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Review

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Boris I. Kharisov, Oxana V. Kharissova, Hector Leija Gutierrez, and Ubaldo Ortiz Me#ndez

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Recent Advances on the Soluble Carbon Nanotubes

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Recent literature (2000−2008) on the functionalization methods leading to soluble carbon nanotubes is reviewed. Carbon nanotubes (CNTs) can be solubilized by a series of methods, including their functionalization by the aryl diazonium process, use of elemental metals, simple inorganics, acids, esters, aldehydes, amines, aromatics, macrocycles, thiols, biomolecules, polymers, and using such techniques as pulsed streamer discharge, microwave treatment, cryogenic crushing, or γ-irradiation. In a difference with the functionalization methods applied in the past decade of the 20th century (frequent use of strong acidic media as a first step and further attachment of various organic moieties), current techniques involve a much wider number of functionalizing agents paying main attention to macrocycles, biomolecules, and polymers, as well as using such special techniques as use of radionuclides, irradiation, microwave treatment, or pulsed streamer discharge. Reactivity, physicochemical properties, and main applications of soluble CNTs are analyzed.

Introduction

The functionalization of carbon nanotubes (CNTs) is a very actively discussed topic in contemporary nanotube literature because the planned modification of CNTs properties is believed to open the road toward real nanotechnology applications.[1] Because of their exceptional combination of mechanical, thermal, chemical, and electronic properties, single-walled (SWNTs or SWCNTs) and multiwalled carbon nanotubes (MWNTs or MWCNTs) are considered as unique materials, with very promising future applications, especially in the field of nanotechnology, nanoelectronics, and composite materials. Additionally, CNTs are becoming highly attractive molecules for applications in medicinal chemistry. At present, potential biological applications of CNTs have been little explored. The main difficulty to integrate such materials into biological systems derives from their lack of solubility in physiological solutions. Functionalization of CNTs with the assistance of biological molecules remarkably improves the solubility of nanotubes in aqueous or organic environment and, thus, facilitates the development of novel biotechnology, biomedicine, and bioengineering.

Nonfunctionalized CNTs are difficult to dissolve or disperse in most organic or inorganic solvents because of their long structured features, large molecular size, or severe aggregation. The common agents used to help disperse carbon nanotubes are surfactants, which, however, can only increase the dispersibility to a limited extent, and surfactants do not affect the solubility of carbon nanotubes. Current chemical methods for water-suspended SWNTs require harsh sonochemical treatments in order to effectively disperse nanotubes. However, these methods are currently incapable of conferring thermodynamically stable water-based dissolutions of carbon structures since surfacted SWNTs solutions are simply metastable colloidal suspensions, where they transiently individualize but always reaggregate over time since this is their thermodynamically favorable state. Therefore, true water-soluble nanotube solutions are those solutions that entropically favor individualized nanotubes,[2] where the reaggregation of CNTs in a solvent is less favored, on a thermodynamic basis, than their continued solvated state.[3] In some embodiments, the extent of functionalization is dependent upon a number of factors, e.g., the reactivity of the CNTs, the reactivity of the functionalizing agent, steric factors, etc. In some such embodiments, as a result of such dependencies, the extent of functionalization can be in the range of from at least about one functional group per every 1000 CNT carbons to at most about one functional group per every two CNT carbons.

In the last years, the carbon nanotubes, soluble in water or organic solvents, have been mentioned in a series of monographs, including book chapters on the CNTs.[4−8] Some recent reviews were dedicated to the strategic approaches toward the solubilization of CNTs using chemical and physical modifications,[9−11] environmental, toxicological, and pharmacological studies related with use of CNTs,[12,13] the main methods for the modification of CNTs with polymers,[14] applications of functionalized CNTs,[15,16] in particular, as biosensors,[17] and discussions on the possibility of the existence of SWNTs in organic solvents in the form of clusters.[18] A fundamental review[19] was devoted to electronic and vibrational properties of the SWCNTs.

Among many others, currently used functionalization agents include aryl diazonium moieties, halogen, oxy, carbon [alkyl, alkenyl, alkynyl, aryl, and acyl (RCO′)], and metal-based radicals. CNTs can be functionalized by oxidation (peroxyacids, metal oxidants, such as osmium tetraoxide, potassium permanganate, chromates; ozone, oxygen, superoxides) or reduction reactions, interactions with thiols, carbenes, dienes, etc. In the present review, we generalized the most recent advances in this area, leading to CNTs soluble in water or/and common organic solvents.

Functionalization Leading to Soluble CNTs

Functionalization by Use of Elemental Metals, Inorganics, and Grignard Reagents. Generally, elemental metals have been used in the form of nanoparticles (Au, Fe, Co) or solutions in liquid ammonia (alkali metals) through with organic linkers. Thus, water-soluble hybrids of MWNTs and *gold* nanoparticles (Au@MWNTs) were fabricated via the in situ solution method using an optoelectronic-active compound of *N*,*N*′-bi(2-mercaptoethyl)-perylene-3,4,9,10-tetracarboxylic diimide as interlinker and stabilizer.[20] It was found that the formed hybrid exhibited strong visible luminescence under UV lamp irradiation, which might extend its potential applications to biological labeling.

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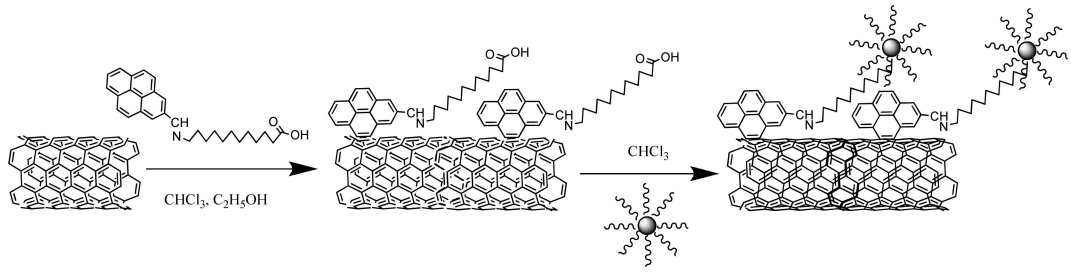


Figure 1. Modification of CNTs by capped magnetic nanoparticles.

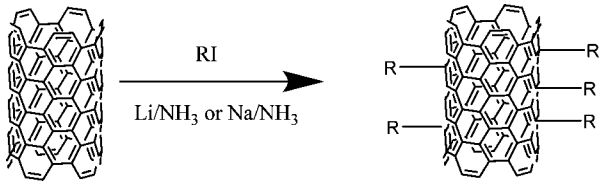


Figure 2. Functionalization of MWCNTs by the Billups reaction.

In another report, dedicated to gold−CNTs hybrids, the efficient aqueous dispersion of pristine HiPco SWNTs with ionic liquid surfactants 1-dodecyl-3-methylimidazolium bromide (D) and 1-(12-mercaptododecyl)-3-methylimidazolium bromide (M), the thiolation of nanotube sidewalls, and the controlled self-assembly of positively charged SWNT−D,M composites on gold were studied.[21] *Iron*-filled Fe@MWCNTs were surface-modified with various functionalities via a rapid, single-step process involving ultrasonication-assisted and microwave-induced radical polymerization reactions.[22] The offered process is universal for both hydrophobic (e.g., polystyrenes and poly(methyl methacrylate)) and hydrophilic (e.g., polyacrylamide, poly(acrylic acids), and poly(allyl alcohols)) polymer chains (see also the polymer section below), which can be chemically grafted onto the surface of MWCNTs in the same conditions within ∼10 min. The solubilities of the formed functionalized MWCNTs are in the range of 1200−2800 mg/L in solutions. An intriguing method for CNTs derivatization with magnetic nanoparticles is described in ref 23. Capped iron oxide or *cobalt and cobalt/platinum* magnetic nanoparticles were attached to carbon nanotubes by means of an interlinker molecule, a carboxylic derivative of pyrene (Figure 1) (see also the section below on the functionalization with aromatic molecules). The available carboxylic groups of pyrene derivative can be further linked to metal or metal oxide nanoparticles. The formed composites were highly soluble in organic solvents, such as chloroform, toluene, and hexane.

Sidewall-functionalized nanotubes, soluble in organic solvents, were prepared by alkylation of nanotube salts obtained using either *lithium, sodium, or potassium* in liquid ammonia (*Billups* reaction).[24] Such reactions can produce different types of derivatized CNTs. It was shown that the alkali metal intercalates into the SWNT ropes (in case of further reaction of nanotube salts Na−CNTs with PhI, the arylated CNTs can be produced); alkali metals used behave differently requiring distinct temperature ranges (the least range corresponds to Li). The Billups reaction protocol involving dissolving metal reduction of MWNTs and their subsequent alkylation or arylation was shown to produce functionalized MWNTs that were soluble in either organic or aqueous solvents. This method allows for the attachment of alkyl or aryl pendent groups, using either lithium or sodium, and has been used to produce gram quantities of alkylated MWNTs[25] (Figure 2).

