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Noncovalent Functionalization of Carbon Nanotubes

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1.1 Introduction

Within the past decades extensive research has shed light into the structure, reactivity and properties of carbon nanotubes (CNTs) [1–3]. This new carbon allotrope is theoretically constructed by rolling up a graphene sheet into a cylinder with the hexagonal rings joining seamlessly. Commonly, carbon nanotubes are classified into single-walled carbon nanotubes (SWCNTs) which consist of one cylinder and multi-walled carbon nanotubes (MWCNTs) comprising an array of tubes being concentrically nested. Depending on the roll-up vector which defines the arrangement of the hexagonal rings along the tubular surface, single-walled carbon nanotubes exhibit different physical and electronic properties, e.g. they either possess metallic or semiconducting character.

Apart from their outstanding electronic properties providing the foundation for multiple applications as nanowires, field-effect transistors and electronic devices [3–5], carbon nanotubes surmount any other substance class in their mechanical properties. The exceptionally high tensile modulus (640 GPa) and tensile strength ($\approx$100 GPa) together with the high aspect ratio (300–1000) make nanotubes an ideal candidate for reinforcing fibers and polymers [6, 7].

However, in order to tap the full potential of nanotubes in electronics, photonics, as sensors or in composite materials, two major obstacles have to be overcome, e.g. separation

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according to diameter and/or chirality on the one hand and uniform dispersability in a solvent or matrix on the other hand. Responding to a growing interest, progress in the diameter control during carbon nanotube production has been achieved [8]. However, up to now, the as-produced material contains nanotubes of differing lengths, diameters and chiralities, therefore including semiconducting and metallic nanotubes. This inhomogeneity still forms the bottleneck for nanotube-based technological progress. Furthermore, the strong intertube van der Waals interactions of 0.5 eV/μm, which render nanotubes virtually insoluble in common organic solvents and water also constrict any application [9, 10].

Among the efforts to increase processability of this unique material, chemical and especially noncovalent functionalization represents a cornerstone, as in its nondestructive meaning it does not alter the intrinsic properties of CNTs. Furthermore, tailoring of the surface properties of carbon nanotubes is accessible, boosting solubility in a variety of solvents and increasing matrix interactions, as will be summarized within this chapter.

1.2 Overview of Functionalization Methods

In CNT functionalization chemistry four main approaches are at hand, as outlined by Figure 1.1. The covalent attachment of groups onto the nanotube scaffold includes defect functionalization on the one hand and direct sidewall functionalization on the other hand. Defect functionalization is associated with chemical transformation of defects already present or induced. Contrarily, direct sidewall functionalization is directly related to rehybridization of the sp^2 carbon atoms of the CNT framework into sp^3 carbon atoms. Even though no further defects like kinks and holes in the nanotube walls are created hereby, both covalent methods disrupt the sp^2 carbon network of the nanotube resulting in mostly undesirable alterations of the physical and chemical properties of this extraordinary material. Certainly, covalent functionalization is a prosperous field of research for modifying surface properties of carbon nanotubes, as it allows attachment of a large variety of groups, which is nicely documented in a series of review articles related to this topic [11–18].

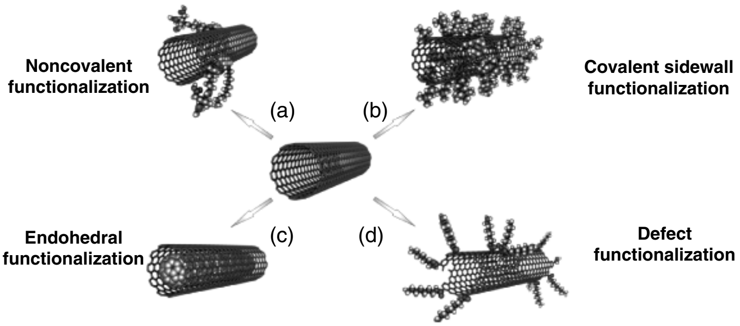


Figure 1.1 *Overview of nanotube functionalization methods; (a) noncovalent functionalization, (b) covalent functionalization, (c) endohedral functionalization, (d) defect functionalization*

Opposed to covalent functionalization, endohedral functionalization [17, 19] is concerned with filling the inner cavities of carbon nanotubes to store guest molecules like fullerenes or small proteins inside the nanotube. However, this approach only slightly influences the surface properties and therefore represents a special case in nanotube functionalization.

Noncovalent exohedral functionalization takes advantage of the supramolecular approach and involves adsorption of various inorganic and organic molecules onto the sidewall of a nanotube via noncovalent interactions including π-π-stacking, van der Waals or charge transfer interactions. The great potential of this method has been realized within the past years [6, 20–25], as it is completely nondestructive and preserves the intrinsic structure of the tubular network without changing the configuration of the carbon atoms.

The following chapter shall mainly deal with concepts and progresses towards monodisperse carbon nanotubes by the noncovalent approach, as this functionalization route may pave the road for many nanotube-based applications due to its nondestructive nature and scalability.

1.3 The Noncovalent Approach

1.3.1 Dispersability of Carbon Nanotubes

1.3.1.1 Aim and Prospects

Noncovalent functionalization mainly targets an enhancement in dispersability and solubility of pristine carbon nanotubes. In the following, the term dispersion refers to homogeneously distributed nanotubes in a colloidal state also including small bundles, while solution implies that the nanotubes appear individualized, e.g. the carbon nanotube bundles are exfoliated. The aim and prospects of noncovalent carbon nanotube functionalization are illustrated by Figure 1.2: The introduction of a bifunctional molecule to the sidewall of a nanotube not only serves the purpose of yielding stable nanotube dispersions and solutions (Figure 1.2a), the interaction with a polymer matrix can also be increased (Figure 1.2b). The use of molecules selectively adsorbing on the nanotube sidewall may also be exploited for nanotube purification, as merely the nanotubes are solubilized, while the impurities consisting of amorphous carbon and metal catalyst particles can be removed as precipitate after centrifugation (Figure 1.2c). This concept is especially advantageous over oxidative purification techniques, as it preserves the intrinsic nanotube structure. The major obstacle here is the necessity to completely individualize the nanotubes, as the impurities are often trapped inside the bundles.

The noncovalent approach also opens the door to the separation of SWCNTs according to diameter and/or chirality either by density gradient ultracentrifugation (Figure 1.2d) or selective interaction with bridged mediators acting as nanotweezers to extract nanotubes of a specific diameter (Figure 1.2e).

