Fullerodendron-assisted Dispersion of Single-walled Carbon Nanotubes via Noncovalent Functionalization

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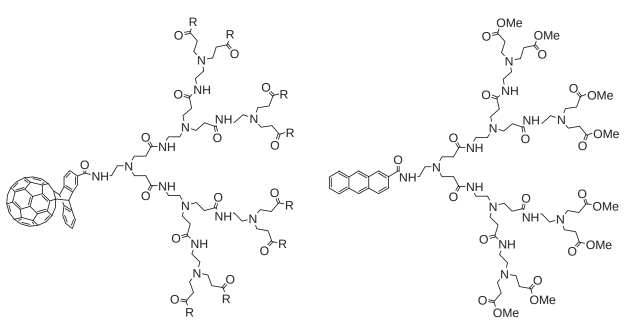
Single-walled carbon nanotubes (SWNTs) were well dispersed in both water and organic solvent by the use of fullerodendron as a dispersant. A C_{60} moiety at the focal point of dendron plays a crucial role in the dispersing process, because dendron having an anthracene unit at the focal point can not disperse SWNTs in THF. The dispersions of SWNTs were characterized by UV–vis–NIR spectroscopy, Raman spectroscopy, SEM, HRTEM, and AFM.

Since their discovery in 1993,[1] single-walled carbon nanotubes (SWNTs) have attracted considerable attention because of their superb mechanical and electrical properties as well as their promise in the area of materials chemistry.[2,3] However, chemical and biochemical approaches using this material have been very much limited,[4,5] since polydispersity and poor solubility of carbon nanotubes (CNTs) in both aqueous and nonaqueous solution prevent chemical modification and characterization. In this point of view, noncovalent sidewall-functionalizations of the nanotube with aromatic molecules (e.g., pyrenes[6] and porphyrins[7]) have been extensively reported, because the study would lead to the chemical and biochemical design to create functional carbon nanotubes in solution systems without alteration of their inherent properties. However, dispersion of CNTs by the use of a fullerene derivative has never been reported. During our studies on the synthesis, characterization, and property of fullerodendron,[8–11] we found that this molecule strongly interacted with carbon nanotubes and act as a dispersant of them. Here, we report that a solution of fullerodendrons (**1a**) or (**1b**) disperses SWNTs via noncovalent functionalization. Furthermore, although there are several reports described the covalent attachment of dendritic wedges to CNTs,[12,13] to our knowledge, this is the first example of noncovalent sidewall-functionalization of SWNTs with dendritic wedges (Scheme 1).



1a R = OMe
1b R = O⁻K⁺

2

Scheme 1.

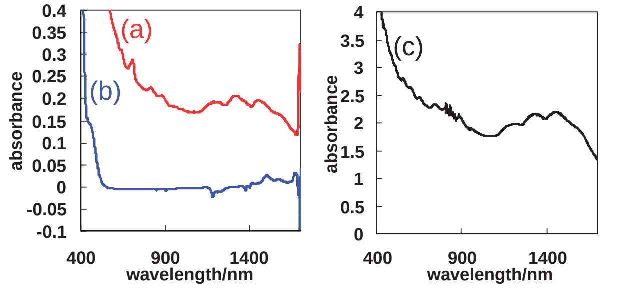


Figure 1. UV–vis–NIR spectra of SWNTs (a) in THF with fullerodendron **1a** (red), (b) with dendron **2** (blue), (c) in D_2O with fullerodendron **1b** (black).

Bundled SWNTs were effectively dispersed in THF by their sonication in the presence of fullerodendron **1a** (0.1 mM). On the other hand, no such black-colored THF solution was obtained in the absence of fullerodendron **1a**. Optical absorption spectroscopy and scanning electron microscopy (SEM) measurements provide evidence for well-dispersed SWNTs via formation of fullerodendron-functionalized SWNTs. When the THF solution of fullerodendron **1a** (0.1 mM) was employed, the characteristic absorption derived from SWNTs appeared around a 700–1700 nm region in the UV–vis–NIR spectrum (Figure 1a).[14] In contrast, the absorption band of SWNTs was not observed by the use of a THF solution of dendron **2** (1.0 mM), which have not C_{60} but an anthracene at the focal point (Figure 1b). This result suggested that the C_{60} moiety at the focal point of dendron **1a** played a crucial role in the dispersing process. Furthermore, a SEM image of SWNTs–fullerodendron dispersion showed the presence of polymer-wrapped SWNTs (see Supporting Information Figure S1).