Use of Li as the mostly used alkali metal in these processes was in situ Raman-studied in detail.[26] It was shown that addition of 1-iodododecane to the lithiated SWNTs resulted in the covalent attachment of dodecyl groups. The intercalation of lithium throughout the SWNT ropes led to complete dodecylation of all individual SWNTs. Lithuim was also applied to yield a water-soluble poly(ethylene glycol) PEG−CNT conjugate in a two-step process, including the reaction of lithium, SWCNTs, and 11-bromoundecanoic acid in liquid ammonia forming carboxylic acid derivatized SWCNTs (Figure 3) and further interaction of the obtained product with H_2N−PEG−OMe in mixture of solvents.[27,28]

Simple inorganic compounds are capable to solubilize CNTs even without formation of direct chemical bonds "CNTs−substrate". Thus, MWCNTs were dispersed in aqueous solutions through *alumina-coated silica* (ACS) nanoparticle halos.[29] MWCNTs were directly dispersed into a highly charged ACS nanoparticle aqueous solution, which was stable for weeks after ultrasonication, without functionalization of their surfaces. A stable, water-soluble suspension of CdS/aligned-MWCNT heterostructures with electron transfer from CdS nanoparticles to aligned MWCNTs, implying potential applications in photovoltaic cells, photocatalysis, and solar energy conversion, was reported.[30] CdSe quantum dots were noncovalently attached to SWNTs through an intermediary 1-pyrenebutyric acid *N*-hydroxy-succinimide ester molecule.[31] Use of *Grignard reagents* RC(═S)SMX (wherein R is alkyl, alkenyl, or aryl, wherein any alkyl, alkenyl, or aryl may be optionally substituted; M is Be, Mg, Ca, Sr, or Ba, and X is Cl, Br, or I) in functionalization of CNTs is also known.[32]

Functionalization of CNTs in Strong Acidic Media and with Oxygen-Containing Moieties. Generally, suitable acid media include any acidic medium capable of dispersing CNTs in a substantially individualized state. By first dispersing CNTs in an acidic medium, bundled CNTs can be separated as individual CNTs, affording exposure of the CNT sidewalls, and thereby facilitating the functionalization of such CNTs, wherein functional groups are attached to the subsequently exposed sidewalls of these individualized CNTs. Strong acids, oxidizing CNTs surface, lead to formation of COOH groups, so use of sulfuric or/and nitric acid can be a first step of CNTs functionalization, followed by further reaction of COOH groups with, for example, $SOCl_2$ or other substances which are present in solution.

A few recent patents and articles are dedicated to use oleum in order to functionalize CNTs. Thus, the functionalization of SWNTs in oleum via *diazonium species* generated in situ (Figure 4) was reported in refs 33 and 34. In a typical example, purified SWCNTs were dispersed in oleum (20% free SO_3) at 80 °C; then sulfanilic acid was added to the dispersion followed by sodium nitrite and 2,2′-azo-bis(isobutyrylnitrile) (AIBN), and the mixture was stirred for 1 h being further filtered and washed. In other reports,[35,36] the phenylated SWNTs, obtained from SWNT and distinct quantities of benzoyl peroxide to reach the most-, medium-, or least-functionalized level, were further

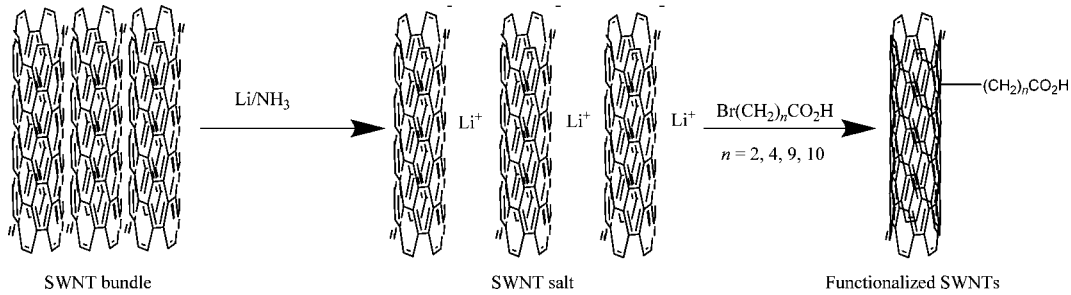


Figure 3. General procedure for the synthesis of carboxylic acid derivatized SWNTs.

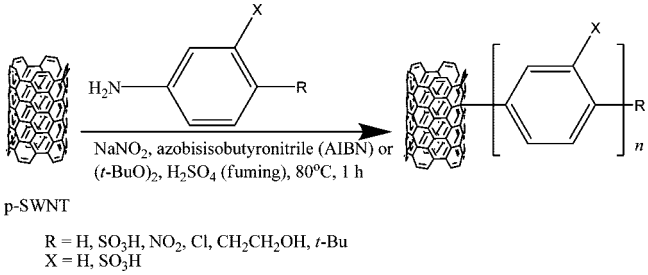


Figure 4. Functionalization of SWNTs in oleum via diazonium species generated in situ.

sulfonated by reaction of phenylated SWNTs with sulfuric acid (simply dispersing the phenylated SWNTs in oleum), wherein $-SO_3H$ substitutes for $-H$ on the phenyl groups at a position para to their attachment to the SWNT (Figure 5). Phenyl-sulfonated SWNTs are found to be true water-soluble carbon nanotubes and can serve as a platform technology for the development of SWNTs for several industries including pharmaceutical, energy, and electronics. Degree of functionalization was determined both qualitatively using Raman spectroscopy and quantitatively using thermogravimetric analysis and X-ray photoelectron spectroscopy. Similar derivatization of SWCNTs using the diazonium-species technique was reported in refs 37 and 38.

Aqueous solutions of SWNTs (0.03−0.15 mg/mL), stable for more than 1 month, were obtained by functionalization with carboxylate groups, formed as a result of acid/oxidant treatment (mixture of 9:1 concentrated H_2SO_4/30% H_2O_2).[39] It is noted that the optical absorption of the first interband transition of as-treated water-soluble semiconducting SWNTs reversibly responds to the pH change in aqueous solutions. In another report,[40] soluble (2 wt %), ultrashort (length <60 nm), carboxylated SWCNTs were prepared in the process, predicated on oleum's ability to intercalate between individual SWNTs inside SWNT ropes; this is a procedure that simultaneously cuts and functionalizes SWNTs using a mixture of sulfuric and nitric acids. Long-time-stable solutions of carbon nanotubes, functionalized with carboxylic acids, among other species (nitrates, hydroxyls, sulfur-containing groups, carboxylic acid salts, and phosphates), were also described in the patent.[41] It was noted that most preferred pH ranges from 3 to 6, the most preferred level of functionalized carbons on the SWCNT is 0.5−20 atom %, and the functionalized carbons may exist anywhere on the nanotubes (open or closed ends, external and internal sidewalls). Additionally, behavior of CNTs, treated with acids, was studied in solvents of different polarity and in water of different pH as a function of acid treatment conditions. In a difference of untreated CNTs, soluble or dispersible in non- or low-polar solvents (acetone, alcohols), the treated CNTs were found to be soluble or dispersed in the deionized water, but not in acetone or alcohols, increasing solubility with pH from 4 up to 10.[42]

Among O-containing organic groups, CNTs were solubilized by functionalization with *ester* moieties, for instance, esters with *n*-pentyl,[43] other alkyl chains (*n*-butyl, *n*-hexyl, *n*-octyl, *n*-dodecyl, and *n*-hexadecyl),[44] or dendron-type moieties with long alkyl chains[45] (Figure 6), *crown ether* (4′-aminobenzo-15-crown-5-ether),[46] or *aldehydes* (anisaldehyde together with 3-methyl-hippuric acid).[47]

Functionalization with Compounds Containing Alkyl and Aromatic Moieties. High-speed vibration mill (HSVM) mechanochemical technique was applied to prepare SWCNTs, functionalized with some alkyl and aryl groups (Figure 7). As a result, SWNTs with long alkyl chains can be dissolved in many common organic solvents.[48] In another report, highly soluble pyridyl-functionalized SWCNTs were obtained by a 1,3-dipolar cycloaddition of a nitrile oxide on the SWNT walls (Figure 8), similar to 1,3-dipolar cycloadditions that are common for fullerene functionalization (Figure 9), and characterized by NMR, FT-Raman, and electron microscopy.[49] The CNTs here were *doubly functionalized*: at the tips with pentyl esters (to provide sufficient solubility in organic solvents) and on the walls by pyridyl isoxazoline groups (they are capable to coordinate the metalloporphyrin to the pyridyl group). This composite was further used as a precursor in the synthesis of CNTs−Zn−porphyrin analogue of fullerene-C_{60}−Zn−porphyrin. The occurrence of this complex is clearly revealed by optical spectroscopy and by the shifts in cyclic voltammetry (CV) potentials of Zn−porphyrin in the presence of Py−SWNT, similar but larger than for the corresponding fullerene analogues.

Functionalization of SWCNTs with *phenol* groups by 1,3-dipolar cycloaddition reaction and further derivatization of the products with 2-bromoisobutyryl bromide resulted in the attachment of atom transfer radical polymerization initiators (active in the polymerization of *t*-butyl acrylate from the surface of the nanotubes) to the sidewalls of the nanotubes (Figure 10).[50,51] The obtained SWCNTs, functionalized with poly(*t*-butyl acrylate), were soluble in a variety of organic solvents (see the section on polymers below).

Polynuclear aromatics—ionic *pyrene* and *naphthalene* derivatives (Figure 11)—were used for obtaining water-soluble SWNT polyelectrolytes (SWNT-PEs), which are analogous to polyanions and polycations.[52] The nanotube−adsorbate interactions consist of $\pi-\pi$-stacking interactions between the aromatic core of the adsorbate and the nanotube surface and charge transfer between them. Pyrene-containing moieties in construction of soluble CNTs were also reported in refs 53 and 54.

The SWNTs, functionalized by *ferrocene*-grafted poly(*p*-phenylene ethynylene), were found to gelate common organic solvents such as chloroform forming a freestanding CNTs organogel that cannot be redispersed in any organic solvents and can be applied for obtaining an insoluble, homogeneous, electroactive SWNT film.[55] Ferrocene units can be covalently

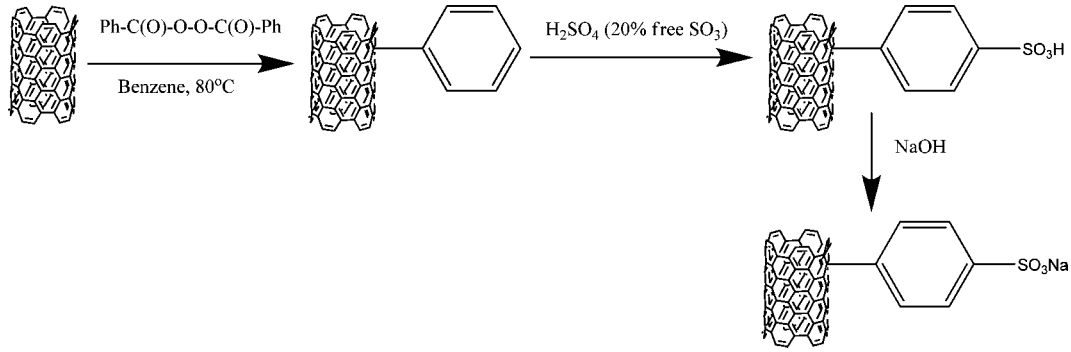


Figure 5. Synthesis of sulfonated SWNTs.

