

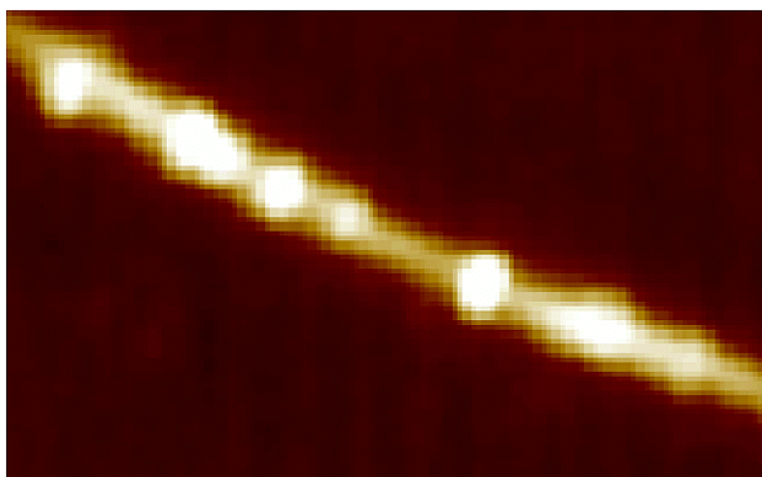
Communication

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J. Am. Chem. Soc., **2003**, 125 (29), 8722-8723 • DOI: 10.1021/ja0355675 • Publication Date (Web): 25 June 2003

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Functionalization of Single-Walled Carbon Nanotubes via the Bingel Reaction

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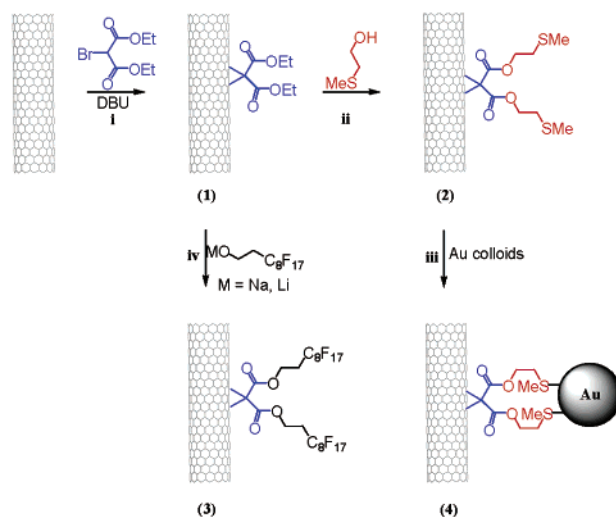
Because of their impressive electrical and mechanical properties, single-walled carbon nanotubes, SWNTs, have stimulated much interest over the past few years. SWNTs can be metallic or semiconducting depending on their structure and have a high Young's modulus of around 1 TPa.¹ It is clear, however, that to be able to take full advantage of these unique properties of SWNTs it will be necessary, in many cases, to attach them to other molecules or surfaces to fabricate nanodevices or composites. To achieve this, it is essential to be able to functionalize the SWNTs with chemical groups.

Carboxylate groups have been introduced on to the surface of SWNTs by reaction with strong oxidizing agents such as HNO₃² and can be modified further to form amides.^{3–5} Similarly, acid–base chemistry⁶ and ester linkages⁷ have been utilized to attach long chain alkyl groups to the SWNT walls to alter their solubility properties. SWNT modifications using cyclization reactions are also possible using exceptionally reactive carbene and nitrene reagents to attack the SWNT wall.^{8,9} Similarly, the 1,3 dipolar addition of azomethane ylides to SWNTs, with the driving force of the reaction being the release of dinitrogen, has been reported.¹⁰ Here, we describe the cyclopropanation of SWNTs under Bingel reaction conditions, and we have used “chemical tagging” procedures to identify the presence of reacted surface sites using atomic force microscopy (AFM), and ¹⁹F NMR and X-ray photoelectron spectroscopy.