1.3.1.2 Aqueous Dispersions

The most widespread noncovalent functionalization method to obtain nanotubes dispersed and dissolved in aqueous media is their encapsulation in surfactant micelles. In general,

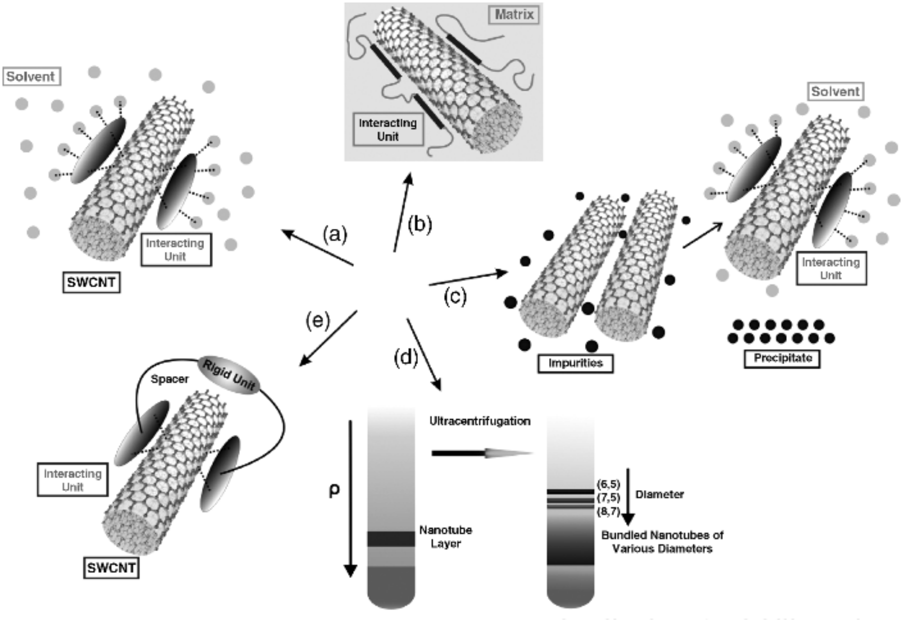


Figure 1.2 *Aim and prospects of noncovalent functionalization: (a) solubility tuning, (b) composite reinforcement, (c) purification, (d) separation of different tube species by density gradient ultracentrifugation, (e) separation of different tube species by selective interaction*

surfactants can be described as molecules with a hydrophilic region usually referred to as polar head group and a hydrophobic region denoted as tail. Due to this amphiphilicity they tend to adsorb at interfaces and self-accumulate into supramolecular structures.

Three adsorption mechanisms of surfactants onto SWCNTs have been proposed as depicted by Figure 1.3. In analogy to the epitaxial adsorption of surfactants on graphite, specific self-alignment as cylindrical micelles (Figure 1.3a) or hemimicelles (Figure 1.3b) has been suggested [26, 27]. More recently, structureless random adsorption has been favored [28]. In this case, no preferred arrangement of the head and tail groups stabilizes the dispersion/solution (Figure 1.3c).

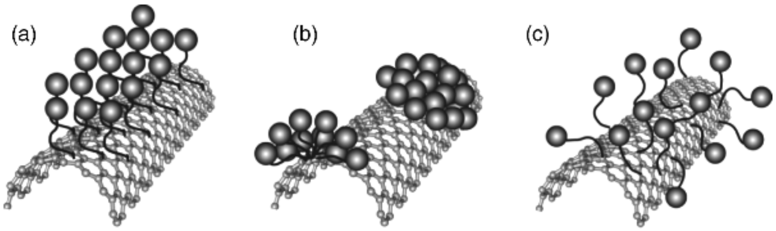


Figure 1.3 *Adsorption of surfactants: (a) SWCNTs encapsulated in a cylindrical micelle by aligned adsorption of the amphiphiles, (b) hemimicellar adsorption, (c) random adsorption*

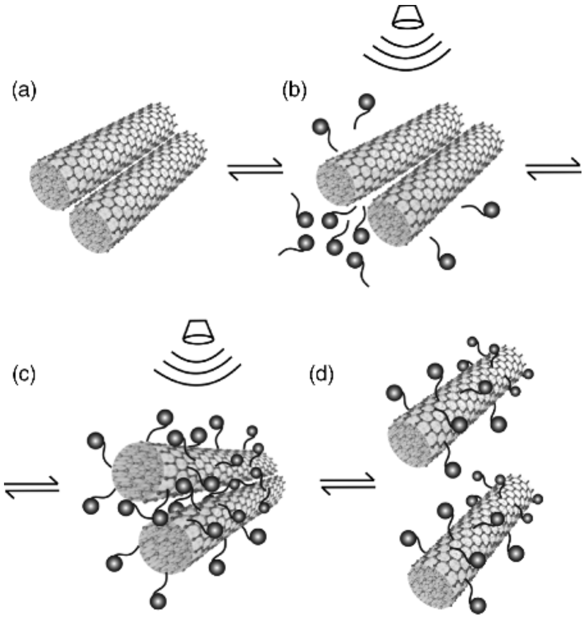


Figure 1.4 *Mechanism of nanotube exfoliation from bundles with the aid of a surfactant and ultrasonication according to the unzippering mechanism*

According to the unzippering mechanism proposed by Strano *et al.* [29], nanotubes are isolated from bundles by ultrasonication in the presence of a surfactant (Figure 1.4). During the first step, the energy input by ultrasonication provides high local sheer, resulting in dangling ends in the nanotube bundles (Figure 1.4b) which become adsorption sites for surfactants preventing the loosened tubes from reaggregation (Figure 1.4c). Due to the relative movement of the partly individualized nanotube relative to the bundle, the surfactant continuously progresses along the nanotube length resulting in the isolation of the individual tube (Figure 1.4d). Hereby, an equilibrium is established between free individuals and bundled aggregates limiting the concentration of stably individualized SWCNTs.

The exfoliation of SWCNTs is specifically important for their characterization. A cornerstone in nanotube characterization has been laid by O'Connell *et al.* who have first reported on the observation of nanotube fluorescence directly across the bandgap of semiconducting SWCNTs [26]. They have revealed that photoemission is only observed when nanotubes are exfoliated, as aggregation otherwise quenches the fluorescence by interaction with metallic nanotubes. Based on this finding, Bachilo *et al.* have used spectrofluorimetry to assign the optical transitions to specific (n,m)-nanotubes for determining the detailed composition of a bulk sample of individualized SWCNTs [30]. Exfoliation in both cases was achieved by the anionic detergent sodium dodecyl sulfate (SDS) nicely underlining the importance of nanotube solubilization by surfactants.

Surfactants are usually classified according to the nature of the head charge, e.g. anionic, cationic, nonionic and zwitterionic. A variety of nanotube surfactants (Figure 1.5) has been investigated including the most common detergents sodium dodecyl benzene sulfonate