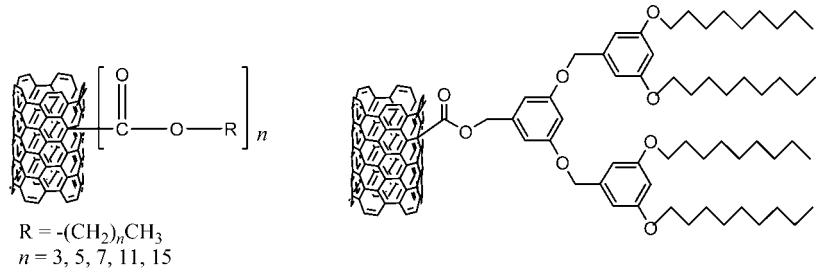


Figure 6. Ester-functionalized CNTs.

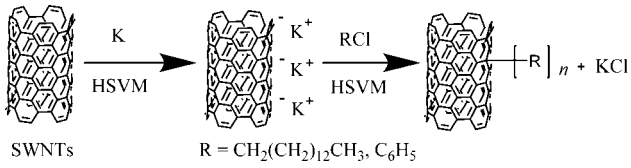


Figure 7. SWCNTs functionalized with alkyl and aryl groups.

introduced onto SWNTs also by 1,3-dipolar cycloaddition of azomethine ylides, thus solubilizing them.[56]

Functionalization with Aliphatic and Aromatic Amine-(amido)-Containing Moieties. Generally, the amino functionalization of MWNTs can improve their dispersion in H_2O; however, other reactions may also have occurred, which influenced their dispersity in organic solvents.[57] Among other reports on the use of these moieties,[58,59] a series of amines [octadecylamine (ODA), 2-aminoanthracene, 1-H,1-H-pentadecafluorooctylamine, 4-perfluorooctylaniline, and 2,4-bis(perfluorooctyl)aniline] was reported to interact with SWCNTs, previously thermally treated in air and optionally purified with nitric acid. The formed products exhibit different solubility in dependence of amines and solvents used.[60] For one of the most frequently applied amines, ODA,[61] it was revealed that the ODA chains grafted on MWNT are partially crystallized.[62] Similar functionalization of SWCNTs with octadecylamido moieties allowed creating soluble nanotubes (s-SWNT−CONH-$(CH_2)_{17}CH_3$), where the mentioned groups are attached in the end groups and at defect sites; the weight percentage of the octadecylamido functionality in the s-SWNTs is about 50%.[63] A representative reaction between ODA and SWCNTs is shown in Figure 12.[64] Additionally, a total aromatic polyimide was found[65] to have a high potential to solubilize SWNTs individually in organic solutions. When SWNTs concentrations increase, the solutions became viscous and then changed to gels.

A series of *aniline derivatives* (4-pentylaniline, 4-dodecylaniline, 4-tetradocylaniline, 4-pentacosylaniline, 4-tetracontylaniline, 4-pentacontylaniline) as well as amines (octadecylamine, nonylamine, dodecylamine, pentacosylamine, tetracontylamine, pentacontylamine), etc. and mixtures thereof were used for functionalization of CNTs.[66,67] The formed composites are soluble in carbon disulfide and common organic solvents as chlorobenzene, dichlorobenzene, trichlorobenzene, tetrahydrofuran (THF), chloroform, methylene chloride, diethylene glycol dimethyl ether, benzene, toluene, tetrachlorocarbon, pyridine, dichloroethane, diethyl ether, xylene, naphthalene, nitrobenzene, ether, and mixtures thereof. The solubilities of the carbon nanotubes in these solvents range from about 0.01−5.0 mg/mL. For a completely soluble optically active polyaniline−MWCNT composite, it was found[68] that the polymer's optical activity was retained in the presence of carbon nanotubes. Solutions were found to be easily processable into thin films, which exhibited dendritic structures only in the presence of nanotubes. Aniline was also used as a solvent for MWCNTs, grafted by the carboxylic acid group.[69] These nanotubes were rapidly (30 min) dissolved in aniline under microwave treatment. The solubility of SWNT in aniline is up to 8 mg/mL.[70]

Functionalization with Sulfur-Containing Moieties. Among *sulfur-containing* surfactants or functionalizing agents, we note the surfactants sodium dodecyl sulfate $C_{12}H_{25}OSO_3Na$ (and sometimes sodium dodecyl benzenesulfonate), whose presence together with hydroxypropyl methyl cellulose[71] or HNO_3/H_2SO_4 mixture[72] helps to assist the dispersion of CNTs. Dodecanethiol as the reaction agent was used to obtain a stable suspension of thiolated SWCNTs in toluene; the thiolation process is also observed on the exposure of the nanotubes to toluene solutions of dodecanethiol-stabilized Au nanoparticles, using them for labeling or manipulating the location of the chemical reaction sites on the tube wall.[73] Similarly, cyclic disulfides were also used for introduction of sulfur-containing functional groups onto SWNTs and further treatment with gold nanoparticles.[74]

Functionalization with Macrocycles. Classic macrocycles *porphyrins* and *phthalocyanines* have been successfully applied as precursors for solubilization of CNTs. Thus, the authors of ref 75 established that porphyrin molecules can dissolve SWNTs in organic solutions and the SWNTs−porphyrin hybrid nanomaterials can be separated from the solutions; moreover, both individually dissolved nanotubes and bundled nanotubes coex-

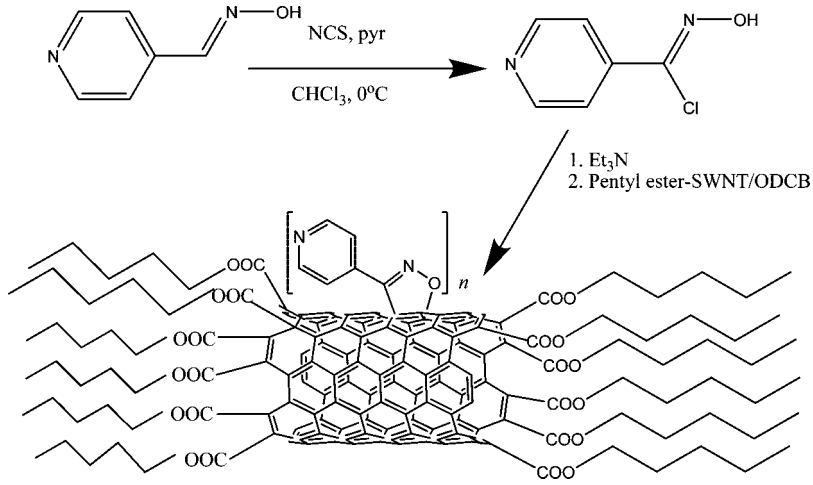


Figure 8. Synthesis of pyridyl-functionalized SWCNTs.

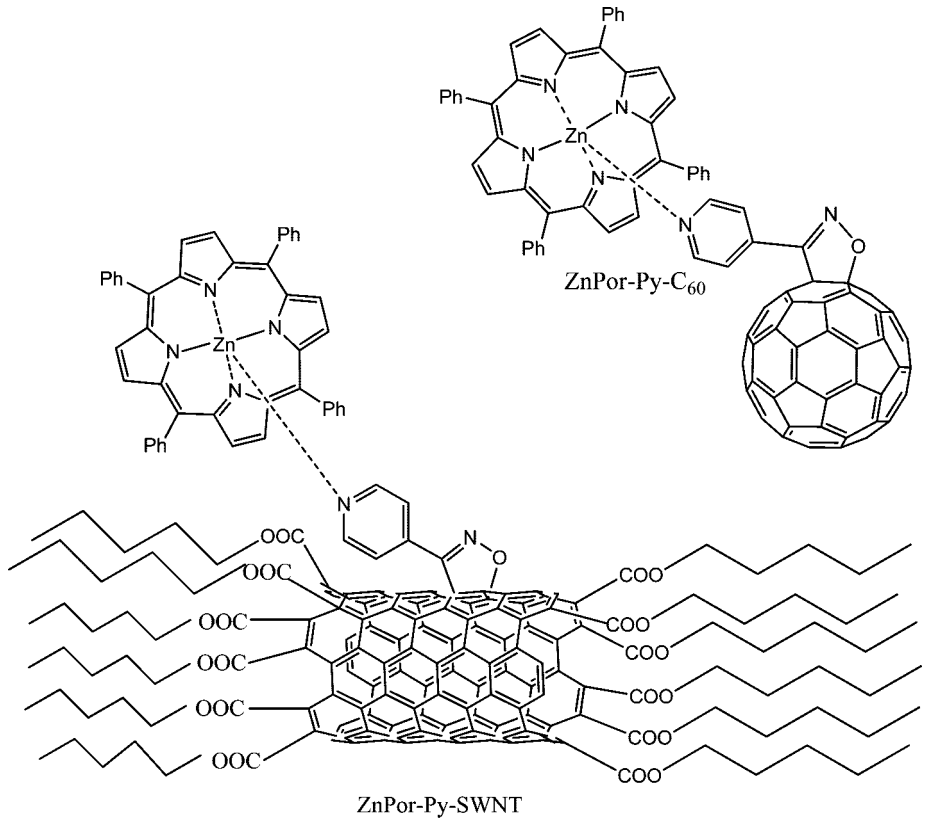


Figure 9. Comparison of Zn−porphyrin complex of pyridyl-functionalized SWCNTs and its fullerene analogue.

isted in the solution. The solid purified SWNTs (p-SWNTs)−porphyrin nanomaterials were readily separated from the p-SWNTs−porphyrin solution, and this nanomaterial was redissolvable in dimethylformamide. The formed porphyrin−CNTs solutions can be stable for long time; thus, water-soluble porphyrin molecules [*meso*-(tetrakis-4-sulfonatophenyl) porphine dihydrochloride] (Figure 13) were used to solubilize SWNTs, resulting in aqueous solutions stable for several weeks.[76] A suspension, stable more than 1 week, was prepared with use of an anionic tetra(*p*-carboxyphenyl) porphyrin (TCPP) and MCNTs, and as an application, a spectrofluorometric method of DNA hybridization was proposed.[77] Spectroscopic changes of tetraphenylporphyrin CNTs composites in a variety of chlorinated solvents such as chloroform, dichloroethane, and dichlorobenzene as a result of sonication were studied.[78] It was established that protonation of the porphyrin core nitrogen atoms occurs as a result of sonodegradation of the solvent molecules.

