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A Short, Rigid, Structurally Pure Carbon Nanotube by Stepwise Chemical Synthesis

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S *Supporting Information*

ABSTRACT: The inaccessibility of uniform-diameter, single-chirality carbon nanotubes (CNTs) in pure form continues to thwart efforts by scientists to use these ultrathin materials in innovative applications that could revolutionize nanoscale electronics. Stimulated by the challenge to address this long-standing problem, we and other organic chemists have envisioned a new production strategy involving the controlled elongation of small hydrocarbon templates, such as hemispherical nanotube end-caps, prepared by bottom-up chemical synthesis; the diameter and rim structure encoded in the template would dictate the diameter and chirality of the resulting CNT. Toward that objective, a short [5,5] CNT has now been synthesized by stepwise chemical methods. This $C_{50}H_{10}$ geodesic polyarene has been isolated, purified, crystallized, and fully characterized by NMR spectroscopy, UV−vis absorption spectroscopy, high resolution mass spectrometry, and X-ray crystallography.

The discovery of carbon nanotubes in 1991[1] almost instantly inspired dreams among scientists and engineers about how these lightweight, super strong, heat resistant, ultrathin nanowires could someday be used to miniaturize electronic devices down to the nanometer scale, well beyond the limits of what can ever be achieved by lithography on silicon chips.[2,3] Unfortunately, not all carbon nanotubes (CNTs) are alike. Some are semiconductors, whereas others are highly conductive, like metals, with current carrying capacities up to 1000 times greater than that of copper wire.[3] Despite two decades of extensive experimentation worldwide, however, all known preparation methods still yield mixtures of different types of CNTs that are virtually impossible to separate into their individual components in useful amounts.[4,5] More controlled methods for synthesizing CNTs are clearly needed.[6]

If access could be gained to a small hydrocarbon template, such as a short CNT (*e.g.*, **1**), and it could be elongated by the repetitive addition of carbon atoms to annulate new six-membered rings, as outlined in Figure 1, then every resulting CNT would be of the same type;[7] the diameters of all the CNTs produced and the orientations of the six-membered rings along their sidewalls (their "chiralities") would all be identical. The dimensions and structure of the template rim would dictate the diameter and chirality of the resulting CNTs. From nanotube **1**, for example, elongation would yield exclusively [5,5] CNTs having a 1 nm diameter (Figure 1). All [*n*,*n*] CNTs belong to the so-called armchair nanotube family and are expected to exhibit the metal-like electrical conductivity required for use as nanowires.[2,3]

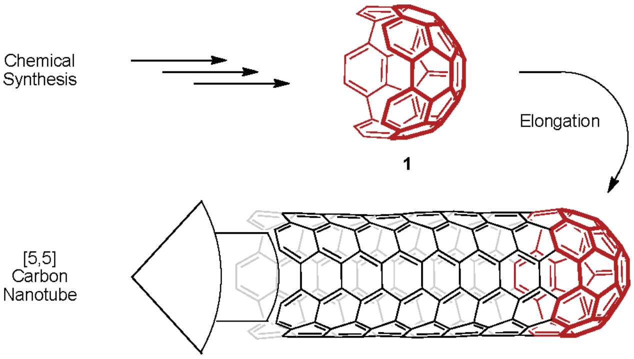

Figure 1. Strategy for the bottom-up synthesis of uniform diameter, single chirality carbon nanotubes. The diameter and rim structure encoded in the hemispherical $C_{50}H_{10}$ template (**1**), a short nanotube, will dictate the diameter and sidewall structure of the resulting elongated carbon nanotube and, thereby, its electrical conductivity.

The first major hurdle that must be overcome before this strategy can be tested is the preparation of a small hydrocarbon with a cylindrical rim that is suitable to use as a template for nanotube growth.[7,8] This communication reports the successful synthesis and unambiguous characterization of the first such hemispherical polyarene (**1**). Previous work in our laboratory[9] and elsewhere[10] has produced dozens of less curved geodesic polyarenes but never a fully hemispherical nanotube end-cap. Because the 50 carbon atoms of hydrocarbon **1** comprise both a complete end-cap and the beginnings of the sidewalls of a CNT, theoreticians have regarded this previously unknown polyarene as not just an end-cap but as a short, full-fledged carbon nanotube.[11]