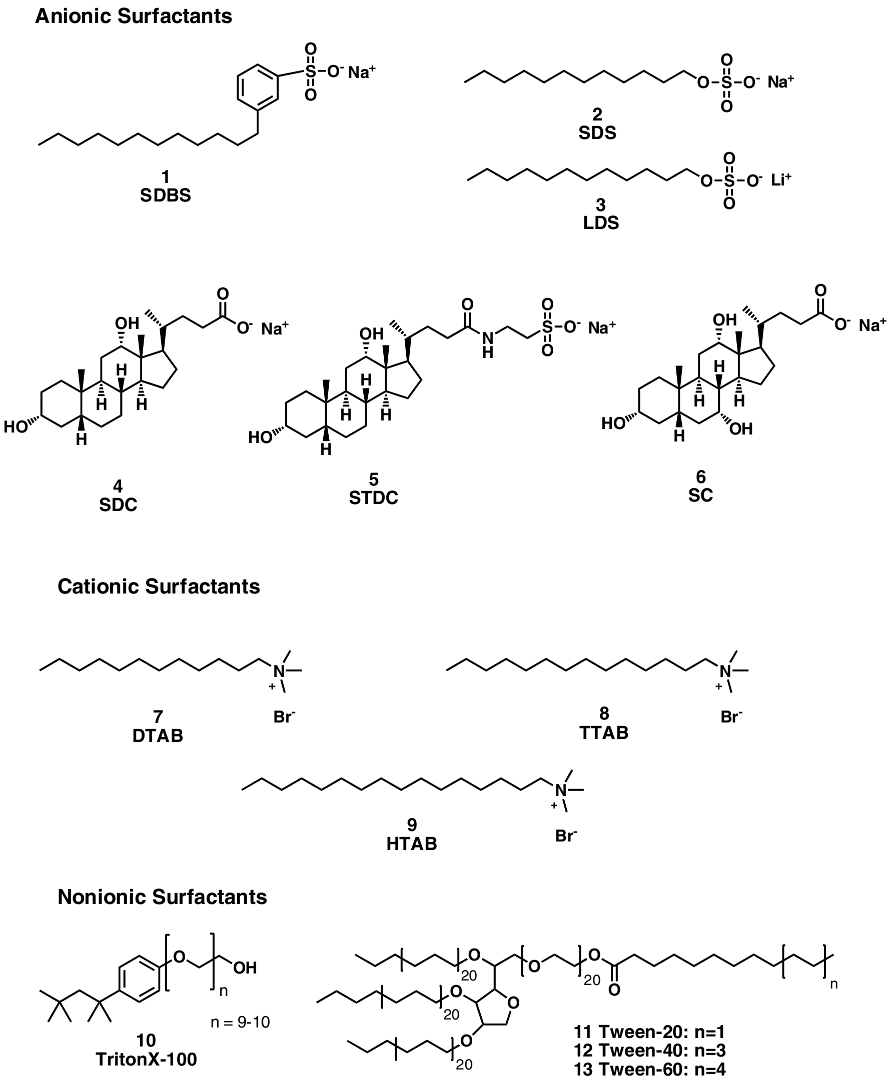


Figure 1.5 *Structure of the most common SWCNT detergents*

(SDBS **1**), sodium dodecyl sulfate (SDS **2**), lithium, dodecyl sulfate (LDS **3**), the bile salts sodium deoxycholate (SDC **4**), sodium taurodeoxycholate (STDC **5**) and sodium cholate (SC **6**) as representatives of anionic surfactants, dodecyltrimethylammonium bromide (DTAB **7**), tetradecyl trimethyl ammonium bromide (TTAP **8**), hexadecyltrimethylammonium bromide (HTAB **9**) among cationic surfactants and TritonX-100 **10**, Tween-20 **11**, Tween-40 **12** and Tween-60 **13** as nonionic surfactants.

A comparative study of SDS, SDBS and TritonX-100 has shown that SDBS and TritonX-100 are more effective than SDS in dispersing SWCNTs [31]. It has been suggested that the aromatic rings in SDBS and TritonX-100 have a positive effect due to additional π-stacking interactions with the nanotube sidewall when adsorbed in a hemimicellar fashion (compare Figure 1.3b). The transmission electron microscopic (TEM) investigations of Mioskowski *et al.* [27] on SWCNTs dispersed in SDS, however, support a cylindrical adsorption of the detergent, as the TEM images have revealed that SDS forms supramolecular structures consisting of half-cylinders.

In a detailed study on the dispersion of arc discharge SWCNTs by various surfactants, Wenseleers *et al.* [32] have observed no spectral shift in the characteristic nanotube absorption bands in aqueous solutions of SDBS and TritonX-100. They have concluded that π-stacking of the benzene rings is therefore not likely, as interaction with the nanotubes would cause the spectral features to be red-shifted. They have assigned their observation to steric hindrance of the rather bulky substituents in TritonX-100 and SDBS. Additionally, the benzene ring in SDBS is located at the polar end of the detergent rendering it unfavorable for interacting with the nanotube. Furthermore, their analysis has revealed that bile salt detergents (SDC, STDC and SC) are highly effective in dispersing SWCNTs before centrifugation. In order to probe the stability of the dispersion and solubility of the nanotubes, the dispersed nanotubes have been characterized by Raman, nIR emission and UV/Vis/nIR absorption spectroscopy after ultracentrifugation which serves the purpose to remove coarse aggregates and nanotube bundles. In the case of the bile salts, the absorption, emission and Raman intensity is high, yielding well resolved features strongly supporting also efficient individualization. This superior dispersion behavior has been ascribed to the ability of the bile salts to stack into ordered layers due to the hydrophobic and hydrophilic face of the apolar half of the molecule: depending on the position of the hydroxyl group in the semi-rigid cholesterol unit the molecule has a more polar and a more apolar side. The high ability of the bile salts to form stable nanotube dispersions and solutions has also been confirmed by other groups [33–35].

The solubilization and individualization of SWCNTs in aqueous solutions of SDBS, SDS and SC can be probed by photoluminescence mapping [36], as fluorescence is known to be quenched in nanotube bundles. It has been indicated that SDS and SC preferentially solubilize smaller-diameter nanotubes, while SDBS shows no significant diameter selectivity within the range of $d = 0.83–0.97$ nm.

Within the group of the nonionic surfactants an increase in the molecular weight has a positive impact on the dispersability of nanotubes [37]. This behavior is traced back to the lack of Coulomb repulsion in the head groups resulting in the long and/or branched disordered polar chains (usually poly(ethylene glycol)) to be the key factor in nanotube dispersability.

As outlined in the section above, the results especially concerning the adsorption mechanism partly appear contradictory, nicely demonstrating that the dispersability and solubility of carbon nanotubes is highly sensitive to the environment and the dispersion parameters, e.g. ultrasonication power and time [38], centrifugation or precipitation conditions, temperature, etc. Furthermore, it has been shown that the concentration of the nanotube [39], as well as the detergent [40, 41] has a tremendous impact on both, the quality of the dispersion and the general dispersion behavior. The composition of the pristine nanotube material (amount of impurities, diameter distribution, etc.) constitutes a further impediment towards comparability [38].

In a systematic study, the effect of purification, sonication time and surfactant concentration on the dispersability of SWCNTs in an aqueous solution of SDBS has also been investigated [42]. It has been revealed that the purification method has an impact on the surface properties of the nanotube, e.g. the point of zero charge (PZC). However, the introduced positive or negative charges on the nanotube, being dependent on the pH, only influence the interaction with the negatively charged SDBS molecules at pH values far from the PZC, indicating that the nanotube-detergent interactions are hydrophobic in nature. Further adsorption studies have shown that, at saturation, the detergent molecules cover the nanotubes as monolayer with the tails oriented vertically on the surface. This indicates that the nanotubes are rather dispersed by adsorption of the SDBS molecules than by enclosing the SWCNTs in cylindrical micelles. It has also been pointed out that the sonication time plays a key role in nanotube dispersion and dissolution, as dispersion remained ineffective without the aid of sonication. Finally, the investigations have unveiled that nanotubes can be dispersed in an aqueous solution of SDBS below the critical micelle concentration (cmc) of SDBS further underlining that the formation of micelles is not a requirement for suspendability. The dispersability of the nanotubes reaches a maximum at [SDBS] = 2.5 mM (0.87 wt%) under the experimental conditions chosen.

