# Chemistry of Single-Walled Carbon Nanotubes

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## ABSTRACT

In this Account we highlight the experimental evidence in favor of our view that carbon nanotubes should be considered as a new macromolecular form of carbon with unique properties and with great potential for practical applications. We show that carbon nanotubes may take on properties that are normally associated with molecular species, such as solubility in organic solvents, solution-based chemical transformations, chromatography, and spectroscopy. It is already clear that the nascent field of nanotube chemistry will rival that of the fullerenes.

## Introduction

Fullerenes were immediately recognized as a new molecular form of carbon,[1,2] even though they have produced novel materials with itinerant properties.[3] Since their inception,[4] carbon nanotubes have been regarded as materials,[5] and most naturally related to the other intractable carbon allotropes—graphite and diamond. It has been the goal of our group to bring these fascinating one-dimensional (1D) carbon structures into the fold of (macro)molecular chemistry.[6] Recent work has shown that with appropriate processing carbon nanotubes may take on properties that are normally associated with molecular species,[7] such as solubility in organic solvents, solution-based chemical transformations, chromatography, and spectroscopy. In this Account we summarize the progress and the promise of the new field of carbon nanotube chemistry.

We focus on single-walled carbon nanotubes (SWNTs) which were first reported in 1993.[8,9] The SWNTs are characterized by strong covalent bonding, a unique one-dimensional structure, and nanometer size which impart unusual properties to the nanotubes—including exceptionally high tensile strength, high resilience, electronic properties ranging from metallic to semiconducting, high current carrying capacity, and high thermal conductivity. Chemical processing of the SWNTs will play an essential role in the realization of the promise of this material.

## Preparation and Solid State Properties

When carbon is dissolved in a transition metal nanoparticle melt, most commonly Ni/Co, Ni/Y, Rh/Pt, or Fe, and
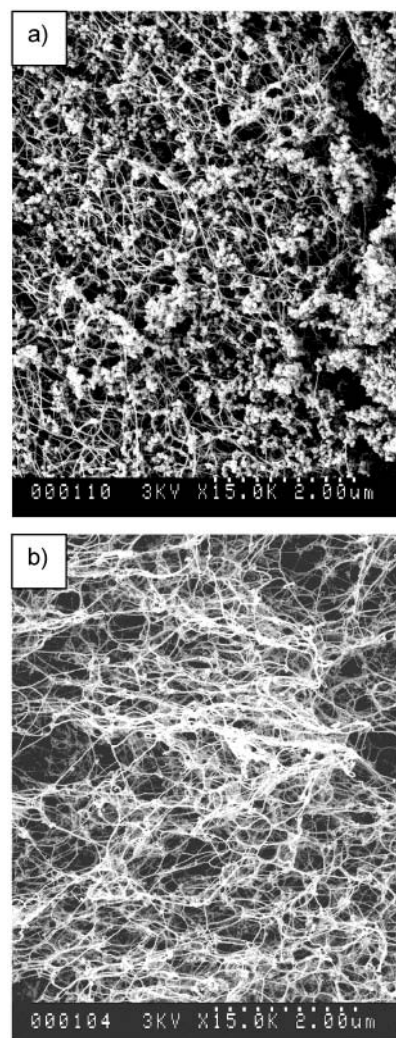
**FIGURE 1.** Scanning electron micrograph of SWNT soot prepared by the arc process with Ni/Y catalyst: (a) typical purity, (b) high purity region of the same sample. (Reproduced with permission from Carbon Solutions, Inc. Copyright 2000.)

allowed to supersaturate,[10,11] a cylindrical graphitic carbon network is extruded. This structure can grow in the form of a cylinder to a length of micrometers in a few milliseconds,[10,12] and it is thought that such structures can grow indefinitely provided the correct phase properties for the particular metal–carbon alloy are maintained.[13–18] The SWNTs thus formed have diameters on the order of a nanometer when prepared by current techniques.[19–21] Typically, the as-prepared SWNT soot (AP-SWNTs) from the electric arc procedure contains metal particles, metal clusters coated with carbon, amorphous carbon, and in some cases fullerenes, with a 30 wt % abundance of carbon nanotube ropes (Figure 1).

