Functionalization of Single-Walled Carbon Nanotubes

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Abstract: Through chemical functionalization of single-walled carbon nanotubes, the prerequisites for possible applications of such nanostructures are established. The derivatized tubes differ from the crude materials in their good solubility, which enables both a more extensive characterization and subsequent chemical reactivity. Current derivatization methods include defect and covalent sidewall functionalization, as well as noncovalent exo- and endohedral functionalization. In this way, for example, a range of nanotubes can be prepared: with sidewall substituents, wrapped with polymers, or with guest molecules included. The current state of the literature is presented in this Minireview.

1. Introduction

Research into carbon nanotubes has, in the past, mainly concentrated on the investigation of their physical properties.[1–4] The size of these macromolecular carbon allotropes and the continuous development of the fields of scanning tunneling microscopy and electron spectroscopy has made it possible to conduct precise investigations of individual molecules. Thus it was demonstrated that carbon nanotubes possess an array of unprecedented structural, mechanical, and electronic properties. For example, carbon nanotubes can exhibit metallic conductivity at the same time as: a) chemical and thermal stability, b) extremely high tensile strength and elasticity, c) the ability to absorb gas molecules as nanocapillaries, d) solubility when treated with surfactants, and e) the potential of further chemical functionalization. Uniquely, these are stable organic molecules that require no additional doping to become metallic conductors. Once this property profile was known, the question of technological applications quickly arose. In reaching this goal, however, it is necessary that not only single molecules, but also large ensembles, of the most pure and uniform nanotubes possible can be manipulated and investigated by analytical methods. This goal is currently a great challenge for chemists and materials scientists. In this context, chemical functionalization is an especially attractive target, as it can improve solubility[5] and processibility and allows the unique properties of single-walled nanotubes (SWNTs) to be coupled to those of other types of materials. Carbon nanotubes can be divided into SWNTs and multi-walled nanotubes (MWNTs). In this Minireview, the focus is on SWNTs, as their monomolecular character and the related simpler structure, and easier handling for chemical functionalization make them especially interesting (Figure 1).

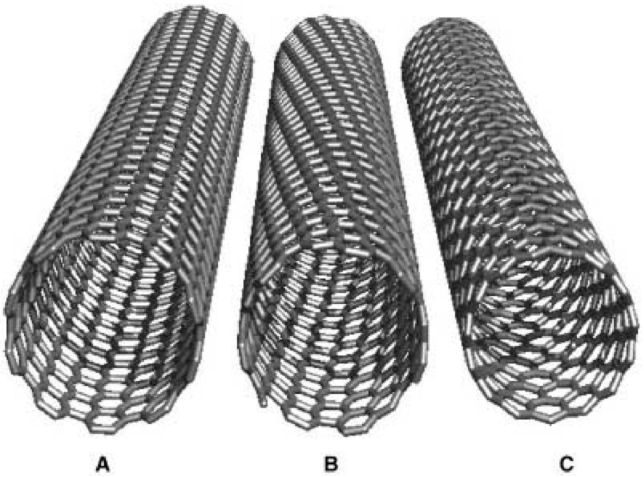

Figure 1. Idealized representation of defect-free (n,m) SWNTs with open ends. A) A metallic conducting (10,10) tube ("armchair"), B) a chiral, semiconducting (12,7) tube, and C) a conducting (15,0) tube ("zigzag"). The armchair (A) and zigzag (C) tubes are achiral. All the (n,n) armchair tubes are metallic, whilst this is only the case with chiral or zigzag tubes if $(n-m)/3$ is a whole number, otherwise, they are semiconductors.[1–4]

2. Synthesis and Purification of SWNTs

Several methods are known for the synthesis of SWNTs.[4] The first synthesis proceeded by arc discharge of graphite in the presence of metal catalysts (e.g. Fe, Co, Ni)[4]. Alternative routes are based on the laser vaporization of graphite–Ni–Co mixtures or chemical vapor deposition (CVD), in which carbon sources such as acetylene, metallocenes, $Fe(CO)_5/C_2H_2$, and CO can be used.[4] With one particular method, in which CO serves as the carbon source, very thin nanotubes