Based on preliminary research on the zeta potential of aqueous nanotube dispersions [43], Coleman and coworkers [44] have been able to relate the zeta potential of detergent coated SWCNTs to the quality of the dispersion. The zeta potential in colloidal science can be defined as the electrical potential in the vicinity of the surface of the colloid dispersed, e.g. the nanotube. By a detailed atomic force microscopy (AFM) analysis on nanotubes dispersed in SDBS, SDS, LDS, TTAP, SC and fairy liquid (a common kitchen surfactant) they have quantified the quality of the dispersion by four parameters: the saturation value (at low concentration) of the root-mean-square bundle diameter, the maximum value of the total number of dispersed objects per unit volume of dispersion, the saturation value (at low concentration) of the number fraction of individual tubes and the maximum value of the number of individual nanotubes per unit volume of dispersion. They have included the four parameters in a metric, allowing quantification of the quality of the dispersion. The dispersion quality metric scales very well with the zeta potential decreasing in the following order: SDS > LDS > SDBS > TTAB > SC > fairy liquid. Dispersion and solubilization of nanotubes by ionic surfactants imparts an effective charge on the nanotube, stabilizing the nanotubes from reaggregation due to electrostatic repulsion. Thus, it is reasonable that higher zeta potentials are related to an increased stability of the dispersion. This means that the number of adsorbed surfactant molecules per unit area of tube surface should be maximized. In a preliminary study, White *et al.* [43] have demonstrated that the zeta potential of a dispersion of nanotubes in SDS augments with increasing the SDS concentration (for a fixed nanotube concentration). Furthermore they have shown that the zeta potential is increased when reducing the chain length of the detergent. Both observations are consistent with the zeta potential scaling with the total charge in the vicinity of the nanotube. Typical values of the zeta potential in the study range from –20 mV for the SC solution to –72 mV for the LDS dispersion (for a nanotube concentration of 0.065 g/l) [44]. It has clearly been outlined that the dispersion quality can presumably be significantly improved by using surfactants coating the nanotubes to give hybrids with magnitudes of the zeta potential of 100 mV and higher.

Additionally to the readily available detergents, bifunctional polycyclic aromatic compounds are also excellent candidates for the dispersion/dissolution of nanotubes. In principal, a strong and specific interaction with the nanotube can be ensured *via*

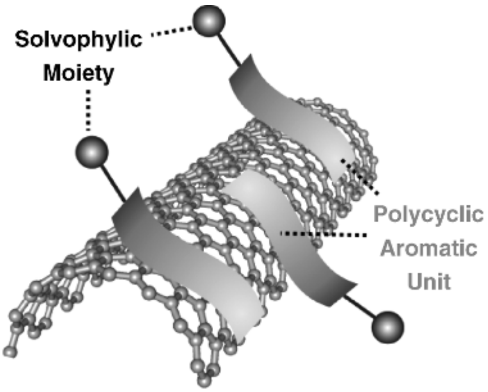
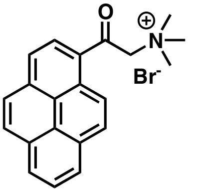


Figure 1.6 Concept of nanotube dispersion by polycyclic aromatic compounds equipped with a solvophylic moiety

π-π-stacking which is, in many cases, favorable over the nonspecific hydrophobic interaction being exploited by detergents. Water solubility is provided by solvophylic moieties covalently attached to the aromatic backbone of the dispersing agent (Figure 1.6).

Pyrene derivatives, especially trimethyl-(2-oxo-2-pyrene-1-yl-ethyl)-ammonium bromide **14** are prominent examples nicely underlining the effectiveness of this concept. It has been demonstrated that **14** is capable of dispersing and individualizing both as-produced and purified SWCNTs under mild dispersion conditions [45, 46]. Photoluminescence measurements have revealed that a significant red-shift of the nanotube spectral features occurs, being indicative for the π-π-stacking interaction. Furthermore, semiconducting nanotubes in the diameter range of 0.89–1.00 nm are preferentially individualized. TEM results have indicated that purification of the raw nanotube material occurs upon dissolution in **14**, as fewer catalyst particles are observed compared to nanotubes dispersed in an aqueous solution of HTAB. Since the finding of **14** being an excellent nanotube solubilizer, the pyrene moiety has widely been applied as noncovalent anchoring group, for instance, for the immobilization of fullerenes, proteins, porphyrins and metal nanoparticles (ref [25] and references therein).



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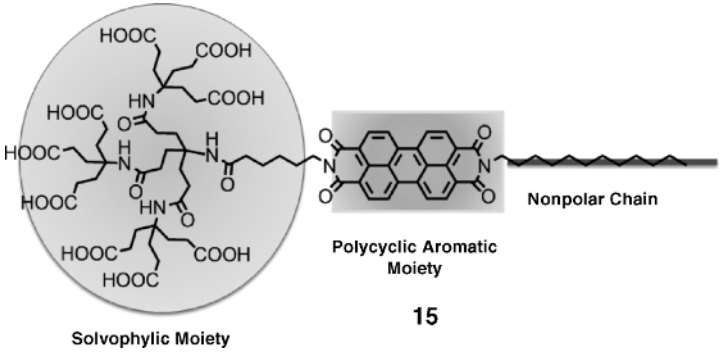
The dispersion of SWCNTs by noncovalent functionalization with ionic pyrene and naphthalene derivatives has been explored [47]. The nondestructive nature of the interaction has been confirmed by UV/Vis/nIR absorption, emission and Raman spectroscopy, as well as by X-ray photoelectron spectrum (XPS). Presumably, charge transfer from the adsorbate to the nanotube takes place, as a shift to higher binding energies in the XPS C1s core level spectra has been observed. The presence of a free amino group, especially in the case of the naphthalene derivatives, plays a key role in the dispersion process due to an increased interaction with the nanotube. Thus, specific interactions between the adsorbate's substituents, e.g. by charge transfer and cation-π interactions additionally to the π-π-stacking interaction has been unveiled as important, especially in the case of rather small aromatic molecules. Furthermore, the XPS measurements have shown that the ionic surface charge density on the nanotubes in the composites is almost constant indicating that electrostatic repulsion between the adsorbate molecules is the limiting factor for noncovalent functionalization of SWCNTs with water soluble polycyclic aromatic compounds.

Furthermore, water soluble perylene bisimide derivatives are highly effective in individualizing SWCNTs [48]. The perylene derivative **15** represents a novel class of SWCNT surfactants, as it can be regarded as three-component molecule bearing a 2G-Newkome dendrimer as solvophylic moiety, a perylene bisimide unit for interacting with the nanotube surface *via* π-π-stacking interactions and an aliphatic tail responsible for the highly amphyphilic nature. In fact, it has previously been shown by cryo-TEM that **15** forms regular micelles with a diameter of approximately 16 nm in buffered aqueous media (pH = 7.2) [49].