Ultra-high-vacuum (UHV) scanning tunneling microscopy (STM) has allowed atomic resolution imaging of the surface of SWNTs, and I/V spectroscopy has provided direct measurement of the electronic band structure.[22–25] It is now known that SWNTs can behave as metals, semiconductors, or small band-gap semiconductors,[26–28] depending upon their diameter and chirality.[29] Electronic
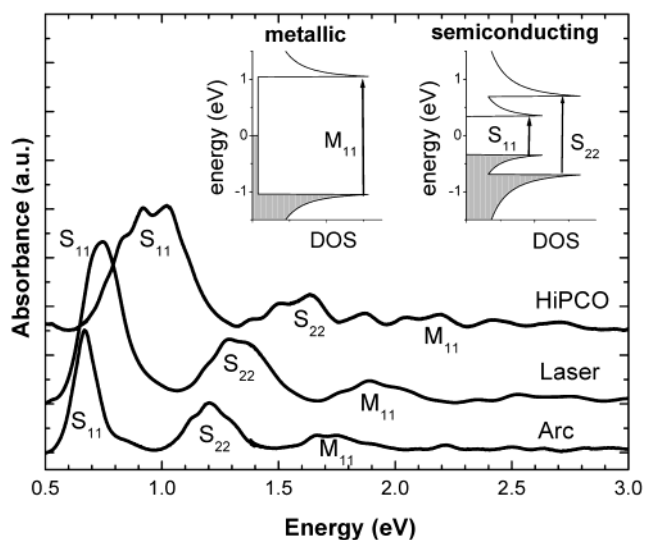
**FIGURE 2.** Electronic transitions between the energy bands of SWNTs, observed by transmission spectroscopy of films, together with a schematic of the nomenclature used to designate the interband transitions.[30]

transitions between the energy bands of SWNTs (Figure 2) can be observed by standard spectroscopic techniques.[7,27,30] Besides the heterogeneity of the samples with respect to the tube diameters and helicities, impurity doping contributes to the breadth of the absorption features.[27] Since the band gaps are inversely proportional to the tube diameters, structural information can be derived from the band transition energies.[31]

## Electronic Structure and Chemical Reactivity

The reactivity of the fullerenes is primarily driven by the enormous strain engendered by their spherical geometry as reflected in the pyramidalization angles of the carbon atoms.[32] For an sp²-hybridized (trigonal) carbon atom, planarity is strongly preferred, and this implies a pyramidalization angle of $\theta_P = 0°$, whereas an sp³-hybridized (tetrahedral) carbon atom requires $\theta_P = 19.5°$ (Figure 3b). All of the carbon atoms in $C_{60}$ have $\theta_P = 11.6°$, and it is immediately clear that their geometry is more appropriate for tetrahedral than trigonal hybridization. Thus the chemical conversion of any trivalent carbon atom in $C_{60}$ to a tetravalent carbon atom relieves the strain at the point of attachment and mitigates the strain at the 59 remaining carbon atoms.[32] Hence reactions that serve to saturate the carbon atoms are accelerated by strain relief, and this strongly favors fullerene addition chemistry.[32−34]

Just as in the case of a fullerene, a perfect SWNT is without functional groups; therefore these quasi-1D cylindrical aromatic macromolecules are chemically inert. However, curvature-induced pyramidalization and misalignment of the π-orbitals[6,30,32,35−41] of the carbon atoms induces a local strain (Figure 3), and carbon nanotubes are expected to be more reactive than a flat graphene sheet. From the standpoint of the chemistry, it is conceptually useful to divide the carbon nanotubes into two regions: the end caps and the side wall. The end caps of the carbon nanotubes resemble a hemispherical fullerene, and because it is impossible to reduce the maximum
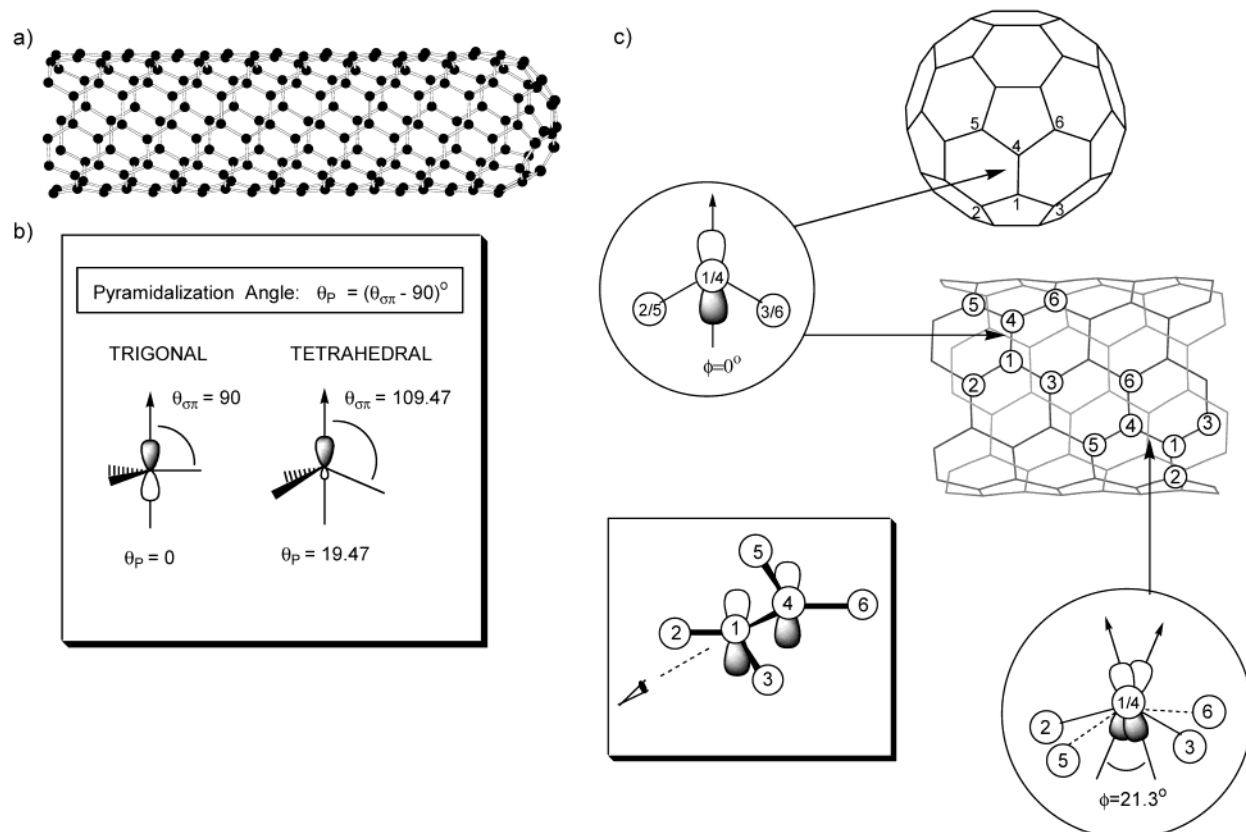