Additionally to free porphyrins, their zinc-containing complexes, which are usually used for functionalization of fullerenes, are also standard solubilizing agents for CNTs. Thus, a highly soluble, conjugated Zn−porphyrin polymer was synthesized in presence of trifluoroacetic acid in THF and found to strongly interact with the surface of SWCNTs, producing a soluble polymer−nanotube complex, which remains soluble after excess free polymer was removed from solution and could be centrifuged at high speed with no observable sedimentation.[79] The carbon nanotubes can be *purified* (see the section on the CNTs purification below) from a large quantity of impurities such as carbon nanoparticles by executing a step of adding the carbon nanotubes into a solution (in THF, chloroform, dichloromethane,

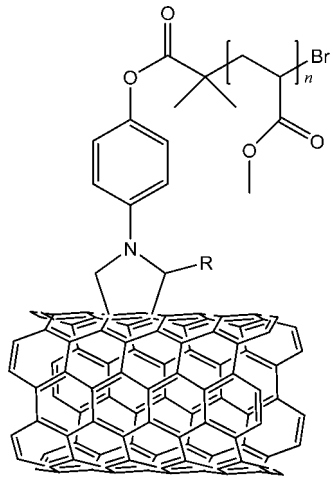


Figure 10. CNTs obtained by 1,3-dipolar cycloaddition reaction.

toluene, benzene, chlorobenzene, dimethylformamide, dimethyl sulfoxide, hexane, acetone, methanol, ethanol, 2-propanol, butanol, acetonitrile, or diethyl ether) using Zn−porphyrin complex with their further recovering[80] (Figure 14). Additional details on the use of porphyrin salts in CNTs functionalization were reported in ref 81.

In comparison with porphyrins, soluble *phthalocyanine*−CNTs composites are considerably less represented. Thus, a water-soluble composite of oxidized multiwall carbon nanotubes and sulfonic acid sodium salt derivatized copper phthalocyanine for application in bilayer organic solar cells is reported.[82] CNTs−molecular semiconductor thin films on the phthalocyanine basis were patented in refs 83 and 84.

Among other nonbiological molecules, used for CNTs functionalization to make them soluble, we note *diazo dyes* were reported to be functionalizing agents for CNTs. Thus, the mixture of SWNTs and a rigid, planar and conjugated diazo dye, Congo red (CR), can be dissolved in water with a solubility as high as 3.5 mg/mL for SWNTs.[85] The authors noted that the π-stacking interaction between adsorbed CR and SWNTs was considered responsible for the high solubility. Among other numerous functionalities, *calixarenes*,[86] *carbenes*[87] (Figure 15a), *carboranes*[88] (Figure 15b), *phenosafranin* (3,7-diamino-5-phenylphenazinium chloride),[89] and many more compounds[90−92] have been used for CNTs functionalization.

Functionalization with the Use of Biomolecules. Soluble CNTs, and especially water-soluble ones functionalized with biomolecules, could get many applications in medicinal chemistry; that is why a host of efforts has been dedicated to CNTs treatment with biologically active species, such as, for example, *carbohydrates*.[93] It was shown that high solubility of CNTs in water can be reached by functionalization with *amino acids*.[94] Thus, in case of reaction of $NH_2(CH_2)_nCO_2H$ with fluoronanotubes, the solubility in water is controlled by the length of the hydrocarbon side chain.[95] The authors showed that the 6-aminohexanoic acid CNTs derivative is soluble in aqueous solution (0.5 mg/mL) between pH 4 and 11, whereas the glycine and 11-aminoundecanoic acid derivatives are insoluble across all pH values. Highly water-dispersed MWCNTs (stable concentration as high as 10 mg/mL in deionized water) were obtained by attaching the lysine $HO_2CCH(NH_2)(CH_2)_4NH_2$ onto MWCNTs by producing acyl chloride on the carboxylic groups associated with the nanotubes.[96] The functionalized MWNTs can be dispersed in water under a wide range of pH values (5−14).

Biologically active *peptides* can be easily linked through a stable covalent bond to CNTs. Thus, a CNTs-bound peptide from the foot-and-mouth disease virus retained the structural integrity; this is immunogenic, eliciting antibody responses of the right specificity.[97] In order to explore the utilization of CNTs in solvent and the affinities of CNTs for different peptides, binding free energies of peptides to SWCNTs were calculated and analyzed.[98] Simulation of interactions between different peptides and SWCNTs was carried out using molecular dynamics methods, and estimation of the binding free energies of peptides onto the outer surface of the SWCNTs was based on thermodynamics theory. A good agreement between theoretical and experimental results was observed.

Different *proteins* such as bovine serum albumin, cytochrome *c*, and horseradish peroxidase were used to solubilize SWNTs in water aided by sonication.[99] Among other proteins used, the egg white lysozyme dispersed SWNTs, whereas papain and pepsin could not.[100] The authors concluded that the main driving force to the hydrophobic interactions between the sidewall of the SWNT and the inner hydrophobic domain exposed to the solvent during the three-dimensional change of the protein was induced by sonication. A gonadotrophin releasing hormone (GnRH), which was overexpressed in the plasma membrane of several types of cancer cells, was covalently anchored onto the surface of the oxidized MWCNTs via an amide linkage.[101] Sidewall coverage of MWCNTs by the GnRH was about 0.7% of the available surface area. It was also shown that the GnRH−MWCNTs entered the cells and showed toxicity in the malignant cells. The CNTs were successfully suspended in aqueous buffer solutions by their functionalization with a specific bifunctional molecule that is "sticky" to proteins 1-pyrene butanoic acid succidymidyl ester (1-pbase).[102] Among other reported proteins attached to CNTs making them soluble, we note Cy5-labeled goat antirabbit IgG (anti-IgG−Cy5), chemically bonded to CNTs via a two-step process of diimide-activated amidation and observed successfully using fluorescence microscopy, obtaining the fluorescent image of highly oriented f-CNTs at first time,[103] the foot-and-mouth disease virus (FMDV), leading to mono- and bis-derivatized CNTs b and c (Figure 16) starting from the precursor a possessing free amino groups,[104] and more.[105−108] Protein−CNTs nanocomposites can be potentially applied for biosensor and biofuel cell applications. A comparison of protein-dispersing media for various engineered carbon nanoparticles is given in ref 109.

Enzymes, belonging to proteins, have also been extensively studied as solubilizing agents for CNTs. Thus, a variety of enzyme−MWNT conjugates in aqueous solutions, their high activity and stability, and reusability, were reported in refs 110 and 111. The formed products are soluble in aqueous buffer, retained a high fraction of their native activity, and are stable at higher temperatures relative to their solution-phase counterparts. With use of noncovalent functionalization by the surfactant Triton X-100, the hydrophobic surfaces of the CNTs are changed to hydrophilic and interact with the hydrophilic surface of Biliverdin IX β reductase enzyme, creating a water-soluble complex with real interaction between the enzyme and CNT−Triton conjugates.[112] We would like to note glucose oxidase[113] among other enzymes[114] forming soluble composites with CNTs. Some protein conjugates possess the attributes of both soluble enzymes—high activity and low diffusional resistance—and immobilized enzymes—high stability—making them attractive choices for applications ranging from diagnostics and sensing to drug delivery.

Other recently reported biomolecules, used as dispersing agents for CNTs, are on the sugar basis. Thus, HSVM technique was applied to obtain water-soluble SWNTs−*nucleotide* com-

