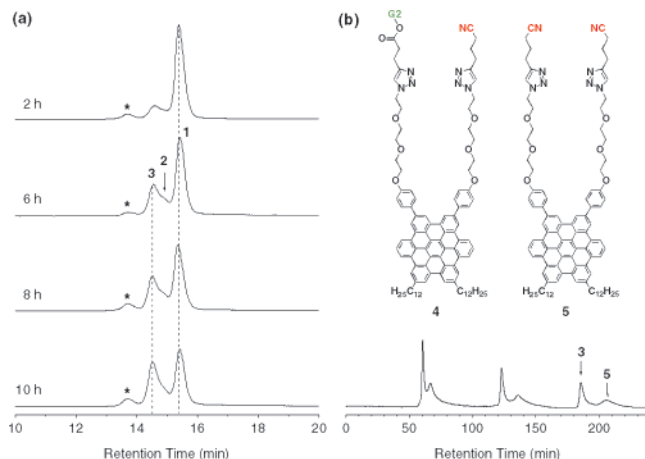
<sup>†</sup> ERATO–SORST Nanospace Project (JST).

<sup>‡</sup> The University of Tokyo.

<sup>§</sup> Biological Information Research Center (AIST).



**Figure 2.** SEM and TEM (inset) micrographs of air-dried suspensions of self-assembled nanotubes (a) formed by vapor diffusion of hexane into a THF solution of **1**, (b) after the first-click reaction with G2-alkyne, (c) after the second-click reaction with 5-hexynenitrile, and (d) after the second-click reaction with 5-hexyn-1-ol.



**Figure 3.** (a) Analytical SEC traces ( $\text{CHCl}_3$ , 360 nm) of the reaction mixtures in 2, 6, 8, and 10 h after starting the click reaction of tubularly assembled **1** with G2-alkyne. The traces were normalized with respect to the total peak area. Asterisk indicates dimeric byproducts.<sup>11</sup> (b) A recycling preparative SEC trace ( $\text{CHCl}_3$ , 360 nm) of a reaction mixture in 12 h after starting the second-click reaction with 5-hexynenitrile.

single-click **2** as a shoulder. When the click reaction was allowed to continue for 10 h, the peak due to double-click **3** was enhanced at the expense of the peak due to unreacted **1**, while single-click **2** was hardly detected. A nearly identical SEC profile was observed in 12 h. From the derived areas of the SEC peaks, roughly a half amount of **1** remained unreacted. Considering a possible steric congestion of the surface azide groups, a random click reaction on the interior and exterior nanotube surfaces would result in the preferential formation of single-click product **2**. However, the results with SEC suggest the more accessible HBC molecules, located on the outer layer of the graphitic bilayer wall, are fully clicked (dendronized), while the azide groups on the inner layer are mostly intact. In the observed kinetics of the functionalization, the dimensional characteristics of the nanotube play a critical role. For example, in a prolonged reaction, clicking of the interior azide groups started slowly. When the reaction was conducted under stirring, fully clicked nanotubes consisting of **3** resulted.<sup>11</sup>

After selective grafting the G2 dendron on the exterior surface, the interior of the nanotubes was successfully functionalized, with retention of the tubular structure, by the second-click reaction with small alkynes such as 5-hexynenitrile and 5-hexyn-1-ol (Figure 2 parts c and d).<sup>11</sup> Recycling preparative SEC of a 12-h reaction mixture with 5-hexynenitrile gave two well-separated fractions (Figure 3b). By means of MALDI-TOF mass spectrometry, the first

and second fractions were found to contain **3** and **5** (Figure 3b), respectively, with a mole ratio **3/5** of 1.3.<sup>12</sup> On the other hand, diazido-HBC **1** and cross-double-click product **4** (Figure 3b) were hardly detected.

In conclusion, we have developed an innovative method for the preparation of radially diblock graphitic nanotubes, whose functionalities on the interior and exterior surfaces differ from one another. The dendritic grafts on the exterior surface will make it possible to accommodate a greater number of functional groups. The basic rationale of this concept, in principle, is not only limited to the graphitic nanotubes but also can be elaborated into a general method for site-selective and shape-persistent functionalization of potentially labile self-assembled nano-objects.

**Supporting Information Available:** Details of synthesis, characterization, experimental procedures for self-assembly of **1** and click reactions, AFM and SEM micrographs, MALDI-TOF mass and electronic absorption spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) See Supporting Information.
- (12) The volume ratio of 2-nm thick outer/inner layers of a cylinder model with a diameter of 18 nm is 1.3.

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