**FIGURE 3.** Diagrams of (a) metallic (5,5) SWNT, (b) pyramidalization angle ($\theta_P$), and (c) the π-orbital misalignment angles ($\phi$) along the C1−C4 in the (5,5) SWNT and its capping fullerene, $C_{60}$.

pyramidalization angle of any fullerene below about $\theta_P^{max}$ = 9.7°,[42] this ensures that the end caps will always be quite reactive, irrespective of the diameter of the carbon nanotube. In the (5,5) SWNT shown in Figure 3a, which is capped by a hemisphere of $C_{60}$, the pyramidalization angles are as follows: $\theta_P \approx 11.6°$ (end cap) and $\theta_P \approx 6.0°$ (side wall).[30]

The strain in nonplanar conjugated organic molecules arises from two principal sources: pyramidalization of the conjugated carbon atoms, and $\pi$-orbital misalignment between adjacent pairs of conjugated carbon atoms.[35,43] The strain in the fullerenes is primarily from pyramidalization,[44,45] and the large strain imposed by the spheroidal structure accounts for their well-developed (addition) chemistry.[32−34] It is the relief of this strain which accompanies addition reactions that drives the chemistry of the fullerenes.[32] There is very little $\pi$-orbital misalignment in the fullerenes, and in the case of $C_{60}$ the $\pi$-orbital alignment is perfect.[44,46] This is why the pyramidalization angle (alone) provides a useful index of local reactivity in the fullerenes.[32] Clearly the fullerene double bonds that are terminated with carbon atoms of maximum pyramidalization angle ($\theta_P^{max}$) will be the most reactive;[42] this index allows comparisons in reactivity between the carbon atoms in a given fullerene (such as $C_{70}$)[32] and between different fullerenes in terms of the maximum pyramidalization angle which is characteristic of any structure. For example, among those fullerenes with icosahedral symmetry, the fullerene with the minimum $\theta_P^{max}$ value is $C_{240}$, and thus this molecule is expected to be the most chemically inert of the icosahedral (and perhaps all) fullerenes.[42] Because the isolable fullerenes obey the isolated pentagon rule,[47,48] the carbon atom(s) of maximum pyramidalization in any fullerene always lie in a five-membered ring (5−6−6 ring junction), and it appears likely that for all fullerenes, $\theta_P^{max} \geq 9.7°$.[42]

Although the carbon fullerenes and the side walls of the carbon nanotubes are both examples of curved carbon,[49] there are significant structural differences which are expected to be reflected in their chemistry; in particular, the fullerenes are curved in 2D, whereas the nanotubes are curved in 1D. Thus for a curved carbon structure of given radius, the carbon atoms in a fullerene are more distorted than those in the corresponding carbon nanotube. For example, to curve a graphene sheet into a (10,10) SWNT requires a pyramidalization angle for the carbon atoms of about $\theta_P = 3.0°$,[6] whereas the fullerene of equivalent radius, $C_{240}$ [a (10,10) SWNT can be capped by a hemisphere of $C_{240}$],[19] has $\theta_P^{max} = 9.7°$;[42] see also the (5,5) SWNT discussed above. The strain energy of pyramidalization[32,48] is roughly proportional to $\theta_P^2$, so the fullerene must absorb about 10 times the strain energy of pyramidalization per carbon atom, compared to the "equivalent" carbon nanotube at these diameters.