The synthesis of **1** (Figure 2) required years to develop but ultimately has been accomplished in just three steps from corannulene (**2**), a geodesic polyarene that has recently been synthesized by Siegel et al. in kilogram quantities.[12] Direct chlorination of corannulene with iodine monochloride provides 1,3,5,7,9-pentachlorocorannulene (**3**) as the major product,[13] and this versatile compound serves as the foundation onto which the rest of the end-cap and the sidewalls of the nanotube can be built. 5-fold Negishi coupling[14] of **3** with 2,6-dichlorophenylzinc chloride (**4**)[15] adds the remaining 30 carbon atoms to the molecule. The $C_{50}H_{20}Cl_{10}$ compound

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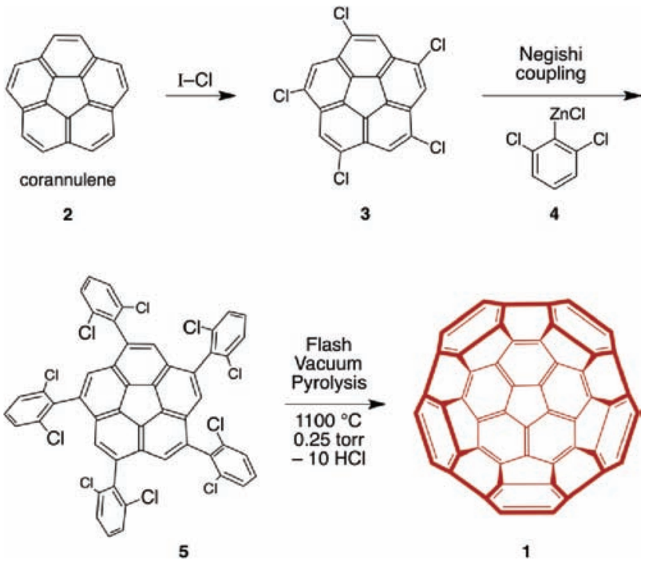

Figure 2. Three-step synthesis of a short [5,5] carbon nanotube (**1**) from corannulene (**2**). The $C_{50}H_{10}$ nanotube shown in Figure 1 (**1**) is depicted here as viewed down its 5-fold axis.

thus obtained (**5**) was characterized by X-ray crystallography and the customary spectroscopic methods (see Supporting Information). Stitching together the five appendages of **5** was achieved by flash vacuum pyrolysis (FVP) at 1100 °C/0.25 Torr. This technique has been used extensively during the past 20 years for the construction of strained geodesic polyarenes[9,16] and also figured prominently in the first rationally designed chemical synthesis of C_{60} (Buckminsterfullerene), likewise from a chlorinated hydrocarbon precursor.[17] At such high temperatures in the gas phase, it is believed that the C−Cl bonds rupture, one at a time, to generate reactive aryl radicals. The high temperatures also provide the energy required to temporarily distort the intermediate species away from their equilibrium geometries, thereby bringing the transient aryl radical centers into bonding distance with otherwise remote atoms in the molecule. The gain in entropy resulting from the loss of 10 chlorine atoms and 10 hydrogen atoms dominates the thermodynamics of this reaction at such high temperatures. Silica gel chromatography of the product mixture obtained from the FVP reproducibly provides pure samples of **1** in 2−3% isolated yield.

The growth of nanotubes from small hydrocarbon templates has the potential to amplify the quantities of material enormously. CNTs exceeding 1 mm in length have been known for more than a decade,[18] and the elongation of a 1 nm template such as **1** to a length of 1 mm would correspond to a 10^6 increase in size. If even a fraction of the template molecules can eventually be grown to a fraction of a millimeter in length, gram quantities of pure, single-index CNTs could be accessible for the first time from the milligram amounts of **1** prepared in the manner described here (3−4 μmol per run).

Hydrocarbon **1** is stable to air, heat, and light; no special precautions are required to handle it under ordinary laboratory conditions. It also exhibits sufficient solubility in common organic solvents (*e.g.*, dichloromethane, chloroform, benzene, and carbon disulfide) to permit routine spectroscopic analysis. The ^{1}H NMR spectrum consists of a single resonance at 7.63 ppm (CD_2Cl_2), which falls in the normal region for hydrogen atoms attached to benzene rings. As expected, the ^{13}C NMR spectrum shows six signals: 154.1, 151.5, 144.7, 137.6, 130.6, 126.4 ppm (CD_2Cl_2). High resolution mass spectrometry (APPI-TOF, negative ion mode) confirms the molecular formula as $C_{50}H_{10}$. Absorption maxima are seen in the UV−vis spectrum of **1** at $\lambda_{\max}$ 268 and 308 nm (CH_2Cl_2), close to those of fullerene-C_{60} ($\lambda_{\max}$ 270 and 329 nm). Additional shoulders and a long absorption tail that extends into the visible region of the spectrum account for the golden color of **1** in solution; the compound appears red-orange in the solid state.