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1433-7851/02/4111-1853 $ 20.00+.50/0

(HiPCO tubes) can be produced.[6] Milligram to gram quantities can currently be manufactured by using such routes, within a matter of hours. The raw material that results contains up to 70% SWNTs by weight. The contaminants are mainly amorphous carbon and catalyst particles, which can be removed by treatment with oxidizing acids,[1–7] microfiltration,[8] or chromatographic procedures.[9, 10]

3. Structural and Physical Properties

What do the nanotubes we obtain look like? Are they well-defined molecules, as is the case with the fullerenes, or polydisperse mixtures? It appears that the situation is much more complicated than with other macromolecular systems because a) the SWNTs preferentially aggregate into bundles of different diameters (Figure 2), b) the nanotubes vary greatly in length, c) the diameters of the nanotubes themselves can vary, d) the nanotubes possess a range of helicities, and e) defects occur, both at the tube ends and on the sidewalls (Figure 3).[11] The probability of finding a pair of identical tubes in a normal macroscopic sample of SWNTs is extremely small.

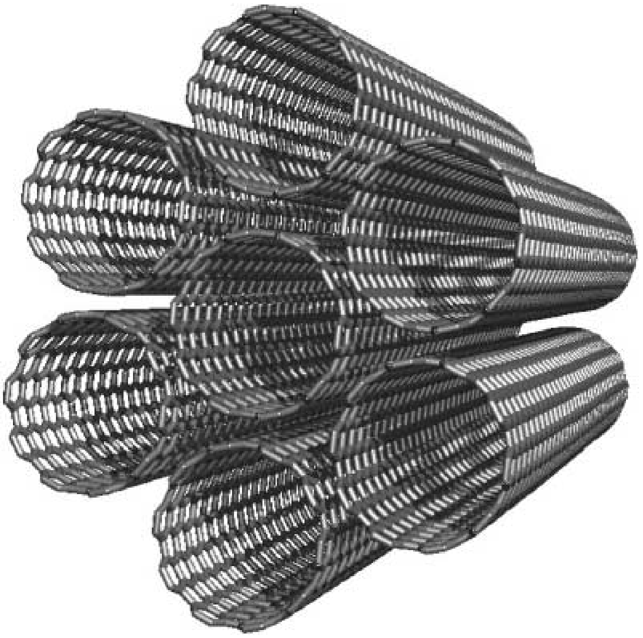


Figure 2. An idealized bundle of (10,10) nanotubes. In such bundles individual tubes are held together with strong $\pi-\pi$-stacking interactions. Almost all the tubes are organized in bundles in a typical sample.

This multitude of possibilities highlights the difficulties that occur in the structural characterization of the resulting mixtures. Enrichment of particular structural forms by use of classical separation techniques (for example, separation according to length, by use of centrifugation) is only possible within narrow limits. The spectroscopic characteristics of subsequently derivativatized nanotubes will always give the average of a polydisperse mixture. Past a certain length, the electronic properties of nanotubes are independent of their length.[11] Therefore, only diameter, helicity, and defects will be considered in the following section, which contains an analysis of structure–property relationships.