However, there is a caveat to this analysis—whereas the $\pi$-orbital alignment in the fullerenes is almost perfect,[44,45] this is not the case for all bonds in the carbon nanotubes. This may be seen in the illustration of an arm-chair (5,5) SWNT shown in Figure 3 (pyramidalization angle, $\theta_P$ =

**Table 1. Pyramidalization ($\theta_P$) and $\pi$-Orbital Misalignment Angles ($\phi$) in ($n,m$) SWNT**

| $n,m$ | diameter (nm) | $\theta_P$ (deg) | $\phi$ (deg) | $n,m$ | diameter (nm) | $\theta_P$ (deg) | $\phi$ (deg) |
|---|---|---|---|---|---|---|---|
| 10,0 | 7.81 | 5.15 | 0, 18.5 | 5,5 | 6.76 | 5.97 | 0, 21.3 |
| 12,0 | 9.37 | 4.30 | 0, 15.3 | 6,6 | 8.11 | 4.99 | 0, 17.6 |
| 14,0 | 10.93 | 3.69 | 0, 13.1 | 7,7 | 9.47 | 4.27 | 0, 15.0 |
| 16,0 | 12.49 | 3.24 | 0, 11.4 | 8,8 | 10.82 | 3.74 | 0, 13.1 |
| 18,0 | 14.05 | 2.88 | 0, 10.1 | 9,9 | 12.17 | 3.33 | 0, 11.6 |
| 20,0 | 15.61 | 2.59 | 0, 09.1 | 10,10 | 13.52 | 3.00 | 0, 10.4 |

6.0°).[30] Although all carbon atoms are equivalent, there are two types of bonds: those that run parallel to the circumference (or perpendicular to the nanotube axis) and those at an angle to the circumference with $\pi$-orbital misalignment angles ($\phi$, deg) of $\phi = 0°$ and 21.3°, respectively. The analogous values for the (10,10) SWNT are $\phi = 0°$ and 10.4°. On the basis of previous calculations of torsional strain energies in conjugated organic molecules,[50] $\pi$-orbital misalignment is likely to be the main source of strain in the carbon nanotubes. This represents a clear contrast with fullerene chemistry, although there are parallels with the reactivity of homofullerenes (fulleroids).[38,39] Just as in the case of the fullerenes, the reactivity of carbon nanotubes arises out of their topology but for different reasons. Furthermore, since the pyramidalization angles and the $\pi$-orbital misalignment angles of SWNTs scale inversely with the diameter of the tubes, a differentiation is expected between the reactivity of carbon nanotubes of different diameters (Table 1).

Maintaining the basic electronic structure of the SWNTs while exploiting the reactivity to bring about appropriate chemical processing and modification remains the central dilemma of the field.[6] The aromatic ring system of the SWNTs can be disrupted by the application of extremely aggressive reagents. When sonicated[51] in the presence of strong oxidizing agents such as $HNO_3$ or $H_2SO_4$ or a mixture of the two,[52] the nanotubes can be functionalized as carboxylic acids or quinones,[53−56] whereas sonication in organic solvents produces dangling bonds in the SWNTs that undergo further chemical reactions.[57] As expected from the foregoing discussion, the oxidative power necessary to incorporate acidic sites into carbon nanotubes varies with the tube diameter. While the largest diameter tubes (made in the electric arc process) require the most strongly oxidative conditions, the smaller diameter HiPco tubes do not survive such harsh treatment.[58,59]