The Bingel reaction is an example of a [2+1] cycloaddition reaction, and fullerenes are known to react with bromomalonates to form up to the hexa-substituted product.^{11–13} The Bingel reaction was performed on 10 mg of purified SWNT material supplied by Carbon Nanotechnologies Inc., TX. The material was annealed under vacuum (10^{−3} mbar) at 1000 °C for 3 h prior to use to remove any carboxylic acid groups present on the surface. To a suspension of the SWNT material in dry *ortho*-dichlorobenzene (*o*-DCB) were added 1.8 mmol of diethyl bromomalonate and 3.3 mmol of 1,8-diazabicyclo[5.4.0]undecene (DBU). The mixture was allowed to react, with stirring, for 2 h, and the modified SWNTs [(COOEt)₂C<SWNT] (1) were isolated from the reaction mixture by filtration and washed thoroughly with *o*-DCB followed by ethanol. Unambiguous characterization of organic group functionalized SWNTs by conventional spectroscopy and electron microscopy is notoriously difficult mainly due to electron beam sensitivity (and resolution), metallic behavior, and low solubility. However, we have recently developed a chemical tagging technique which allows the functional groups to be visualized by atomic force microscopy (AFM). Therefore, Bingel-SWNTs (1), immobilized on a mica surface, were transesterified by prolonged stirring in an excess of 2-(methylthio)ethanol followed by extensive washing with diethyl ether to form [(COOCH₂CH₂SMe)₂C<SWNT] (2), and by exploiting the gold sulfur binding interaction the cyclopropane group was “tagged” using preformed ~5 nm gold colloids, Scheme 1.

Figure 1 shows a typical AFM image of purified SWNTs that have undergone the Bingel reaction and are tagged with gold

Scheme 1. Schematic Representation of the Chemistry Used to Cyclopropanate SWNTs and the Introduction of Chemical Markers for AFM Visualization, and ¹⁹F NMR and XPS Spectroscopy^a



^a (i) Bingel reaction: diethyl bromomalonate and DBU, 24 h room temperature. (ii) Transesterification with 2-(methylthio)ethanol in diethyl ether, 12 h. (iii) Introduction of preformed ~5 nm gold colloids, HPLC grade water, 3 h. (iv) Transesterification with the sodium or lithium salt of 1H,1H,2H,2H-perfluorodecan-1-ol.

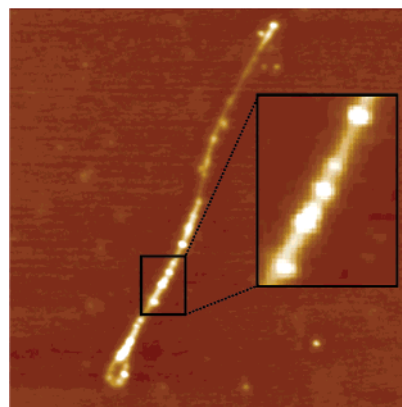


Figure 1. A typical tapping mode AFM (height) image of a SWNT functionalized by the Bingel reaction, [(COOCH₂CH₂SMe)₂C<SWNT], and after exposure to ~5 nm Au colloids (4). The image shown is 900 nm × 900 nm, z scale 0–5 nm. The Au colloids can be seen (light colored features) decorating the complete length of the nanotube.

colloids following the introduction of a thioether linker, as outlined in Scheme 1. The functionalized nanotubes [(COOEt)₂C<SWNT] (1) were deposited onto a mica surface by spin coating a suspension in *o*-DCB. Subsequent reaction steps were then carried out with the nanotubes immobilized on the surface, with thorough washing between each reaction step. Careful control experiments were carried out to ensure that gold colloids were indeed present due to the chemistry described, Figure 2. AFM imaging of pristine SWNTs

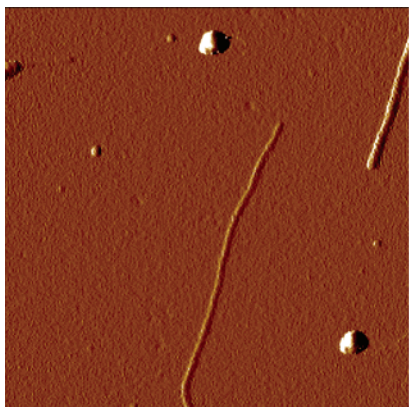


Figure 2. A typical tapping mode AFM (amplitude) image of SWNTs after a control reaction where the Bingel functionalized nanotubes [(COOEt)₂C<SWNT] (1) were exposed to ~5 nm Au colloids in the absence of the thioether linker. The image shown is 1.5 μm × 1.5 μm. Au colloids and what appears to be larger aggregates are only visible on the mica surface and are not present on the walls of the nanotubes. A small bundle containing 2–3 nanotubes is visible in the top right of the image.

prior to any reaction chemistry but after exposure to gold colloids showed no presence of nanotubes decorated with an array of nanoparticles, although occasionally a catalyst particle was observed at the end of a SWNT. Similarly, imaging pristine SWNTs exposed only to 2-(methylthio)ethanol and 5 nm gold colloids showed no signs of nanotube decoration with colloids. Significantly, gold colloids were only observed after the SWNTs were reacted with diethyl bromomalonate in the presence of a base, transesterified with a thio linker, and exposed to gold colloids, suggesting that the nanotubes were indeed cyclopropanated under the Bingel reaction conditions. Noteworthy, gold colloids were observed both on the sides and at the ends of the nanotubes.