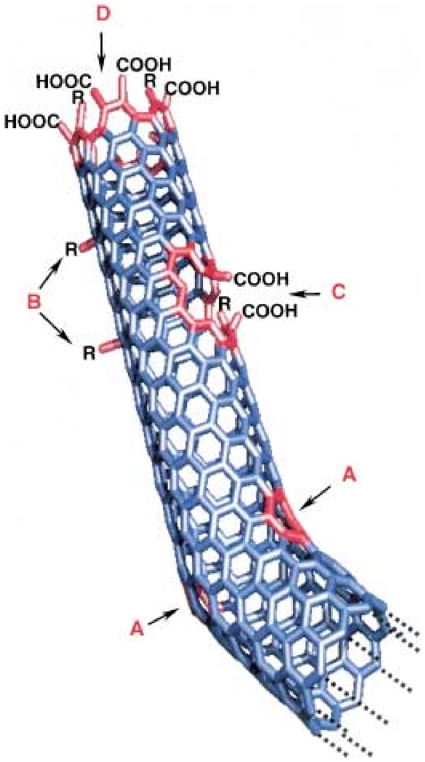


Figure 3. Typical defects in a SWNT: A) five- or seven-membered rings in the C framework, instead of the normal six-membered ring, leads to a bend in the tube, B) sp^3-hybridized defects (R = H and OH), C) C framework damaged by oxidative conditions, which leaves a hole lined with -COOH groups, and D) open end of the SWNT, terminated with -COOH groups. Besides carboxy termini, the existence of which has been unambigously demonstrated, other terminal groups such as $-NO_2$, OH, H, and =O are possible.

3.1. Diameter and Helicity

The electronic properties of carbon nanotubes depend primarily on the roll-up vector $C_h = n a_1 + m a_2$ (Figure 4)[11] and thus on the diameter and helicity. The rolling-up of a 2D graphite sheet to a quasi-1D nanotube causes the formation of so-called van Hove singularities, which are energy levels with a significantly high density of states. Only in some cases, such as (10,10) or (15,0) tubes, does a finite density of states occur at the Fermi level, which results in metallic conductivity. In a typical sample of SWNTs, there is a continuous distribution of tubes with different roll-up vectors.[11] The diameter of the SWNTs lies typically in the range 1–2 nm.[1, 4] In contrast, the diameter of HiPCO tubes is about 0.7 nm.[6]

3.2. Defects

Some defects of the six-membered-ring carbon structure of the nanotubes, such as the inclusion of five- or seven-membered rings in the carbon network, stem from the initial

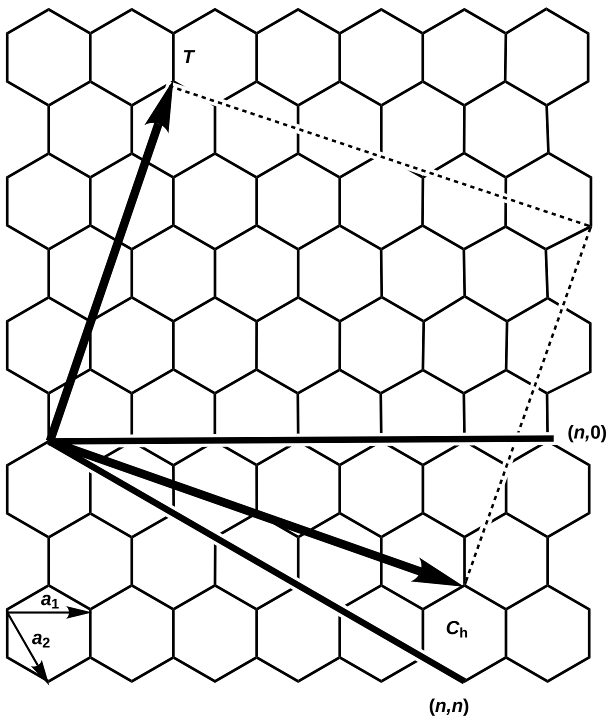


Figure 4. Schematic representation of a 2D graphite layer with the lattice vectors a_1 and a_2 and the roll-up vector $C_h = n a_1 + m a_2$. Achiral tubes exhibit roll-up vectors derived from (n,0) (zigzag) or (n,n) (armchair). The translation vector T is parallel to the tube axis and defines the 1D unit cell. The rectangle represents an unrolled unit cell, defined by T and C_h. In this example, (n,m) = (4,2).[1–4]