The preceding discussion has focused on the local electronic structure, but from the time of their discovery,[8,9] it has been recognized that SWNTs possess a unique electronic band structure (Figure 2). Depending on helicity and diameter, these 1D nanostructures may be metals or semiconductors.[29,60−62] The electronic structure of the SWNTs is related to a 2D graphene sheet, but, because of the radial confinement of the wave function, the continuous electronic density of states (DOS) in graphite divides into a series of spikes in SWNTs which are referred to as Van Hove singularities. Electronic transitions between these singularities give rise to prominent features in scanning tunneling spectroscopy (STS)[22,23] and transmission spectroscopy.[7,17,31,63] As can be seen in Figure 2, the
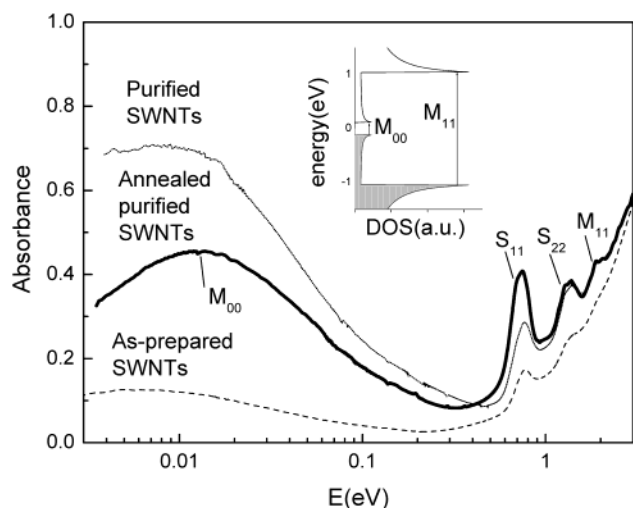
**FIGURE 4.** Fermi level electronic structure of common forms of SWNTs. The low energy (~0.01 eV) features arise from a combination of (1) transitions that are intrinsic to the metallic SWNTs, (2) transitions due to the curvature-induced gap ($M_{00}$) in the chiral metallic SWNTs, and (3) transitions due to purification-induced acid doping of the semiconducting SWNTs.[27]

commercially available SWNT preparations readily allow the observation of the first and second electronic transitions in the semiconducting nanotubes ($S_{11}$ and $S_{22}$) and the first transition in the metallic nanotubes ($M_{11}$).[30] In addition, transitions at the Fermi level (Figure 4) of the metallic SWNTs ($M_{00}$) are observable in the far-IR region of the electromagnetic spectrum.[26,27] This is the most informative region of the spectrum, and in the case of acid-purified SWNTs we have shown that the low-energy feature is partially due to doping of the SWNTs, presumably by nitric acid. Furthermore, the peak at ~0.01 eV may be assigned to the curvature-induced pseudogap in the chiral SWNTs.[64−66]

On a practical note, an important aspect of nanotube chemistry is the level of purity of the starting materials, and most bulk samples are heavily contaminated with non-nanotube impurities. No chemist likes to work with impure starting materials, but this is the usual state of affairs at the present time. The absence of analytically pure bulk samples of carbon nanotubes has been the most important factor in hampering the investigation of their chemistry and characterization of their intrinsic properties.[53,58,67−69] It should be noted that most current techniques do not begin to address the purification of carbon nanotubes by length, diameter, and chirality, although this will clearly be of great future importance.[70−72]
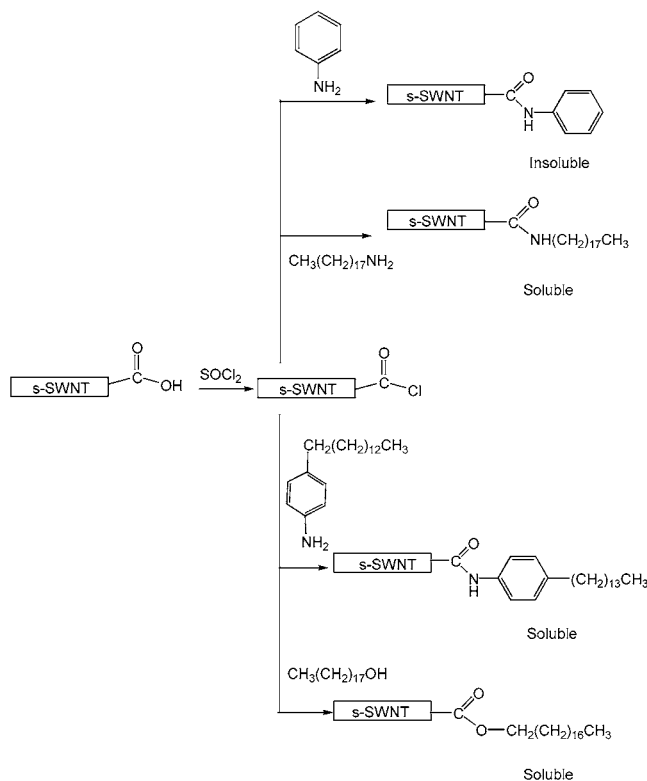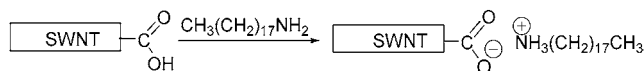
## Dissolution