To further confirm the successful cyclopropanation of SWNTs, a fluorinated marker was introduced by transesterification of a suspension of [(COOEt)₂C<SWNT] (1) with the sodium salt of 1*H*,1*H*,2*H*,2*H*-perfluorodecan-1-ol, followed by extensive washing, to afford [(COOCH₂CH₂C₈F₁₇)₂C<SWNT] (3), Scheme 1. The introduction of the perfluoro group allowed the nanotubes to be probed by ¹⁹F NMR and XPS spectroscopy.

The ¹⁹F NMR spectra were recorded as solutions or fine dispersions (for SWNTs) in 1:1 *d*₇-DMF/DMF. For the SWNT samples, ~1 mg of material was briefly sonicated in the solvent, allowed to stand for 1 h, and the supernatant was collected for spectroscopy. Figure 3 shows the ¹⁹F NMR spectra of the transesterified product and a control sample where pristine SWNTs were exposed to the same concentration of the fluorinated alcohol and subjected to the same degree of washing. It is clear that little or no fluorine-containing groups are present in the control reaction, ruling out physical adsorption as a major contributing factor to the spectra, whereas [(COOCH₂CH₂C₈F₁₇)₂C<SWNT] (3) exhibits resonances [$\delta = -80.9$ CF₃(10), -114.5 CF₂(3), -123.4 CF₂(4), -123.6 CF₂(5,7), -124.4 CF₂(8), -125.3 CF₂(9), 128.0 CF₂(6)] at chemical shifts similar to those observed in the starting alcohol, 1*H*,1*H*,2*H*,2*H*-perfluorodecan-1-ol [$\delta = -81.3$ CF₃(10), -114.0 CF₂(3), -122.8 CF₂(4), -123.0 CF₂(5,7), -123.8 CF₂(8), -124.7 CF₂(9), 127.2 CF₂(6)]. The resonances are slightly broadened presumably due to the sample being finely dispersed and to the restricted mobility caused by the large size of the nanotubes.⁸

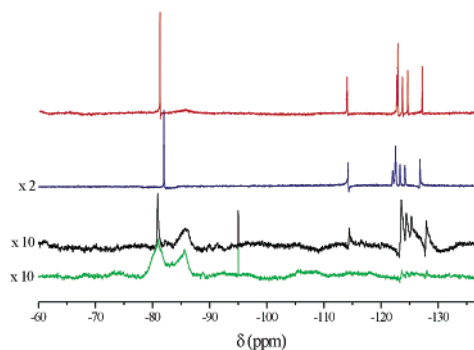


Figure 3. ¹⁹F NMR (*d*₇-DMF/DMF) spectra of 1*H*,1*H*,2*H*,2*H*-perfluorodecan-1-ol (red), sodium salt of 1*H*,1*H*,2*H*,2*H*-perfluorodecan-1-ol [(COOCH₂CH₂C₈F₁₇)₂C<SWNT] (3) (black), and pristine SWNTs exposed to the sodium salt of 1*H*,1*H*,2*H*,2*H*-perfluorodecan-1-ol, the control (green). The broad feature (-85 ppm) and sharp line (-95 ppm) are from the NMR probe and a data spike, respectively.

The XPS spectrum (F1s) of [(COOCH₂CH₂C₈F₁₇)₂C<SWNT] (3) similarly shows the presence of fluorine bound to carbon at a binding energy of 686.2 eV; see Supporting Information. The degree of functionalization was estimated to be ca. 2%.

In conclusion, we have shown that it is possible to functionalize SWNTs with a cyclopropane group using Bingel reaction conditions. AFM in conjunction with chemical tagging techniques has been shown to be a reliable method in locating functional groups and determining their distribution.

Acknowledgment. K.S.C. would like to acknowledge The Royal Society for financial support and the EPSRC for a studentship (S.R.B.).

Supporting Information Available: C1s and F1s XPS spectra of (3). Raman spectra of (2) and (3). Experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0355675