Similarly, optically transparent black-colored dispersion of SWNTs was prepared by sonicating SWNTs for 60 min in aqueous solution of fullerodendron **1b** (0.1 mM). No precipitation was produced for the SWNTs–fullerodendron dispersion even after two months upon storage at room temperature. The characteristic absorption derived from the nanotubes dissolved in water is seen around a 700–1700 nm region in the UV–vis–NIR spectrum (Figure 1c).[14] Furthermore, typical Raman scattering of the radial breathing modes (RBMs) and the tangential displacement mode (TDM) of SWNTs were observed at 189, 274, and 1588 cm^{-1} (Figure S2).[15,16] On the other hand, topographic atomic force microscope (AFM) image for the dispersion of

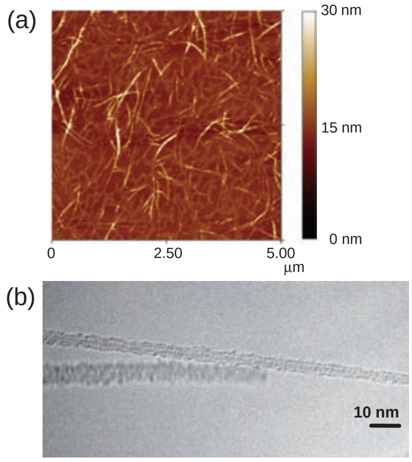


Figure 2. (a) Typical AFM image of the dispersion of fullerodendron-functionalized SWNTs. (b) HRTEM image of fullerodendron-functionalized SWNTs.

SWNTs–fullerodendron in D_2O shows well-dispersed SWNTs with high concentration (Figure 2a), thus strongly suggesting the SWNTs have been functionalized, i.e., the fullerodendron **1b** noncovalently binds to SWNTs and renders them dispersible in D_2O. According to z-scan analysis of AFM, tube diameters ranging from 2.3 to 9.6 nm were observed (Figure S3). Considering that HiPco tubes have a diameter distribution between 0.9–1.3 nm, SWNTs in a D_2O/fullerodendron solution have a polymer-wrapped and less bundled structure. Furthermore, such a picture is supported by the high-resolution transmission electron microscope (HRTEM) result at a higher magnification, which shows soft materials on the surface of small bundle of SWNTs (Figure 2). Comparable TEM image, which revealed a formation of a monolayer of fullerene on the outside of the SWNTs under supercritical conditions, was observed by Britz et al.[17]

The results described herein show the first example of a fullerodendron-assisted dispersion of SWNTs induced by interaction between SWNTs and the C_{60} moiety of fullerodendrons **1a** or **1b**. Although interactions between inner surface of nanotubes and outer surface of fullerene were demonstrated by the use of carbon nanopeapods,[18] no clear-cut example of adsorption of fullerene derivatives on CNTs has been hitherto reported. These results provide a new approach for functionalizing nanotubes noncovalently with dendritic wedge, and a novel category of the fullerene-functionalized CNTs. In this strategy, a great advantage over the "nanopeapod" approach in constructing fullerene-functionalized CNTs is that there is no limitation of a diameter and layer structure of CNTs, i.e., very similar results might be obtained with not only SWNTs having very small diameters but also MWNTs having large diameters. Functionalization of SWNTs with C_{60} could supply the nanotubes with many of the fullerene's unique intrinsic properties, such as electroluminescence, photovoltaic properties, photocatalitic activity, and biocompatibility. Further work is in progress to explore applications and advantages of fullerodendron-functionalized CNTs.

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