Chemistry occurs in solution. Modern synthetic chemistry and biological processes primarily take place in the solution phase. Although we attempted chemistry on as-prepared SWNTs (AP-SWNTs) (Scheme 1), the difficulties associated with characterizing the products[6] forced us to turn our attention to the development of a dissolution process for the SWNTs. SWNTs are extremely resistant to

**Scheme 1. Reactions of AP-SWNTs[6]**
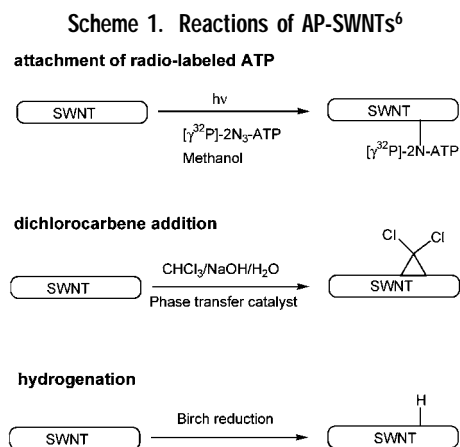


wetting.[73] They typically exist as ropes or bundles 10−25 nm in diameter that are a few micrometers long; the SWNT ropes are entangled together in the solid state to form a highly dense, complex network structure. These factors, coupled with the fact that these pseudo-1D graphitic cylinders do not have any surface functional groups, make them very difficult to disperse in organic media.[6]

It is possible to wet the SWNT raw soot in refluxing nitric acid,[5,55] whereby the end caps of the tubes are oxidized to carboxylic acid and other weakly acidic functionalities.[55,74,75] These "acid-purified" SWNTs can be dispersed in various amide-type organic solvents under the influence of an ultrasonic force field.[76] The nitric acid purifies the carbon nanotubes by removal of some of the metal catalysts used in the synthesis of the tubes and some of the amorphous carbon that is a byproduct of most synthetic methods. However, the nitric acid treatment introduces defects on the nanotube surface,[52] oxidizes (hole dopes) the carbon nanotubes, and produces impurity states (Figure 4) at the Fermi level of the nanotubes.[27] This latter effect may be viewed as an intercalation of the nanotube lattice by oxidizing agents, with concomitant effects on the electronic properties of the nanotubes,[77,78] a process which is quite familiar from the intercalation of graphite and fullerene lattices by various redox reagents. The defect sites that are introduced into the carbon nanotubes can be used to shorten and eventually destroy the carbon nanotubes under similar oxidizing conditions.[55,79−82] The shortened tubes (s-SWNTs) are better solvated by amide solvents than are the full-length SWNTs.

We envisioned that the addition of a long-chain hydrocarbon at the ends of the shortened (100−300 nm) carbon nanotubes[55] might render the functionalized SWNTs soluble in organic solvents. Thus we set out to convert the acid functionality in the s-SWNTs to the amide of octadecylamine (ODA, Scheme 2), and this led to the first shortened soluble SWNTs (s-s-SWNTs).[7] The formation of the amide bond can be monitored using mid-IR spectroscopy, and the SWNTs exhibit a number of clear spectroscopic signatures that suggest the material is in solution. Direct reaction of the acid-purified s-SWNTs with long-chain amines led to soluble materials by the formation of zwitterions (Scheme 3).[83]
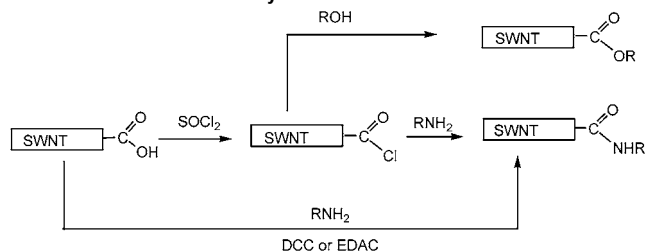
**Scheme 2.  Covalent Chemistry at the Open Ends of s-SWNTs[7,83,115]**



**Scheme 3.  Zwitterionic Functionalization of SWNT (s-I-SWNT)[84]**



**Scheme 4.  Carboxylic Acid Derivatization Protocol**



Some insight into the mechanism of dissolution was obtained by functionalization with 4-tetradecylaniline and with aniline (Scheme 2). While the tetradecylaniline functionalization yielded s-s-SWNTs soluble in THF, $CS_2$, and aromatic solvents, the aniline derivatives were appreciably soluble only in aniline.[83] It may thus be inferred that the long-chain hydrocarbon plays an important role in disrupting and compensating for the loss of the van der Waals attraction between the carbon nanotubes.