Crystals of **1** were grown by slow evaporation of a solution in CS_2, CH_2Cl_2, and hexanes. X-ray crystallographic analysis gives the structure for nanotube **1** shown in Figure 3. The bowl depth is 5.16 Å. The shortest distance from the 5-fold axis of the hydrocarbon to that of its nearest neighbor in the crystal is 9.4 Å, which corresponds to a nanotube diameter of just under 10 Å (~1.0 nm). The X-ray CIF file is available in the Supporting Information and has also been deposited in the Cambridge Crystallographic Data Centre (CCDC 831391).

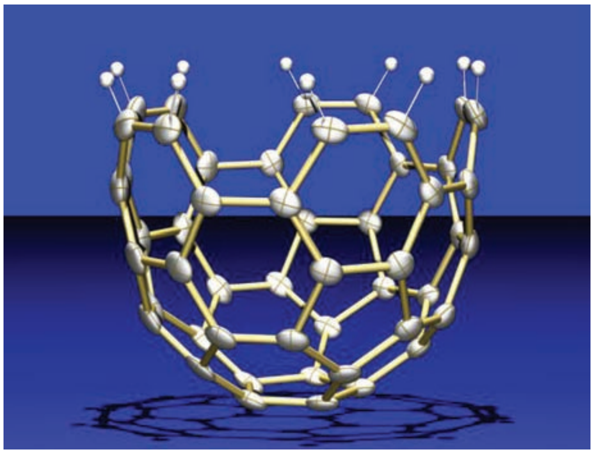

Figure 3. Molecular structure of the short, $C_{50}H_{10}$ carbon nanotube (**1**), as determined by X-ray crystallography. Carbon atom positions are indicated with 50% probability ellipsoids.

The crystal structure further reveals that the cavity of every nanotube is occupied by a carbon disulfide molecule, with the axes of the CS_2 and the nanotube aligned collinearly (Figure 4). A second CS_2 of crystallization is located outside, filling the interstices between neighboring nanotubes in the crystal lattice (see Supporting Information). The sulfur atom inside the cavity of the nanotube sits just 0.64 Å above the centroid of the 50 carbon atoms, and the carbon atom of the same CS_2 guest sits

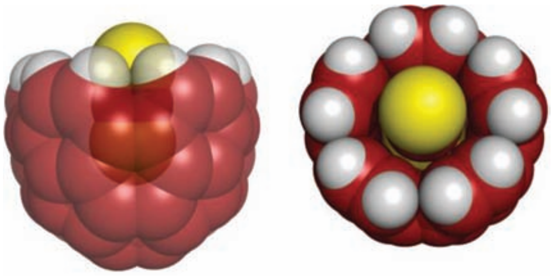

Figure 4. . Space-filling view of the short, $C_{50}H_{10}$ carbon nanotube (**1**). A carbon disulfide molecule from the solvent of crystallization was found to occupy the cavity of each nanotube in the crystals used for X-ray crystallography (yellow = sulfur, white = hydrogen, red = carbon).

just 0.21 Å below the plane of the 10 carbon atoms that define the rim of the nanotube, all of which have radially oriented p-orbitals.[19]

The results reported here prove that short, rigid, isomerically pure carbon nanotubes can now be synthesized in the laboratory by rational chemical methods. Furthermore, they instill confidence that short CNTs of different diameters and rim structures will likewise become accessible in the future, either by other annulations of polycyclic aromatic hydrocarbon bowls[10,20] or, alternatively, by molecular surgery, starting from C_{60} or higher fullerenes.[21] Larger diameter hemispherical polyarenes will be less strained than **1** and, in this respect, actually represent less demanding targets for directed chemical synthesis. Belts of aromatic rings that are open at both ends[22,23] and the less rigid cycloparaphenylenes[22,24] likewise represent potential templates from which to grow structurally uniform CNTs. Finding or inventing methods to elongate nanotube **1** and other templates remains a significant challenge;[25] however, there is no longer any room for doubt that modern methods of synthetic organic chemistry can deliver the hydrocarbon templates required to test this approach to the controlled synthesis of carbon nanotubes.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures for the synthesis of new compounds **1** and **5**; spectra for **1** and **5** and CIF files for their X-ray crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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