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After sonicating SWCNTs immersed in a buffered aqueous solution of **15**, with a concentration as low as 0.01 wt%, stable dispersions are formed. After centrifugation (25 000 g), the population of individual SWCNTs is much higher compared to nanotubes dispersed in a solution of SDBS, under the same experimental conditions, as demonstrated by statistical AFM analysis. Adsorption of the perylene unit of **15** has been indicated by the red-shift of the characteristic absorption and emission features of the nanotubes. This has further been supported by the fluorescence quenching of the perylene unit. Cryo-TEM imaging has also underlined the high degree of individualization and revealed that less catalyst particles are present when nanotubes are dispersed with the perylene bisimide derivative **15** compared to a dispersion of nanotubes in SDBS (Figure 1.7).

Additional to pyrene **14** and perylene **15**, porphyrin derivatives represent a third class of polycyclic aromatic surfactants to aid the dispersion of nanotubes in water or organic solvents (see Section 1.3.1.3). Porphyrin derivatives are highly efficient in constructing SWCNT-nanohybrids. However, only the water-soluble porphyrin derivative **16** (*meso*-(tetrakis-4-sulfonatophenyl)porphyrin) will be mentioned in this section. It has been demonstrated by fluorescence and absorption spectroscopy that the free base of **16** is

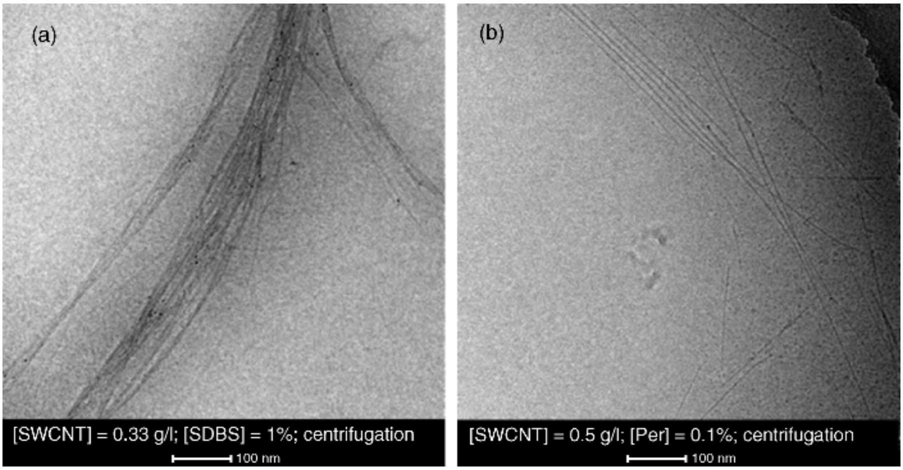
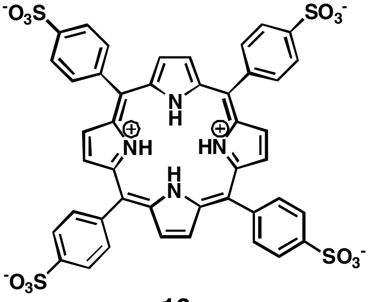


Figure 1.7 *Representative cryo-TEM images of SWCNTs dispersed in an aqueous solution of (a) SDBS and (b) perylene* ***15****. Reprinted with permission from reference [48]*

responsible for dispersing SWCNTs in water [50]. The stabilizing interaction upon adsorption of the porphyrin to the nanotube sidewall renders protonation to the diacid form more difficult. At pH = 5, the nucleation of *J*-aggregates being unstable in solution cause the nanotube porphyrin complex to precipitate. Furthermore, the porphyrin functionalized nanotubes can be precisely aligned on poly(dimethylsiloxane) (PDMS) stamps by combing. Printing then allows transfer of the nanotubes to a silicon surface as imaged by AFM (Figure 1.8).



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1.3.1.3 Dispersion in Organic Solvents

Only limited research has thus far focused on the dispersion of nanotubes in organic solvents compared to water-based systems. Since carbon nanotubes are hydrophobic, they are expected to be wetted by organic solvents as opposed to aqueous media. However, pristine CNTs are colloidally dispersed only in a limited number of solvents, e.g. *o*-dichlorobenzene (ODCB) [51–55], *N*-methyl-2-pyrrolidone (NMP) [56–60], *N,N*-dimethylformamide

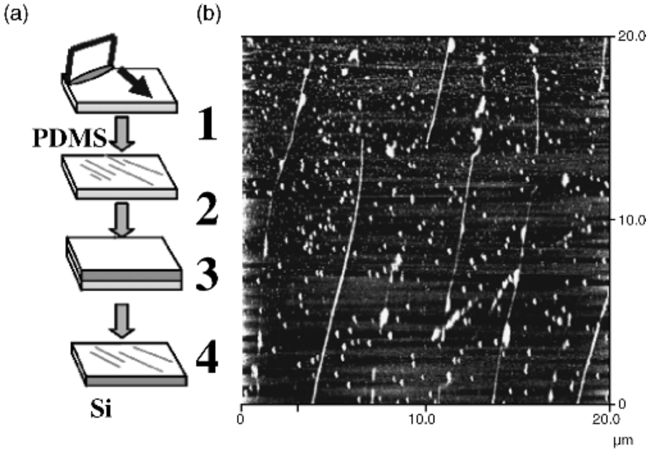


Figure 1.8 (a) Alignment of porphyrin functionalized SWCNTs onto PDMS stamps by combing followed by transfer printing of the aligned nanotubes onto a silicon substrate, (b) AFM image of aligned SWCNTs. Reprinted with permission from reference [50]

(DMF) [56–61] and *N,N*-dimethylacetamide (DMA) [57, 60]. Even though dispersion in such solvents is convenient, it is important to note that the stability of the dispersion is usually poor being accompanied by the formation of nanotube aggregates within hours or days.

Dispersability of carbon nanotubes in ODCB has been the topic of discussion, as ODCB was found to degrade upon sonication which is commonly used in carbon nanotube processing. In 2003 Niyogi *et al.* [53] have pointed out that the sonochemical decomposition and polymerization of ODCB results in additional stabilization of the nanotube dispersion. The dispersion stability has been found to be drastically reduced when adding ethanol which may act as radical quencher in inhibiting the polymerization of ODCB. Interestingly, if ODCB is allowed to polymerize sonochemically prior to the addition of nanotubes, the SWCNTs are not efficiently dispersed indicating that dispersion of nanotubes in ODCB upon sonication follows a more complex mechanism. This has further been supported by the observation that nanotubes are irreversibly damaged upon extended sonication in ODCB. Two years later Geckeler and coworkers [54] have demonstrated that by-products of sonochemical degradation of ODCB such as sonopolymers can be removed by ultracentrifugation (325 000 g). However, small oligomeric species are still present in the supernatant solution. After ultracentrifugation, they have found that nanotubes are highly exfoliated containing 85 % of individual nanotubes as shown by statistical AFM analysis. In a recent study, Moonoosawmy *et al.* have revealed that the electronic band structure of SWCNTs is disrupted by sonication in chlorinated solvents such as ODCB, dichloromethane, chloroform and 1,2-dichloroethane due to p-type doping [62]. Chlorinated solvents are sonochemically decomposed to form species like hydrogen chloride and chlorine gas. These, in turn react with residual iron catalyst often present in the SWCNT pristine material to form iron chlorides being identified as p-dopant by XPS. The doping behavior is characterized by a loss of intensity in the shoulder of the Raman G band, an increase in relative intensity of the G band, as well as an upward shift of the D* band. Furthermore, it has been recently demonstrated that nanotube dispersions in chlorinated aromatic solvents such as ODCB produced by mild sonication exhibit are highly light scattering, interfering with the acquisition of conventional absorption spectroscopic measurements [61].