Full-length SWNTs (l-SWNTs) are the ideal material for composites and nanoscale conductors. Thus we sought a dissolution process for unshortened, full-length SWNTs, and this was accomplished by direct reaction of the SWNT-COOH with octadecylamine (s-l-SWNT, Scheme 3).[83,84] Ionic functionalization has the following advantages:[7] (1) The acid–base reaction represents the simplest possible route to soluble SWNTs and can be readily scaled-up at low cost. (2) Unlike the covalent amide bond, the cation ($^+NH_3(CH_2)_{17}CH_3$) in the ionic bond of SWNT–$COO^-$ $^+NH_3(CH_2)_{17}CH_3$ can be readily exchanged by other organic and inorganic cations. Furthermore, such an ionic feature may allow electrostatic interactions between SWNTs and biological molecules and can serve as the basis for developing biocompatible SWNTs.

Since our initial work, the protocol of adding a bulky side chain to the SWNT ends via amide or ester bond formation (Scheme 4) has been applied by other groups,[85–92] thus establishing the generality of the process.
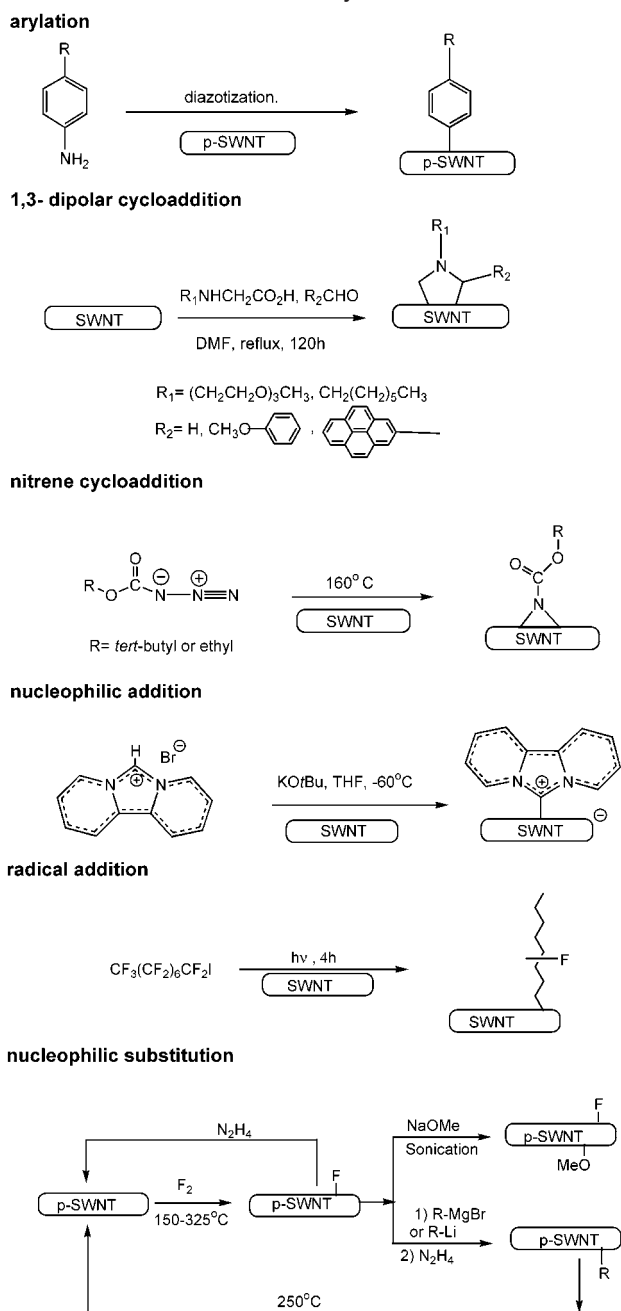
As noted above, the chemistry of the carbon nanotubes is conveniently divided into two parts: the end caps and the side wall. In our approach, the end caps are first removed and then the open ends of the nanotubes functionalized, perhaps together with functionalization of defects and associated carbons. Nevertheless, a primary goal of our work was the preservation of the essential aspects of the carbon nanotube electronic structure.[6,7] The alternative method (Scheme 5) to functionalization makes use of side wall chemistry[93–97] with concomitant loss of the carbon nanotube conjugated electronic structure in order to render the SWNTs soluble.[95–97]

The dissolution methods discussed above make use of ionic or covalent functionalization of the carbon nanotubes. Noncovalent functionalization has also been shown to be effective in the dissolution of the carbon nanotubes,[98,99] together with polymer wrapping procedures.[100–102]