formation of the tubes (Figure 3 A). No intact endcaps which, like fullerenes, possess a curvature enforced by the presence of five-membered rings, have been observed. The open ends of the tubes are often closed by particles of catalyst in the crude material. These catalyst particles can be removed by oxidative workup with, for example, HNO_3, which results in ends largely decorated with carboxy groups (Figure 3 B).[7, 12–16] However, defects in the sidewalls can also be introduced under such drastic conditions. The appearance of carboxy groups in these positions[12, 13] can only be explained by the tube structure breaking open. Defects in SWNTs are important in the covalent chemistry of the tubes because they can either serve as anchor groups for further functionalization, or be created by the covalent attachment of further groups. The evidence collected to date indicates that nanotubes can tolerate a limited number of defects before a macroscopic sample loses its special electronic and mechanical properties.[15, 17, 18] Defects are therefore a promising starting point for the development of the covalent chemistry of SWNTs.

In recent years, several approaches to the functionalization of SWNTs have been developed, in both molecular and supramolecular chemistry. These approaches include defect functionalization, covalent functionalization of the sidewalls, noncovalent exohedral functionalization, for example, formation of supramolecular adducts with surfactants or polymers, and endohedral functionalization (Figure 5).

4. Defect-Group Chemistry

As mentioned in Section 2, the purification of SWNTs involves the removal of metal particles or amorphous carbon from the crude material by oxidative methods. Under harsh conditions, the SWNTs themselves are also attacked, which results in the formation of very short tubes (pipes) of lengths 100–300 nm.[7] These small nanotubes, 300 nm long and with a diameter of 1.4 nm, contain around 50000 C atoms in about 25000 benzene rings, which corresponds to a molecular weight of about 600000. These properties are similar to those of high-molecular-weight polymers. It was shown that defects are present in the sidewalls of these pipes, as well as at the open ends.[12, 13, 16]An analysis in which the evolution of CO or CO_2 upon heating the tubes was measured, demonstrated that about 5 % of the C atoms in a pipe are localized at defects.[13] Reactive groups, suitable for further functionalization of the tubes, lie at these defect positions. Thus, long-chain alkylamines were coupled to carboxy groups activated with $SOCl_2$ (Scheme 1).[14, 15]

The functionalized tubes are more soluble in organic solvents than the starting material, so their spectroscopic characterization in the liquid phase is possible. The bundles of pipes are broken up into smaller bundles or individual tubes during the functionalization. The space available within most of the tubes is sufficient to allow the uptake of solvent molecules.[15] An IR spectroscopic estimate of the degree of