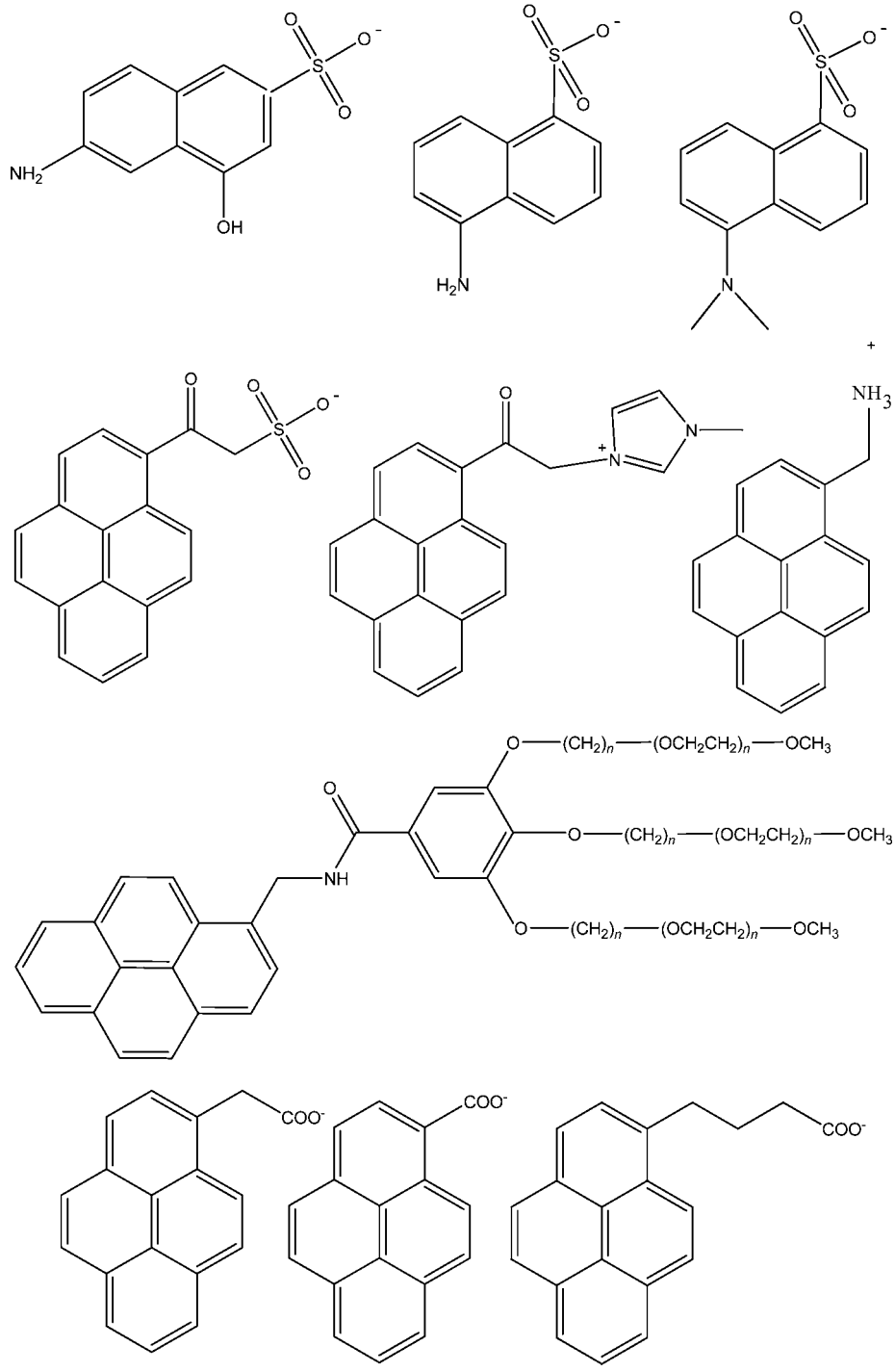


Figure 11. Polynuclear aromatics, used for obtaining water-soluble SWNT polyelectrolytes.

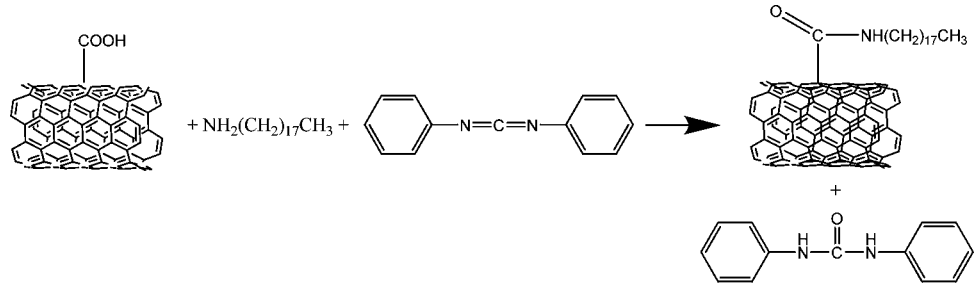


Figure 12. Amidation of SWNTs with octadecylamine.

posites, whose solubility depend significantly on the number of phosphate groups and the kinds of bases employed.[115] The complex amylose−nanotube system was studied by molecular dynamics simulation for elucidation of the mode of interaction

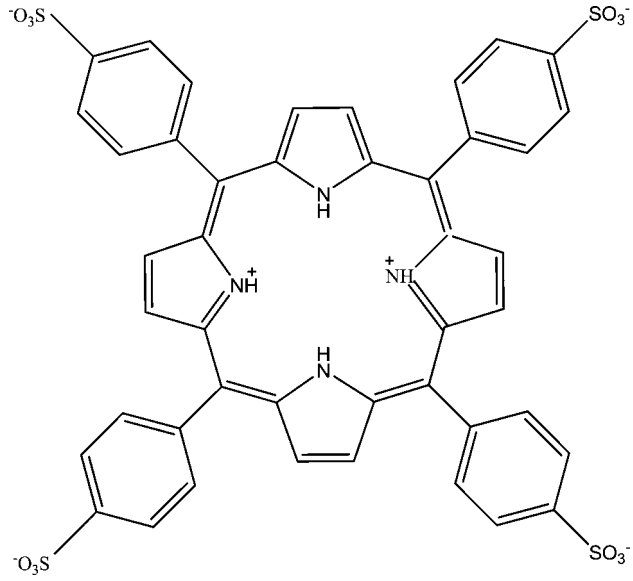


Figure 13. *meso*-(Tetrakis-4-sulfonatophenyl) porphine dihydrochloride.

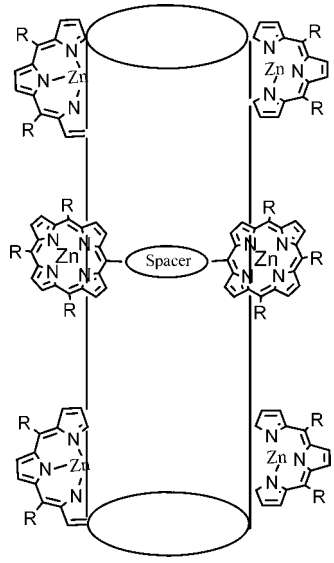


Figure 14. Zn−porphyrin complex/SWNT intermediate compound, used for CNTs purification.

between the initially separated amylose and SWNT fragments, which can be either wrapping or encapsulation.[116] The authors found that amylose molecules can be used to bind with nanotubes due to the dominance of the van der Waals force and, thus, favor noncovalent functionalization of carbon nanotubes. The functionalized SWCNTs, having substantial solubility in dimethyl sulfoxide and dimethylformamide, were obtained from oxidized SWCNTs by acyl halogenation with thionyl chloride and dimethylformamide and further interaction with *methyl-β-cyclodextrin* and ODA simultaneously.[117] Such systems offer considerable advantages over polymer-based composites due to their biocompatibility and noncovalent coupling which can potentially preserve the unique properties of the tubes.[118] The mechanism of interaction for such systems has been proposed to be dominated by hydrophobic and hydrophilic interactions along the surface of the tube.

A certain attention has been paid to composites of CNTs with a linear polysaccharide *chitosan* (CS).[119,120] Thus, a new amperometric biosensor for hydrogen peroxide was developed[121] based on cross-linking horseradish peroxidase (HRP) by glut-

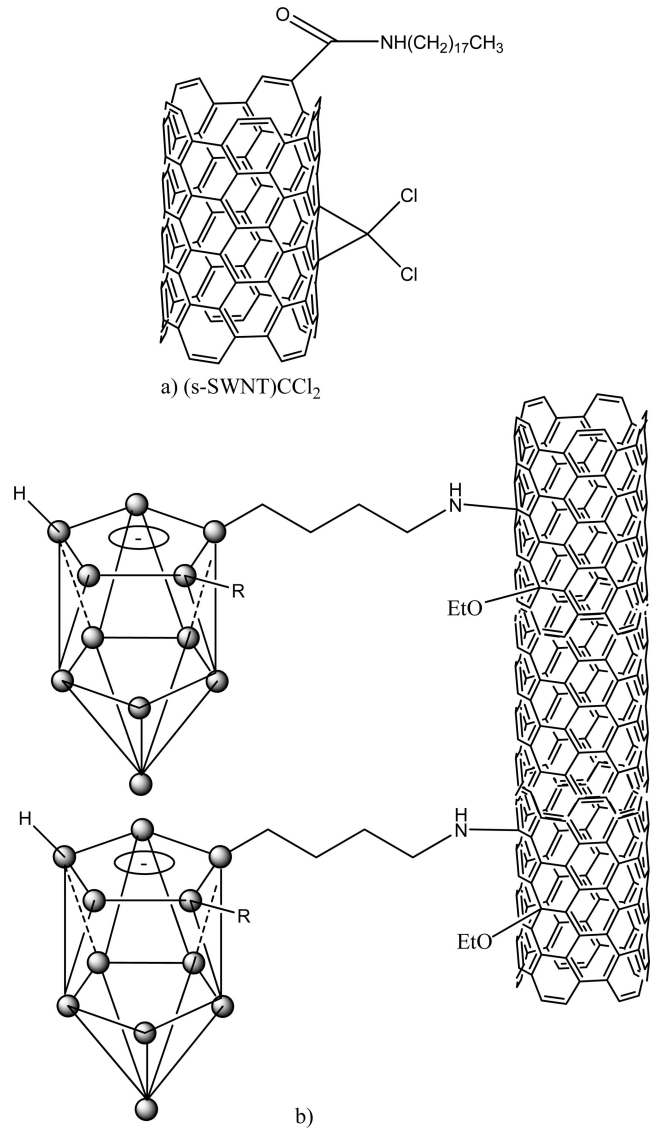


Figure 15. Carbene (a) and carborane (b) functionalized SWNTs.

araldehyde with multiwall carbon nanotubes/chitosan (MWNTs/chitosan) composite film coated on a glassy carbon electrode. The biosensor had good repeatability and stability for the determination of H_2O_2. In general, the CNTs−CS composite provides a suitable biosensing matrix due to its good conductivity, high stability, and good biocompatibility.[122] Additionally to H_2O_2, these composites can detect different substrates (ABTS, catechol, and O_2), possessing high affinity and sensitivity, durable long-term stability, and facile preparation procedure. Chitosan−CNTs composites were also obtained in the form of fibers with a wet-spinning method.[123]

DNA functionalization of CNTs holds interesting prospects in various fields including solubilization in aqueous media, nucleic acid sensing, gene therapy, and controlled deposition on conducting or semiconducting substrates.[124] Thus, a solid-state mechanochemical reaction was used for obtaining DNA-wrapped nanotubes of both MWCNTs and SWCNTs, resulting in a high aqueous solubility of the products with a stability of >6 months.[125] It was established that the nanotubes were cut into shorter lengths and were fully covered with DNA, which in the product is intact. DNA−SWCNTs were also prepared by another method, the *layer-by-layer technique*,[126] where poly(diallyldimethylammonium) (PDDA), a positively charged polyelectrolyte, and DNA as a negatively charged counterpart