Additionally to ODCB, HiPco SWCNTs can be dispersed and exfoliated in NMP without additional dispersants by diluting stock solutions [63]. The number fraction of individual nanotubes approaches 70 % at a concentration of 0.004 g/l as revealed by statistical AFM analysis, while the number density of individual nanotubes has a maximum at a concentration of 0.010 g/l. The presence of an equilibrium bundle number density has been proposed so that the dispersions self-arrange themselves and always remain close to the dilute/semidilute boundary. Optical absorption and emission, as well as Raman investigations have confirmed the presence of individualized SWCNTs at all nanotube concentrations and have underlined the conclusions drawn from the AFM analysis. The dispersions are stable against aggregation and sedimentation for at least two weeks as shown by absorption spectroscopy and AFM [63, 64].

Recently, it has been pointed out that γ-butyrolactone (GBL), often referred to as liquid ecstasy, is a suitable solvent for the dispersion and solubilization of SWCNTs [65]. In contrast to NMP, the dispersions show an anisotropic, liquid crystalline behavior at nanotube concentrations above 0.105 g/l as revealed by absorption spectroscopy, crossed polarized microscopy and scanning electron microscopy (SEM). The aligned liquid crystalline phase (Figure 1.9) can be removed by mild centrifugation. The upper limit of the pure isotropic phase has been detected to be at a nanotube concentration of 0.004 g/l. At intermediate concentrations, the dispersion can be regarded as biphasic. As shown by sedimentation and AFM measurements, the isotropic dispersions obtained after centrifugation are stable against aggregation. Since the degree of individualization is increased

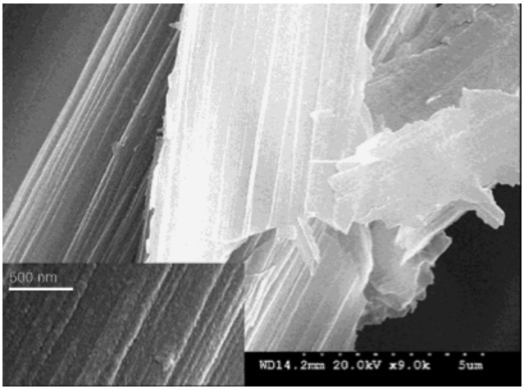
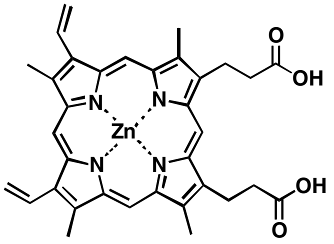


Figure 1.9 SEM image of SWCNT anisotropic phase after centrifugation of SWCNTs in GBL. Shown in the bottom left corner is a magnified region depicting aligned (gold-coated) bundles with diameters of the order of 100 nm. Reprinted with permission from reference [65]

in dispersions of low nanotube concentrations, the presence of an equilibrium characterized by a maximum number density of bundles has been suggested, similarily to the NMP dispersions described above. The maximum fraction of individual nanotubes, approaching 40% at a concentration of 0.6 mg/l, is however lower than for the NMP dispersions.

Before the discovery that GBL is a suitable solvent for nanotubes, it was widely recognized that the required characteristics for a nanotube dispersing solvent are large solvent-nanotube interactions relative to the nanotube-nanotube and solvent-solvent interactions in combination with the absence of ordering at the nanotube-solvent-nanotube interface. Ausman *et al.* [56], as well as Landi *et al.* [57] and Furtado *et al.* [59] have subsequently pointed out that nanotube dispersing solvents are characterized by a high electron pair donicity suggesting that a weak charge transfer from the nitrogen electron lone pair in NMP or DMF to the nanotube results in an increased solvent-nanotube interaction. Furthermore Landi *et al.* [57] have proposed that alkyl groups attached to the carbonyl group of the amide solvents stabilize the double bond character in the amide and thus the dipole moment resulting in a stronger solvent-nanotube interaction. However, both criteria are fulfilled by dimethylsulfoxide (DMSO) which is not a suitable nanotube dispersing solvent, while GBL matches none of the criteria. Based on these data, Coleman and coworkers have followed a different approach to shed light into the dispersion of nanotubes by organic solvents [66]. They have asserted that the ideal situation for the dispersion of nanotubes would be to find a true solvent where the free energy of mixing is negative, i.e. the solution is thermodynamically stable. They have pinpointed that nanotube dissolution is prohibited by the small entropy of mixing due to the large molecular weight and high rigidity of the nanotubes on the one hand and the positive enthalpy of mixing due to the strong mutual attractions between the nanotubes on the other hand. Thus, the goal is to find solvents leading to an enthalpy of mixing close to zero resulting in a slightly negative free energy of mixing. This would lead to spontaneous exfoliation of nanotubes without the aid of ultrasonication. They have clearly been able to demonstrate by optical absorption spectroscopy and AFM that this is the case upon diluting SWCNT-NMP dispersions, as a dynamic equilibrium, characterized by a significant population of nonfunctionalized individual nanotubes and small bundles, is formed. The exfoliation process is therefore concentration dependent and can be accelerated by sonication; however, sonication is not a prerequisite for the dissolution of nanotubes. In general, they have pointed out that nanotube dispersability is maximized in solvents for which the surface energy matches that of graphitic surfaces, finally answering the fundamental question of nanotube solubility in organic solvents and thus providing the cornerstone for solution based experimental and processing procedures in a two component system consisting of nanotubes and solvent only.

Similar to the concept of dispersion of nanotubes in aqueous media by the addition of dispersants, the dispersability of nanotubes in organic solvents can also be increased by designed additives. However, one main driving force for dispersion in aqueous media, namely the hydrophobic effect, cannot be exploited in this case. Nonetheless, some examples exist, e.g. porphyrins which have shown to also successfully disperse nanotubes in nonaqueous media. The first report appeared in 2003 revealing that zinc protoporphyrin IX (ZnPP; **17**) is capable of dispersing and also individualizing SWCNTs in DMF as shown by AFM and absorption spectroscopy [67]. The filtrated supernatant solution after centrifugation is redispersable in DMF supporting strong noncovalent interactions of porphyrin **17** with the nanotube sidewall.