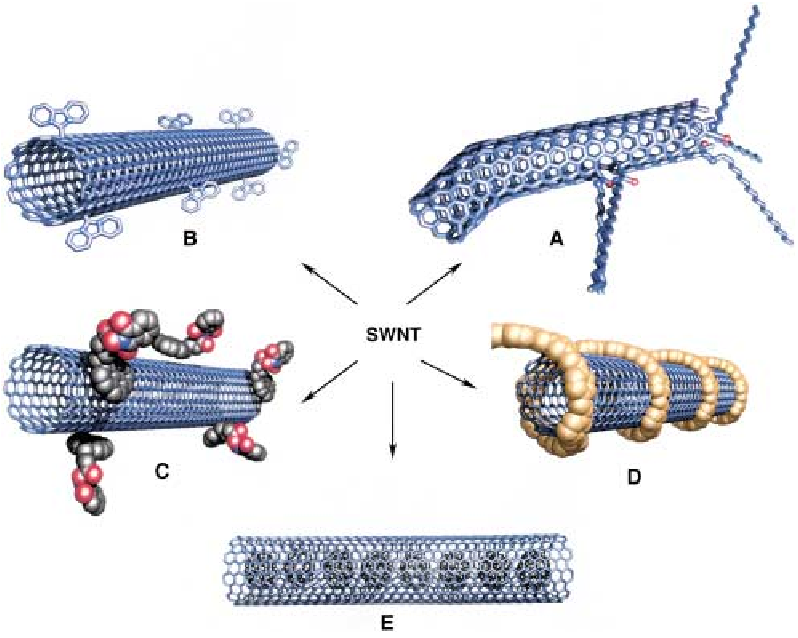
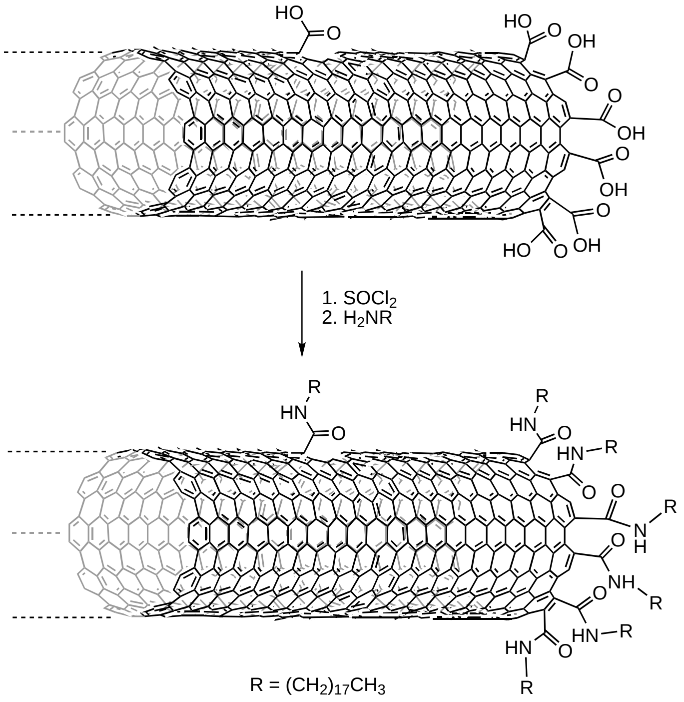


Figure 5. Functionalization possibilities for SWNTs: A) defect-group functionalization, B) covalent sidewall functionalization, C) noncovalent exohedral functionalization with surfactants, D) noncovalent exohedral functionalization with polymers, and E) endohedral functionalization with, for example, C_{60}. For methods B–E, the tubes are drawn in idealized fashion, but defects are found in real situations.



Scheme 1. Defect-group functionalization of SWNTs with octadecylamine.[14]

functionalization of pipes that had been amidated with octadecylamine gave an mass percentage of 55 ± 10% for the added groups; this is a mole fraction of 6%.[12] This high degree of functionalization suggests that a large proportion of the defect sites are located on the sidewalls. Polymers and dendrimers with terminal amino or hydroxy groups were coupled to activated tubes to give amides or esters.[19–23] Monolayers of SWNTs were deposited on surface-modified silicon wafers.[24] Moreover, functionalized SWNTs have been employed as tips for atomic-force microscopy by use of this technique.[25] When the unactivated carboxy groups of the tubes are treated with amines, ammonium salts result, which are also quite soluble in organic solvents.[15, 18] This reaction was also successful with uncut nanotubes, of lengths of over 1 μm.[18] In this case, the tubes were heated in molten long-chain amines. The electronic properties of the tubes remain essentially unaltered after functionalization. The yields of such ionic derivatives are around 30%, which are considerably higher than those of the covalently functionalized amide systems (approximately 5%).