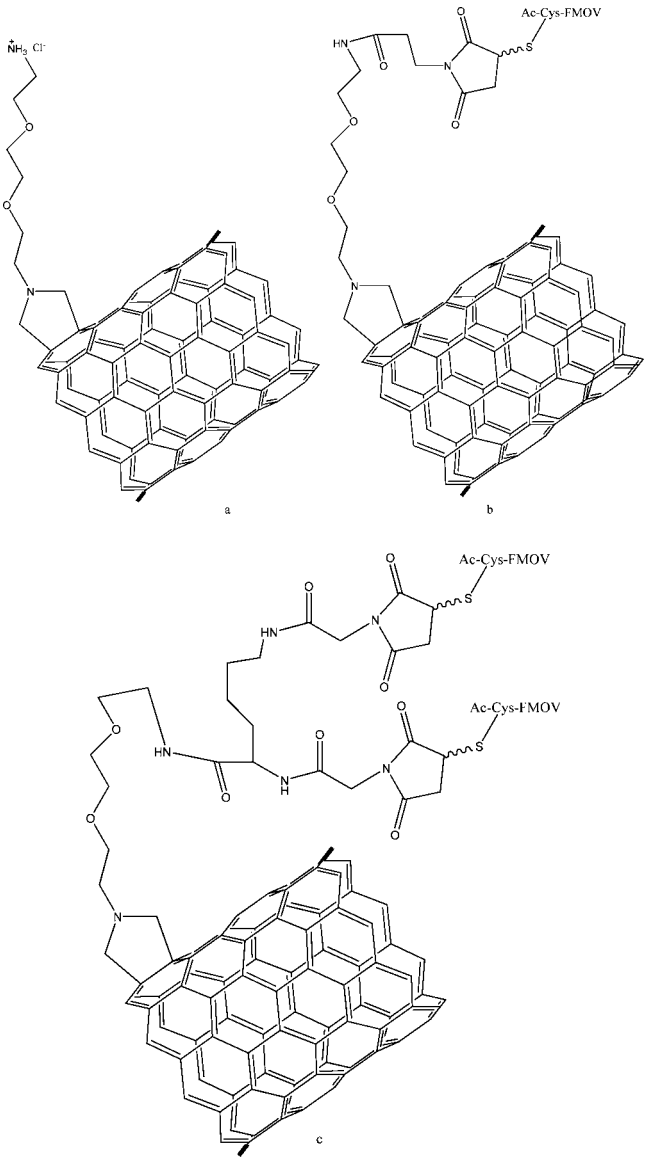


Figure 16. Molecular structures of the CNT derivative (a) and mono (b) and bis (c) conjugates.

macromolecule are alternatively deposited on the water-soluble oxidized SWCNTs (Figure 17). (We note that the same technique was applied also to fabricate a thin film from RNA-dissolved SWNT solutions[127].) As a representative application of the obtained DNA composite, an electrode modified by DNA/PDDA/SWCNTs particles exhibited larger electrocatalytic oxidation current in an aqueous solution of $Ru(bpy)_3^{2+}$; moreover, DNA−CNTs can be used as sensors for NO_2 detection. Other recent achievements on DNA immobilization on the CNTs are reported in refs 128−132.

Functionalization with the Use of Polymers or Their Precursors. In comparison with other functionalizing agents for CNTs, the polymers and their precursors, undoubtedly, have been of the most importance (together with biomolecules) during the last 10 years due to a considerable improvement of mechanical properties and stability of polymer hybrids with CNTs. A host of experimental articles and patents have been published on the basis of results using a broad spectrum of distinct polymers: polystyrene,[133−137] poly(vinylpyrrolidone),[138−140] polybutadiene,[141] poly(*N*-vinylcarbazole),[142] polyaniline,[143,144] poly(ethylene glycol),[145,146] poly(acrylic acid) and related polymers,[147−149] polyurethane,[150] and much more.[151−160] The obtained composites (sometimes in form of films) were soluble in water or common organic solvents, depending on the polymer used. Some representative examples of the synthesis of CNTs−polymer composites and their applications are represented in Table 1.

Special Techniques in the Synthesis and Purification of Soluble CNTs

Functionalization Using Irradiation or Radionuclides. It is well-known that strong sources of irradiation can produce defects and imperfections not only in biological molecules but also in inorganic materials. Carbon nanotubes are not an exception of this rule: additional defects cause higher-scale formation of attached COOH or other functional groups. Thus, MWNTs irradiated with *γ-rays* were subjected to chemical modification with thionyl chloride and decylamine.[181] The results showed that γ-radiation increased the concentration of functional groups bound to MWNTs, which arose due to the increasing number of defect sites created on the MWNTs by γ-photons. In comparison with untreated MWNTs, γ-irradiation significantly enhanced the solubility of MWNTs in acetone and THF. Use of pulsed laser for flocculation of carbon nanotubes was reported in ref 182.

A series of radionuclides has been attached to CNTs with distinct purposes. Thus, *carbon-13* was used to enrich CNTs compositions for improved magnetic resonance imaging.[183,184] An imaging study to determine the tissue biodistribution and pharmacokinetics of prototypical water-soluble DOTA-functionalized CNT labeled with *yttrium-86* (Figure 18) and *indium-111* in a mouse model was undertaken.[185] It was noted that the major sites of accumulation of activity resulting from the administration of ^{86}Y−CNT were the kidney, liver, spleen, and to a much less extent the bone.

Water-soluble MWNTs were labeled with *technetium-99m* (this isotope ^{99m}Tc is one of the most used in medicinal chemistry[186]) to study the distribution of MWNTs modified with glucosamine in mice.[187] It was shown that MWNTs moved easily among the compartments and tissues of the body, behaving like active molecules although their apparent mean molecular weight is tremendously large. Similar results were obtained for *iodine-125* (^{125}I)-labeled CNTs.[188]

Other Synthesis Methods. A very interesting, in our point of view, technique, "*pulsed streamer discharge*", generated in water, involving chemical reactions between radicals appearing by the pulsed streamer discharge and CNTs, allowed the authors to homogeneously disperse and well solubilize them in water for a month or longer.[189] Study of the mechanism revealed that −OH groups, which are known to impart a hydrophilic nature to carbon material, were introduced on the carbon nanotube surface; highly oxidative $O^{\bullet}$ and $H^{\bullet}$ radicals were generated in water and are responsible for the functionalization of the CNTs surface by −OH groups. A great advantage of the proposed method is that there is no need for any chemical agents or additives for solubilization due to their generation from the water itself by the electrochemical reactions induced by the pulsed streamer discharge. This method was improved by the same researchers[190] by the use of gas bubbling in water. Oxygen, argon, and nitrogen were used as bubbling gas in order to clarify the effects of the gas species on the SWCNT solubilization efficiency, and it was established that gas bubbling has positive effects on microplasma-based SWCNT solubilization as a result of enhanced radical formation and functionalization of the SWCNT surface.

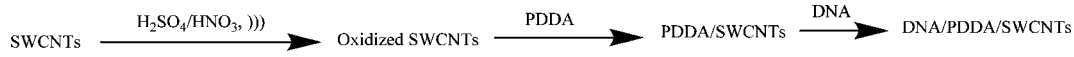


Figure 17. Scheme for fabrication of DNA-modified SWCNTs.

Microwave (MW) treatment, now a common technique in chemistry, was successfully applied for chemical functionalization and solubilization of SWCNTs, for instance, for their amidation and 1,3-dipolar cycloaddition[191,192] or preparation in situ of (MWCNT)/polystyrene or poly(methyl methacrylate) composites soluble in common organic solvents such as 1,2-dichlorobenzene, THF, and chloroform.[193] Solubility was a key feature for a successful MW-heated reaction of cycloaddition of 1,3-dipolar azomethine ylides to the sidewalls of MWNTs, resulting in MWNTs that contain 2-methylenethiol-4-(4-octadecyloxyphenyl), *N*-octyl-2-(4-octadecyloxyphenyl), or 2-(4-octadecyloxyphenyl)pyrrolidine units.[194] All these contain the 4-octadecyloxyphenyl substituent that acts as a solubilizing group. Amount of added groups after only 2 h of MW heating at 200 °C was in the same range as that obtained after 100−120 h of conventional heating of soluble and insoluble MWNTs. Among other techniques, *cryogenic crushing* CNTs at liquid nitrogen temperature allowed them to be shortened and make them appreciably soluble in a solvent without any dispersant.[195] Typical lengths of less than 500 nm were obtained from 30 min of crushing. A two-phase liquid−liquid *extraction process*, allowing extracting water-soluble SWCNTs into an organic phase, is reported in ref 196. The extraction is based on electrostatic interactions between a common phase transfer agent and the sidewall functional groups on the nanotubes.

Purification of Soluble CNTs from impurities (carbon nanoparticles, graphite fragments, etc.) can be carried out by several methods, in particular, by *chromatography*,[197,198] flow field-flow *fractionation*,[199] and *centrifugation*.[200] Thus, through a systemic study of a series of centrifuged solutions, the authors of ref 201 confirmed by Raman spectroscopy that heavily functionalized amorphous carbon was fractionated into the early centrifuged solutions, whereas lightly functionalized graphite fragments as well as polyhedral carbon and metal catalysts particles were fractionated into the late centrifuged solutions and centrifuged residue, and then highly pure and well-dispersed SWNTs were collected from the middle centrifuged solutions. It is proposed that the purity, dispersibility, and aggregation state of SWNTs can be qualitatively estimated by the relative intensity of their absorption features and the fine structure and slope of their absorption curves.

Study of Reactivity and Physicochemical Properties of Soluble CNTs

Special Studies of the Reactivity of Soluble CNTs toward Active Oxygen Sources. Soluble SWCNTs were oxidized with singlet *oxygen* ($^1\Delta_g$), and the reaction progress was monitored utilizing FT-IR and UV−vis−near-IR (NIR) spectroscopy.[202] The results indicated reversible covalent addition of oxygen to the walls of the nanotubes, most likely producing either the [2 + 2] or [4 + 2] cycloaddition product (Figure 19). Dilute aqueous *ozone* solution with or without ultrasound was used to functionalize SWCNTs.[203] Both O_3 and O_3/ultrasound treatments greatly increased the stability of SWCNTs in water. The oxidation pathway was proposed as follows: at the onset of the oxidation reaction, the C═C double bond was first converted to −C−OH which was then oxidized to −C═O and *O*═C−OH concurrently. Ozonating CNTs in fluorinated solvents (perfluorinated polyethers) to functionalize the sidewalls of the carbon nanotubes yielding functionalized CNTs with oxygen-containing functional moieties was reported in refs 204 and 205. Short (about 15 min) and long (about 3 h) exposures to ozone as well as cold (−78 °C), room temperature (r.t.), and hot (50 °C) temperatures were tested.