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The dispersion of SWCNTs in toluene can be increased by the aid of small dye molecules such as terphenyl and anthracene [68]. The π-π-stacking interaction is indicated by the fluorescence quenching of the dye molecules in the nanotube composites. Interestingly, a Raman spectroscopic investigation has revealed the presence of vibrations in the composites that could not be detected in the starting materials, e.g. the nanotubes and the small dye molecules alone. Possibly, the modes arise from intrinsically IR active vibrations becoming Raman active in the composite.

Further investigations on dispersability of nanotubes in organic solvents include the use of tripodal porphyrin hosts to yield stable dispersions of SWCNTs in DMF also containing individualized nanotubes [69]. The same system has previously been shown to bind to C_{60} in a toluene solution to give supramolecular complexes with interesting 3D packing in the crystalline phase. Investigations by microscopic (TEM, SEM, AFM) and spectroscopic (Raman and emission) techniques were combined with density functional theory gas phase modeling to predict a model for the geometry adopted by the preorganized host in the presence of the nanotube guests.

In a supramolecular dispersion approach, a mixture of barbituric acid and triaminopyrimidine has been used for the solubilization of SWCNTs in DMF by sonication and a mechanochemical high-speed vibration milling technique [70]. Since neither barbituric acid nor triaminopyrimidine alone are capable of significantly increasing nanotube dispersability, the formation of a hydrogen-bonding network is responsible for multipoint interactions with the nanotube surface. Similarily, dispersion and precipitation of CoMoCAT SWCNTs can be controlled by using a copper complexed 2,2′-bipyridine derivative bearing two cholesteryl groups [71]. The copper complex shows a reversible sol-gel phase transition by changing the redox state of the Cu^{I}/Cu^{II} complexes. It has been revealed that the Cu^{II} complex is highly efficient in dispersing SWCNTs in chloroform attributed to the expansion of the π-conjugated system in the planar complex (Figure 1.10a). However, upon reduction of the copper Cu^{II} to Cu^{I} the nanotubes are precipitated due to the conformational change to the tetrahedral structure (Figure 1.10b). The precipitation can be reversed by oxidation with O_2.

Furthermore, oligomeric thiophene derivatives act as surfactants and dispersants for SWCNTs in NMP [72]. By systematic variations of the number of the head groups, the regioregularity of the head groups and the head to tail ratio, the structural design of the

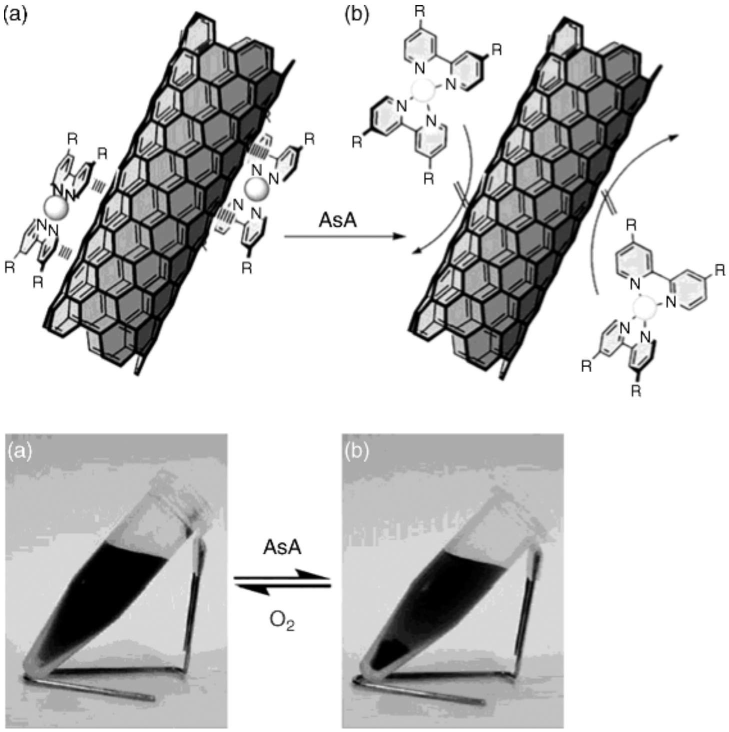
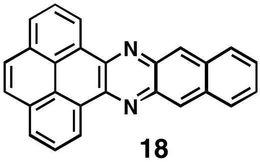


Figure 1.10 Schematic representation of the redox induced conformational change of a copper bipyridyl complex on a SWCNT (top) and the corresponding dispersions of SWCNT in chloroform: (a) the planar Cu^{II} complex is highly efficient in dispersing SWCNTs; (b) upon reduction by ascorbic acid (AsA) the conformation changes to tetrahedral structure which results in the precipitation of the nanotubes. Reprinted with permission from reference [71]

dispersants has been emphasized. The dispersability is improved by increasing the number of head groups in the oligomers. Regioregularity is also found to have an impact on the dispersion behavior of the nanotubes. Raman spectroscopy and XPS furthermore have indicated that a charge transfer from the SWCNT to the strongly electronegative sulfur atom in the thiophene head group is responsible for the strong adsorption of the dispersant on the nanotube sidewall which is responsible for the formation of high quality dispersions at dispersant concentrations as low as 0.1 g/l.

By relying solely on π-π-stacking interactions of an extended diazapentacene derivative **18** with the SWCNT sidewall, it has been demonstrated that stable nanotube dispersions in THF are formed in the presence of **18** as confirmed by AFM and optical spectroscopy [73]. Most interestingly, no solvophobic forces are exploited in this case as indicated by transient absorption measurements so that nanotube dispersions are formed by a noncovalent dispersion approach without alteration of the electronic properties of the SWCNT. This result also suggests that the shifts of nanotube absorption and emission features upon solubilization with aromatic dispersants are widely influenced by solvatochromic effects rather than by the π-π-stacking interaction itself.



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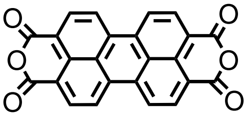
Just recently, a new concept for the exfoliation of SWCNTs in NMP and THF has been introduced in which a perylene dye intercalant is combined with a functionalized peylene derivative dispersant [74]. Owing to its flatness and aromaticity, 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA **19**) has been chosen as additive for the intercalation between the nanotube. The dispersion is then stabilized by a perylene bisimide derivative with polyethylene oxide (PEO) attached as tail group **20** to increase the solubility of the system. As evidenced by TEM and UV/Vis/nIR absorption spectroscopy, the nanotubes are well individualized at a weight ratio of SWCNT to additive of 1 at low concentrations of additives (0.1 g/l).



PTCDA
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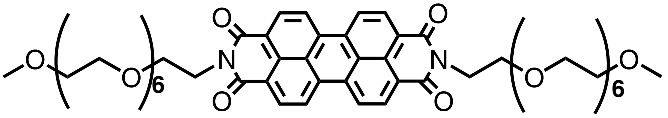

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As outlined in the section above, the prosperous field of nanotube dispersion in organic solvents has born possibilities to overcome the high mutual attraction between the nanotubes either by designed additives or new dispersion concepts. Apart from the monomeric and oligomeric additives described so far, it has also been recognized that polymeric substances are promising in exfoliating SWCNTs as outlined below.