5. Covalent Sidewall Functionalization

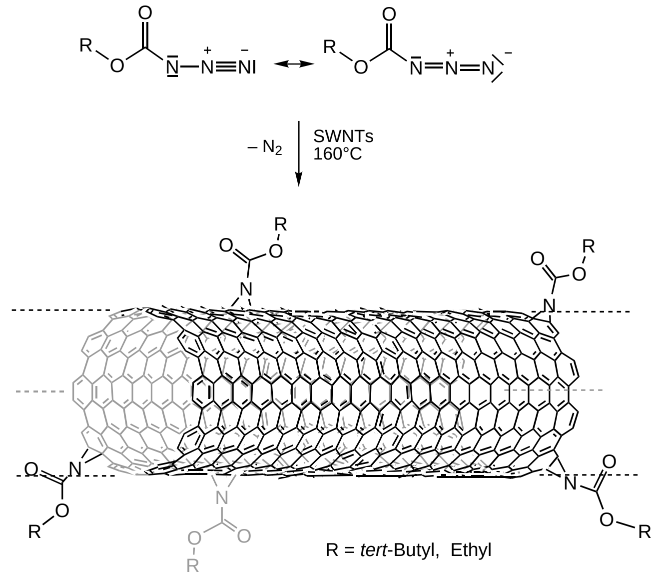
The systematic development of fullerene chemistry has shown that their reactivity in addition reactions depends very strongly on the curvature of the fullerene.[26] An increase of the curvature of the carbon framework leads to a more pronounced pyramidalization of the sp^2-hybridized C atoms and therefore an increased tendency to undergo addition reactions. This effect is clear in the case of C_{70}, in which the [6,6] bonds at the poles are much more reactive than those around the flatter equatorial region. Efficient addition at the equator takes place only with very reactive species, such as arynes, carbenes, or halogens. Normally, SWNTs bear no caps at their poles, and consist instead of graphitic sidewalls, usually with defects. Thus, there are no strongly curved regions that could serve as reactive targets for direct additions. As the typical diameter of a SWNT (1–2 nm) is larger than that of a fullerene, its relative reactivity is even less than that of the flat regions in fullerenes. Further problems in reactions with SWNTs are their low solubility or dispersability, and their occurrence in bundles. Therefore, functionalization of the sidewalls by covalent-bond formation will only be successful if a highly reactive reagent is used. It has not been possible to make quantitative assessments of whether such additions take place preferentially on intact regions of the sidewalls or at pre-existing defect sites.

As discussed in Section 3, the sidewalls of freshly prepared SWNTs are partially attacked under oxidative workup.[12, 13, 16] This attack generates defect sites saturated, for example, with COOH groups. Because SWNT sidewalls are expected to be inert, fluorination was chosen for initial studies as it was described in the chemical transformation of graphite.[27] Highly pure SWNTs[28] were treated with elemental fluorine between 150°C–600°C. For products synthesized at 600°C, the degree of fluorination was 0.1–1. The covalent bond with fluorine was confirmed by IR spectroscopy, through the C–F valence vibration at 1220–1250 cm^{-1}. The fluorination of SWNTs has the consequence that their electronic properties change drastically. Whilst untreated samples of SWNTs exhibit high electrical conductivity, tubes fluorinated above 250°C are insulators. Treatment of these tubes with hydrazine at room temperature causes defluorination. Raman spectroscopy of the defluorinated tubes showed that fluorination at higher temperatures is accompanied by partial fluorolysis of the carbon framework. Molecular modeling results from (10,0) tubes[29] suggested that the formation of a C–F bond is exothermic. The energy of a second C–F bond is highest when the bond forms adjacent to the first. The bond energy of a C–F bond on a tube is, however, lower than that of a C–F bond on an sp^3-hybridized C atom in an unstrained molecule. STM investigations of SWNTs with a fluorination degree of around 0.5 show that the fluorine atoms are grouped into very regular bandlike arrays.

The fluorinated SWNTs can be dissolved in alcohols by ultrasonication[30, 31] and hence become available for transformations using wet chemistry. In this way, the fluorine atoms in fluorinated SWNTs can be substituted for alkyl groups by treatment with alkyl lithium or Grignard compounds.[32] The resulting derivatized nanotubes are soluble, for example, in chloroform (0.6 $mg\,mL^{-1}$) and exhibit a degree of alkylation of about 0.1.