The reaction of H_2O_2 with an aqueous suspension of water-soluble HiPco SWNTs encased in the surfactant sodium dodecyl sulfate was studied.[206] Preliminary studies on the mechanisms suggested that H_2O_2 withdraws electrons from the SWNT valence band by charge transfer, which suppresses the nanotube spectral intensity. CNTs were modified by oxidation with *peroxygen compounds* (inorganic peroxoacids, peroxycarboxylic acids of the formula $Q(C(O)OOH)_n$, hydroperoxides of the formula $Q(OOH)_n$, salts thereof, and combinations of any of the above, where Q is an alkyl, cycloalklyl, aryl, or heterocyclic group of C_1-C_{12} and *n* is one or two).[207] The oxidized CNTs included carbon and oxygen containing moieties, such as carbonyl, carboxyl, aldehyde, ketone, hydroxy, phenolic, esters, lactones, quinones, and derivatives thereof. Oxidation of the nanotubes increases the degree of dispersion of aggregates of nanotubes and aids in the disassembling of such aggregates. The dispersed nanotubes are used to prepare rigid structures and can be used in electrodes and capacitors.

Other Physicochemical Studies. The oxidation of MWCNTs in nitric acid was monitored using sample weight, *Raman spectrum*, solubility, morphology, and alignment.[208] It was noted that high solubility (20−40 mg/mL) is obtained only after prolonged exposure (24−48 h) in concentrated acid (60%) with a considerable loss of the product (60−90%); the MWCNTs are strongly fragmented and covered by amorphous carbon after 48 h of oxidation. Moreover, it was found that the solubility correlates well with the area ratio of the G and D bands from the Raman spectrum. In a similar investigation, aqueous dispersions of SWNTs, prepared using different dispersing agents, were also analyzed by Raman spectroscopy.[209] The influences of different dispersing agents and excitation wavelengths were discussed in comparison with UV−vis spectroscopic analysis data. The authors offered to use the most effective dispersing agent found in this study, sodium dodecylbenzene sulfonate, as a benchmark for future dispersion experiments. EPR studies on pristine, purified, shortened, and soluble SWNTs in various solution phases showed that the soluble SWNTs carry about one unpaired electron per 10 000 carbon atoms and give a free-electron *g*-value.[210] *Density functional theory* calculations were carried out to study the effects of covalently binding isoniazid, an antitubercular compound to functionalized carbon nanotubes.[211] Binding energies, energies of solvation, and quantum chemical molecular descriptors were calculated. Significant differences were observed between SWNTs and MWNTs by investigating them in depth by conventional *electrochemical techniques* in solution.[212,213] Despite that functionalization strongly modified the electronic properties of carbon nanotubes, the enrichment of the density of states of MWNTs with respect to SWNTs, due to larger tube diameters, is still appreciated. The bulk electronic properties of pyrrolidine-functionalized nanotubes (Figure 20) were obtained from CV measurements and discussed in the light of quantum chemical calculations.[214]

^{13}C NMR study of highly soluble ^{13}C-enriched SWCNTs, functionalized with diamine-terminated oligomeric poly(ethylene glycol) (PEG(1500N)), allowed detection of CNTs in solution.[215]

Table 1. Representative Examples of the Composites, Prepared on the Basis of Polymers and Carbon Nanotubes

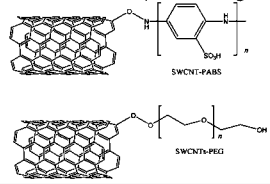
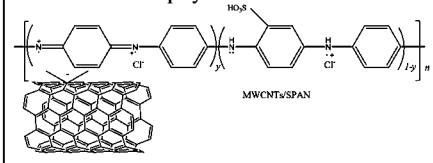
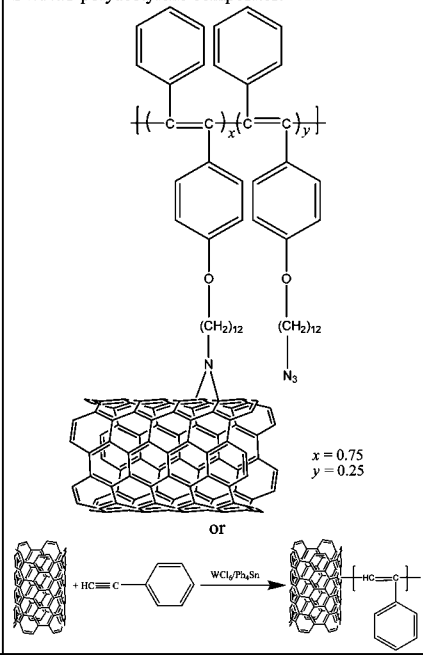
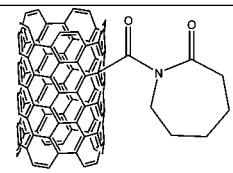
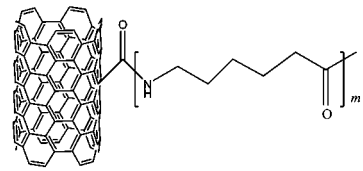
Precursors	Product(s)	Properties and possible applications	Reference
A rigid linear polymer poly(phenyleneethynylene) (PPE) and related compounds, SWNTs.	PPE/SWNTs hybrid	The water solubility of SWNTs was enhanced to 1.8 mg/ml. Used in a photovoltaic cell with the bulk heterojunction configuration.	161, 162
Poly(acrylamide) (PAM), SWNTs (*via* reversible addition–fragmentation chain transfer (reversible addition–fragmentation chain transfer, RAFT) polymerization).	PAM-g-SWNT	Relatively uniform polymer coatings present on the surface of individual, debundled nanotubes.	163
RAFT agents, MWNTs, cationic polymer (poly(2-(dimethylamino) ethylmethacrylate)), anionic polymer (poly(acrylic acid)) and zwitterionic polymer (poly{3-[*N*-(3-methacrylamidopropyl)-*N*,*N*-dimethyl] ammoniopropane sulfonate})	Poly{3-[*N*-(3-methacrylamidopropyl)-*N*,*N*-dimethyl] ammoniopropane sulfonate} functionalized MWNTs, poly(acrylic acid) functionalized MWNTs and poly(2-(dimethylamino) ethyl methacrylate) functionalized MWNTs	Good solubility in aqueous solution.	164
Poly(N-isopropylacrylamide) (PNIPAM), MWNTs, (*via* RAFT polymerization).	MWNT-g-PNIPAM	Good solubility in water, chloroform, and THF. Potential applications by grafting other functional polymer chains onto MWNTs.	165
Poly-*m*-aminobenzene sulphonic acid (PABS) or polyethylene glycol (PEG), SWNTs.	Graft copolymers SWNT-PABS (30% loading SWNTs) and SWNT-PEG (71% loading SWNTs). 	Water-soluble (5 mg/L). Fairly uniform length and diameter.	166, 167
MWNTs. *In situ* polymerization of aniline followed by sulfonation with chlorosulfonic acid in an inert solvent and by hydrolysis in water.	SPAN/MWNTs. SPAN = sulfonated polyaniline 	SPAN/MWNTs are highly dispersible in water. Quinonoid structure of SPAN preferentially interacts with the nanotubes and is stabilized by strong pi-pi interaction between two components.	168
3-Aminophenylboronic acid monomers, DNA, SWNTs.	Poly-(anilineboronic acid)/ss-DNA/SWNT composite (PABA/ss-DNA/SWNT)	Water-soluble; the conductivity of the nanocomposite was much higher than that of the pure self-doped polyaniline in both acidic and neutral solutions.	169
Poly(1-phenyl-1-alkyne) and poly(diphenylacetylene) derivatives carrying azido functional groups at the ends of their alkyl pendants, SWNTs.	SWNTs-polyacetylene composites: 	Soluble in common solvents.	170-173

Table 1. Continued

Precursors	Product(s)	Properties and possible applications	Reference
Double-hydrophilic block copolymer, poly(ethylene oxide)-*b*-poly [2-(*N*,*N*-dimethylamino)ethyl methacrylate] (PEO-*b*-PDMA), MWCNTs.	(PEO-*b*-PDMA)/MWCNTs	Yield 26%. Direct evidence for the individual dispersion. Possible applications: Au and Pt nanoparticles were attached on the sidewall of the modified MWCNTs by using the amino groups of PDMA segments.	174
Poly(ethylene-co-vinyl alcohol) (EVOH) copolymer, SWNTs, carbodiimide-activated esterification reaction conditions.	EVOH-SWNT	Soluble in highly polar solvent systems such as DMSO and hot ethanol-water mixtures. A fabrication of nanocomposites in which the SWNTs are homogeneously dispersed in the polymer matrix is possible.	175
Poly(vinyl alcohol) (PVA), MWCNTs (wet-casting method; esterification reactions).	PVA-MWCNTs films.	Water-soluble. The mechanical properties of the nanocomposite films were significantly improved compared to the neat polymer film. The composite-based electrodes can be used as biosensors for glucose detection.	176-178
Carboxylic acid-terminated hyperbranched poly(ether-ketone)s (HPEKs), MWCNTs or SWCNTs	HPEK-*g*-SWCNT and HPEK-*g*-MWCNT nanocomposites.	The resultant nanocomposites were homogeneously dispersed in various common polar aprotic solvents as well as in concentrated ammonium hydroxide.	179
Thionyl chloride, SWCNTs, caprolactam, metallic sodium	 Caprolactam-functionalized SWCNTS  Caprolactam- and nylon-SWCNTs	Soluble in organic solvents.	180

In-depth studies of CNTs *solubility* in a variety of solvents were carried out by the author of ref 216. Dispersions of SWCNTs in various solvents and aqueous surfactant emulsions were investigated to correlate the degree of dispersion state with *Hansen solubility parameters* $\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$,[217] and it was found that the nanotubes were dispersed or suspended very well in the solvents with certain dispersive component (δ_d) values. They were precipitated in the solvents with high polar component (δ_p) values or hydrogen-bonding component (δ_h) values. The surfactants with a lipophilic group equal to and longer than decyl, containing nine methylene groups and one methyl group, contributed to the dispersion of nanotubes in water. *Molecular dynamics simulations* of liquid water near the external surface of a carbon nanotube bundle were presented in ref 218. Hydrogen bonding, diffusive behavior, and rotational and vibrational motions are analyzed in the low- and high-density regimes. *Supercritical water* in the presence and absence of oxygen was used for the first time for study of the opening and thinning of MWNTs.[219]

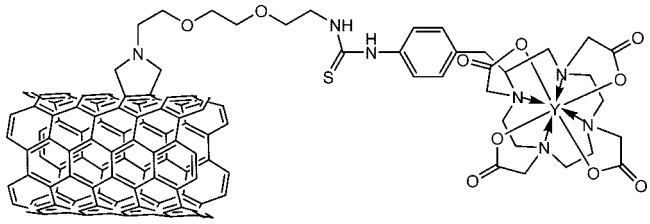


Figure 18. Yttrium-labeled CNTs.