## Covalent Chemistry of the Walls of the Carbon Nanotubes

As noted above, in certain instances covalent chemistry on the walls of the SWNTs is a viable route to soluble material.[95–97] In fact, the ability to carry out controlled (covalent) chemistry on the side walls of the SWNTs is a very important step, and the achievement of a systematic and predictable side wall chemistry is likely to be a precursor to many of the applications that are currently envisioned for carbon nanotubes.[6] We achieved the first covalent side wall chemistry of SWNTs (Scheme 1) when we exposed these solids to a series of aggressive reagents,[6] but it was not until we employed carbene reactions on the s-s-SWNTs using phenyl(bromodichloromethyl)mercury in toluene that we were able to demonstrate the expected modification of the band electronic structure of the SWNTs.[7] Characterization of the functionalized species is a major difficulty in carbon nanotube chemistry, but in the case of wall chemistry, where the band electronic structure is disrupted, solution spectroscopy is a powerful tool; Raman spectroscopy has also been used to study the effects of sidewall functionalization.[93–95,109] Dichlorocarbene is an electrophilic reagent that will add to deactivated double bonds (Scheme 5)[103–105] and to fullerenes.[106,107] Electronic spectroscopy showed that the band-gap transitions in the semiconducting tubes were completely disrupted at a functionalization level of 2% of the available SWNT carbon atoms.[7] Apart from the carbene chemistry,[6,7,96] a number of other chemical processes have been demonstrated on carbon nanotubes (Scheme 5), including nitrene addition,[7,96] hydrogenation via the Birch reduc-

## Scheme 5. Side Wall Chemistry on SWNTs[93−95,97,109,110]

**arylation**



**1,3- dipolar cycloaddition**



$R_1 = (CH_2CH_2O)_3CH_3, CH_2(CH_2)_5CH_3$

$R_2 = H, CH_3O-\bigcirc$ , 

**nitrene cycloaddition**



R= *tert*-butyl or ethyl

**nucleophilic addition**



**radical addition**



**nucleophilic substitution**



tion,[7,108] fluorination,[95,109] alkylation,[110] arylation,[93,94] and 1,3-dipolar cycloaddition.[97]

While the side walls of the carbon nanotubes were once considered impregnable (like the fullerenes),[32,33] there is now an extensive chemistry,[7,93,94,96,97,110] and these initial studies suggest that the chemistry of the carbon nanotubes will ultimately rival that of the carbon fullerenes.

## Ionic Chemistry (Doping)

As noted above, oxidative doping during nitric acid purification exerts a noticeable effect on the electronic transitions seen in the SWNTs (Figure 4). Similar effects may be observed by doping solutions of the nanotubes with halogens.[7,83] Under saturation doping,[7] bromine and iodine completely deplete the electrons from the valence
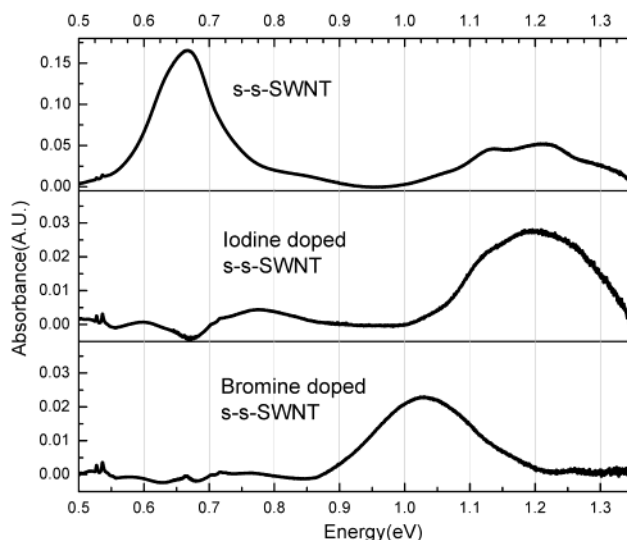
**FIGURE 5.** Change in the interband transitions of s-s-SWNTs after chemical doping with iodine and bromine.[7]

band responsible for the $S_{11}$ transition in the semiconducting nanotubes, and both reagents also affect the $S_{22}$ transition (Figure 5). Similar results were obtained under electrochemical cycling[63] and by controlled doping of thin films of carbon nanotubes.[111,112] Furthermore, solid state doping with halogens has been shown to influence the conductivity and Raman spectra of SWNTs.[113,114]

## Conclusion

Remarkable progress has been made in carbon nanotube chemistry—a field that did not exist five years ago and that was not expected to be possible. Clearly much remains to be accomplished: carbon nanotubes must be made at lower cost and in much improved purity. The heterogeneous bundling of the metallic and semiconducting carbon nanotubes is an additional problem that must be circumvented in order to realize the full nanotechnological potential of SWNTs. Nevertheless, with further developments in chemical processing the unique materials properties of the carbon nanotubes stand poised to revolutionize a number of important industries, from biology and medicine to aerospace and electronics.

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