The direct sidewall functionalization of SWNTs with organic groups is possible by reactive species such as nitrenes, carbenes, and radicals.[14, 33] For example, the thermal reaction of azidoformiates leads to N_2 extrusion and to aziridino-SWNTs (Scheme 2), which dissolve in organic solvents such as DMSO to give black solutions.[33]

Especially stable solutions of functionalized SWNTs are formed from the addition of nucleophilic carbenes.[33] In this case, no cyclopropanation occurs, rather, each added group is



Scheme 2. Sidewall functionalization of SWNTs with alkyl azidoformiates.[33]

bound through just one covalent bond to the tube and is positively charged. One negative charge per added group is transferred to the nanotube framework, as in the analogous reactions with C_{60}. The high solubility of the carbene adducts can be explained through mutual, electrostatic repulsion of the tubes.

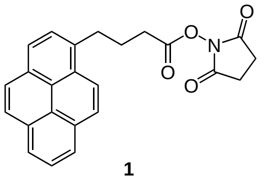
The reaction products of direct sidewall functionalizations can be characterized in solution, for example, by NMR and absorption spectroscopy. Atomic-force micropscopy shows that the original bundles of SWNTs are broken up in the course of adduct formation.[33]

In a similar fashion, SWNTs were functionalized by reaction with azomethinylides.[34] The degree of functionalization of the resulting pyrrolidines is very high, which causes a high solubility in organic solvents.

In one other example of sidewall functionalization, the electrical conductivity of SWNTs was exploited.[35] A solid film of SWNTs (bucky paper) served as the electrode for the electrochemical reduction of aryl diazonium salts. Here, aryl radicals were formed by the extrusion of N_2; these radicals then reacted with the tube walls. Addition degrees of up to 0.05 were recorded, that is, one in 20 C atoms in each nanotube bore an aryl substituent. As with other organonanotubes,[32] the added species could be removed by thermal treatment and the starting materials recovered.

6. Noncovalent Exohedral Functionalization

The formation of noncovalent aggregates with surfactants or wrapping with polymers have shown themselves to be suitable methods for the synthesis of functional SWNTs (Figure 5C, D). In the search for nondestructive purification methods, it has been shown that nanotubes can be transferred to the aqueous phase in the presence of surface-active molecules such as sodium dodecylsulfate (SDS) or benzylalkonium chloride.[8, 9, 36] It is believed that the nanotubes are in the hydrophobic interiors of the corresponding micelles, which results in stable dispersions. When the hydrophobic part of the amphiphile contains an aromatic group, an especially strong interaction results, because effective π–π-stacking interactions can then form with the graphitic sidewalls of the SWNTs. This effect was demonstrated in the aggregation with *N*-succinimidyl-1-pyrenebutanoate (**1**).[37] In these aggregates, the succinimidyl group could be substituted with amino groups from proteins such as ferritin or streptavidin, which caused immobilization of the biopolymers on the tubes. This effect could be interesting for the development of biosensors, because the electronic properties of the tubes can be combined with the recognition properties of the immobilized biosystems.



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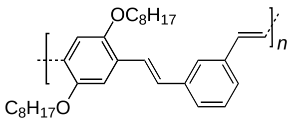

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Direct, nonsurfactant-mediated immobilization of metallothionein proteins[38–40] and streptavidin[41] has also been carried out on MWNTs. The hydrophobic regions of the proteins are probably important for adsorption. A monoclonal antibody, specific for C_{60} fullerenes, could also be bound directly to SWNTs.[42] It was thus shown that the binding site of this IgG antibody is a domain of hydrophobic amino acids. Pronounced noncovalent interactions were also found between SWNTs and anilines[43] or amines.[44] This interaction was detected, for example, by the alteration of the electrical conductivity of SWNTs upon adsorption of primary amines, and through their very high solubility (up to $8\,\mathrm{mg\,mL^{-1}}$) in anilines. Presumably, as in the case of C_{60} fullerenes,[45] donor–acceptor complexes are formed, as the curvature present in both classes of materials lends acceptor character to the corresponding molecular or macromolecular carbon networks.[46] The stable aniline solutions of SWNTs can be diluted with other organic solvents such as acetone, DMF, or THF, without causing precipitation of the tubes.