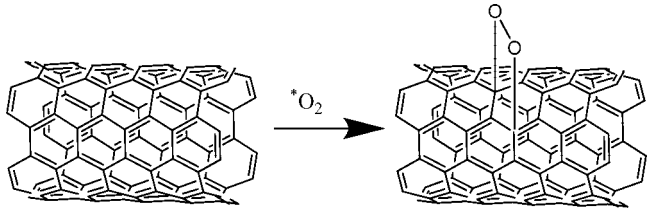


Figure 19. Products of SWCNTs oxidation with oxygen.

Among other recent investigations on CNTs, we note study of optically sensing *sonication effects*,[220] relations between *colloidal stability and percolation* phenomena in aqueous suspensions of MWCNTs,[221] and *toxic effects*.[222] Additionally, a method, a system, and an apparatus to determine a *concentration* of carbon nanotubes in a solution was proposed.[223]

Main Applications of Soluble CNTs

Additionally to such applications of soluble CNTs as biosensors, composites, advanced polymers, etc., mentioned throughout the text, we would like to underline the following uses. Soluble CNTs are applied mainly in nanomedicine[224] for different purposes, the most important of which is the *drug delivery*.[225] Within the family of nanomaterials, CNTs have

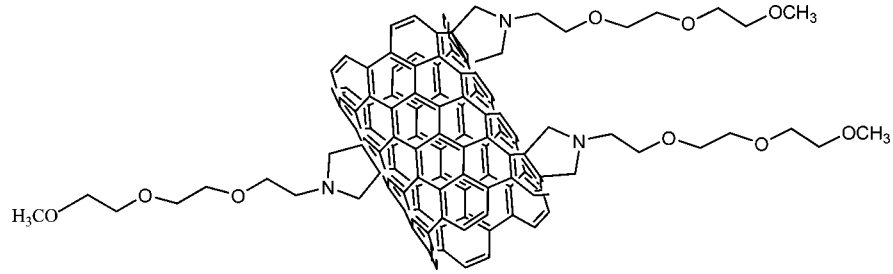


Figure 20. Pyrrolidine-functionalized nanotubes.

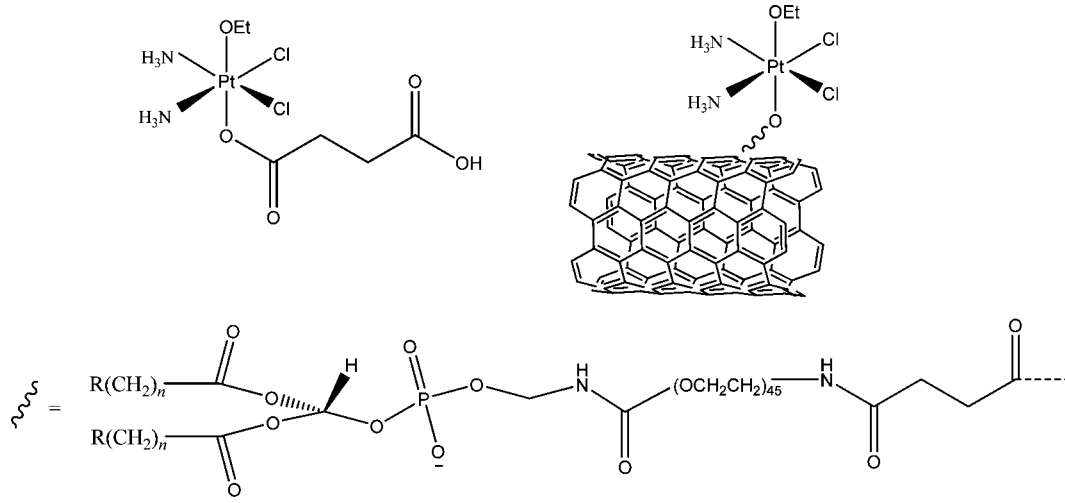


Figure 21. *c*,*c*,*t*-[$Pt(NH_3)_2Cl_2(OEt)(O_2CCH_2CH_2CO_2H)$] and its SWCNTs conjugate.

emerged as a new alternative and efficient tool for transporting and translocating therapeutic molecules. It has become possible after the recent discovery of their capacity to penetrate into the cells. CNT can be loaded with active molecules by forming stable covalent bonds or supramolecular assemblies based on noncovalent interactions. As described above, CNT can be functionalized with bioactive peptides, proteins, nucleic acids, and drugs and used to deliver their cargos to cells and organs. Once the cargos are carried into various cells, tissues, and organs they are able to express their biological function.[226] Because functionalized CNT display low toxicity and are not immunogenic, such systems hold great potential in the field of nanobiotechnology and nanomedicine.[227] Thus, SWNTs and MWNTs were solubilized via the esterification of nanotube-bound carboxylic acids by oligomeric poly(ethylene glycol) compounds.[228] The obtained water-soluble samples were used as starting materials in reactions with bovine serum albumin (BSA) protein in ambient aqueous solutions, yielding SWNT−BSA and MWNT−BSA conjugates. Related information is given in ref 229.

CNT−Alg gel (alginate hydrogel) was reported as useful scaffold material in *tissue engineering* with the sidewalls of CNTs acting as active sites for chemical functionalization.[230] Soluble CNTs were dispersed in sodium alginate solution as a cross-linker. As a result, the CNT−Alg gel showed faster gelling and higher mechanical strength than the conventional alginate gel. *Elimination of cancer cells* using SWNTs is reported in ref 231. The behavior of the functionalized, water-soluble SWNTs under exposition to a noninvasive, 13.56 MHz rf field was studied. Then, human cancer cell lines were incubated with various concentrations of SWNTs and then treated in the rf field. As a result, SWNTs targeted to cancer cells may allow noninvasive rf field treatments to produce lethal thermal injury to the malignant cells. As shown in another "anticancer" report, the platinum(IV) complex *c*,*c*,*t*-[$Pt(NH_3)_2Cl_2(OEt)(O_2CCH_2CH_2CO_2H)$] (Figure 21), which is nearly nontoxic to testicular cancer cells, displays a significantly enhanced cytotoxicity profile when attached to the surface of amine-functionalized soluble SWNTs.[232] The authors noted that, by linking additional groups, such as cancer cell targeting moieties, to the platinated SWNTs as longboat passengers, it may be possible to achieve highly selective constructs for use in clinical trials.

Considerable efforts have been dedicated to preparation, characterization, and search of applications for the *films* on the basis (or starting from) CNTs.[233,234] Thus, free-standing film made of a SWCNT−poly(vinyl alcohol) (PVA) composite material was fabricated by pretreatment of SWCNTs with ultrasonication in water with the aid of a surfactant that promotes unbundling of aggregated SWNCTs.[235] Large-scaled and homogeneous MWNT films were fabricated using the soluble ODA-modified MWNT at r.t. by a spin-coating method.[236] Composite film containing titania electrostatically linked to oxidized MWNTs (TiO_2−s−MWNTs) was prepared from a suspension of TiO_2 nanoparticles in soluble carbon nanotubes. Photoinduced charge transfer between the MWNT and TiO_2 was proposed. One representative application for such films is the modification of electrodes surfaces. Thus, scanning electron microscopy (SEM) and electrochemical studies of water-soluble SWNTs, prepared via noncovalent functionalization by Congo red through a physical grinding treatment and immobilized on the surface of a glassy carbon electrode, showed that SWNTs formed uniform films with porous network structures of nanosizes on the electrode surface, which were stable in neutral and acidic solutions but were unstable in basic media.[237] Examination of potential applications of the films demonstrated that the water-soluble SWNTs were the ideal materials for constructing SWNTs-based electrochemical sensing films.

The directed assembly of SWCNTs at lithographically defined positions on gate oxide surfaces was reported,[238] allowing for the high yield (~90%) and parallel fabrication of SWCNT *device arrays*. The method is based on SWCNTs functionalization through diazonium chemistry, further assembling with HfO_2 surface, and heating to 600 °C. The precision, ease, and resultant high yield of this method provide a promising route to the parallel fabrication of large-scale carbon nanotube electronics. Conducting textiles (*dyes*) can be simply prepared by incorporating carbon nanotubes through a dyeing approach, immersing textiles in an aqueous sulfonated polyaniline−carbon nanotube dispersion acting as a dye.[239] In comparison with textiles dyed with sulfonated polyaniline, the conductivity and capacitance considerably increased. The patent[240] is dedicated to hair coloring using modified CNTs. Other applications are related with use of CNTs in *solar cells*.[241]

Conclusions

As shown above, a series of methods is being currently applied to solubilize both MWCNTs and SWCNTs in water or organic solvents. Formed solutions can be true or dispersions. In the past decade, the most attention has been paid to soluble composites of CNTs with polymers and biomolecules because of the extreme importance of these areas and many potential applications of synthesized composites in medicine and technology.

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