Polymers have also been used in the formation of supramolecular complexes of SWNTs. Thus, the suspension of purified tubes in the presence of polymers such as poly(*m*-phenylene-*co*-2,5-dioctoxy-*p*-phenylenevinylene) (PmPV, **2**), in organic solvents such as $CHCl_3$, leads to the polymer wrapping around the tubes (Figure 5D).[47–49] The properties of these supramolecular compounds are markedly different from those of the individual components. For example, the SWNT/PmPV complex exhibits a conductivity eight-times higher than that of the pure polymer, without any restriction of its luminescence properties. The stable solutions of the SWNT/PmPV complex can be characterized by UV/Vis and NMR spectroscopy. Atomic-force microscopy shows that the polymer coats the tubes uniformly. The small average diameter of the complexes (of around 7.1 nm) suggests that the bundles are mostly broken up on complex formation. The promising optoelectronic properties of the SWNT/PmPV complexes have been used in the manufacture of photovoltaic devices.[48]

The wrapping of SWNTs with polymers that bear polar side-chains, such as polyvinylpyrrolidone (PVP) or polystyrenesulfonate (PSS), leads to stable solutions of the corresponding SWNT/polymer complexes in water.[50] The bundles are again broken up by complex formation in this case. The thermodynamic driving force for complex formation is the need to avoid unfavorable interactions between the apolar tube walls and the solvent water. A range of other, mostly ionic polymers, such as bovine serum albumin, are capable of coating SWNTs. Polymers such as poly(ethylene glycol) and poly(vinyl alcohol) are ineffective in this respect. It is thought that multi-helical wrapping of the tubes with the polymers is most favorable for reasons of strain. Changing to a less polar solvent such as THF causes the polymer complexes to dissociate once more. The SWNT/PVP complexes exhibit liquid-crystalline properties.

7. Endohedral Functionalization

The inner cavity of SWNTs offers space for the storage of guest molecules (Figure 5E). To date, the uptake and the endohedral chemistry of metals and metal salts have been intensively investigated.[51–56] For example, gold and platinum nanothreads have been created in the capillaries of the tubes, by treating the SWNTs with the corresponding perchlorometallic acids at high temperatures. In some cases, the resulting nanothreads are single crystals. The incorporation of fullerenes such as C_{60}[57, 58] (Figure 5) or metallofullerenes such as $Sm@C_{82}$[59] are especially impressive examples of the endohedral chemistry of SWNTs. This incorporation is executed at defect sites localized at the ends or in the sidewalls. The encapsulated fullerenes tend to form chains that are coupled by van der Waals forces. Such arrays are sometimes called "bucky peapods". Upon annealing, the encapsulated fullerenes coalesce in the interior of the SWNTs, which results in new, concentric, endohedral tubes, with a diameter of 0.7 nm. The progress of such reactions inside the tubes could be monitored in real time by use of high-resolution electron microscopy.[59]

8. Concluding remarks

The examples described of the functionalization of single-walled carbon nanotubes demonstrate that the chemistry of this new class of molecules is just beginning. The basis for the exploitation of macroscopic quantities of this carbon allotrope has been laid. The unique properties of SWNTs can now be coupled with those of other classes of material. For the successful future development of this research area, however, it is important to improve the quality of the nanotube raw material, with particular emphasis on the uniformity of the samples. Furthermore, comparative studies on individual nanotubes before and after functionalization are necessary, so that both the dependence of reactivity on electronic structure and the effect of chemical modification on the electrical and mechanical properties can be determined.

This work was supported by the European Union under the 5th Framework Programme 1999, HPRNT 1999-00011 FUNCARS.

Received: December 5, 2001 [M1535]

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