1.3.1.4 Stabilization of Dispersions by Natural and Synthetic Polymers

Designed synthetic, as well as natural polymers such as DNA, peptides and proteins, carbohydrates and lipids partially exhibit excellent nanotube exfoliation capabilities, as will be summarized in the following paragraphs. In general, it is believed that polymers may wrap around a nanotube due to van der Waals and possibly π-π-stacking interactions as depicted by Figure 1.11.

Bioapplications of nanotubes have been predicted and explored ever since their discovery [75–78]. Thus, a combination of SWCNTs and biological molecules is highly desirable in many chemical and biological areas from the viewpoints of both fundamentals and applications. Among natural polymers, the most prominent candidate that exhibits superior SWCNT dissolution is single (ss) and double stranded (ds) DNA. The first publications on

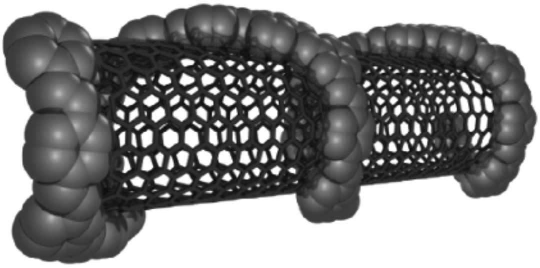


Figure 1.11 *Schematic representation of polymer wrapping on the sidewall of a SWCNT*

DNA-assisted dispersion of SWCNTs appeared in 2003 by Nakashima *et al.* for dsDNA [79], as well as by Zheng *et al.* [80] for ssDNA and short dsDNA. Both groups have revealed that DNA is highly capable of dispersing and individualizing SWCNTs in aqueous media. Simulation studies have shown that the nature of nanotube solubilization by DNA is based on nonspecific DNA-SWCNT interactions due to the nucleic acid base stacking to the nanotube sidewall with the hydrophilic sugar-phosphate backbone pointing towards the exterior, thus guaranteeing water solubility (Figure 1.12). The mode of interaction could thereby be helical wrapping and/or simple surface adsorption. The base stacking mechanism has been supported by the observation that polyadenine and cytosine strands, known to strongly self-stack in solution, exhibit lower exfoliation power than poly guanines and thymines [81]. In their first report, Zheng *et al.* [80] have also indicated that DNA based nanotube dispersions may be applied in the separation of metallic and semiconducting SWCNTs *via* ion-exchange chromatography, as shall be discussed later. To elucidate the nature of DNA interaction with the nanotube, the dispersions have been characterized in detail by fluorescence and Raman spectroscopic investigations revealing a strong diameter dependence of the DNA adsorption or wrapping, respectively [82, 83].

Interestingly, nanotube-DNA dispersions at high concentrations of nanotubes created by simple solvent evaporation have been reported to form a water-based nematic phase of unfunctionalized and freely dispersed SWCNTs [84]. This approach may be versatile in the construction of aligned nanotubes in macroscopic materials.

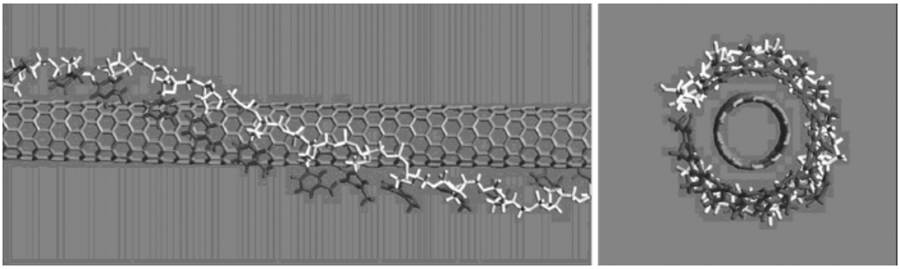


Figure 1.12 *Schematic representation of the helical wrapping binding model of a (10,10)-SWCNT by a polyt(T) DNA sequence. The bases orient to stack with the nanotube framework thus extending away from the sugar-phosphate backbone. Reprinted with permission from reference [80]*

In contrast to the study of Zheng *et al.* [81] having been carried out with nonnatural DNA with an optimal length of less than 150 bases preferably being constructed of guanine and thymine bases, a more recent investigation has focused on the use of long genomic DNA with more than 100 bases of completely random sequence [85]. It has been pointed out that the ability of ssDNA to form tight helices around SWCNTs with distinct periodic pitches is responsible for the dispersion of nanotubes. However, removal of the complementary ssDNA strands is a prerequisite for the wrapping mechanism. When following the same procedure with short 50-base oligomers with random base sequence, the dispersion capability is significantly reduced presumably due to the different folding characteristics of short ssDNA opposed to long genomic DNA.

Furthermore, it has been outlined that natural salmon testes DNA is indeed a powerful dispersing agent, as this additive is capable of exfoliating SWCNTs in water spontaneously, e.g. without the need of ultrasonication and ultracentrifugation by merely diluting a stock dispersion as revealed by statistical AFM analysis and photoluminescence spectroscopy [86]. At lower nanotube concentration, the amount of individualized nanotubes increases. The maximum number fraction of individual nanotubes reaches 83% at a nanotube concentration of 0.027 g/l.

In general, DNA-nanotube conjugates which combine the unique properties of SWCNTs with the sequence-specific pairing interaction and conformational flexibility of DNA have been extensively pursued [87–89] for their promising prospects in a number of applications, such as nanoscale devices, nanotube separation, biosensors, electronic sequencing and therapeutic delivery.

The second class of nanotube dispersants for biological applications has been presented by Dieckmann and coworkers who have designed an amphiphilic helical peptide they denoted as **nano-1** [90]. They have constructed their artificial peptide on the basis of the preliminary works of Wang *et al.* [91] who used phage display to identify several peptides with a high affinity for carbon nanotubes. An analysis of the peptide conformations has suggested that the binding sequence is flexible and folds into a structure matching the geometry of the nanotube [91]. Figure 1.13 schematically illustrates the structure of the peptide and its interaction with a SWCNT. When folded into an α-helix, as proposed on the basis of CD spectroscopy, the hydrophobic valine and phenylalanine residues in positions *a* and *d*, respectively, create an apolar surface of the peptide suitable for interacting with the nanotube sidewall. The introduction of polar residues in positions *e* and *g* generate favorable helix-helix interactions, while the oppositely charged residues in positions *b* and *f* provide favorable interactions between the helices from different peptides. Specifically the latter factor can be easily influenced by changing the solution's ionic strength resulting in controlled solubility characteristics, modulated by influencing peptide-peptide interactions. Nanotubes dispersed and exfoliated by **nano-1** can then be assembled into ordered fiber-like hierarchical structures [92], presumably by end-to-end connections [93].

Selective individualization of SWCNTs according to diameter has been achieved by reversible cyclization of artificial peptides [94]. After wrapping the peptides of specific lengths around the nanotube, a head to tail covalent bond formation has been induced between the thiol moieties of the peptide termini. Enrichment of certain diameters after the solubilization process has been monitored by absorption and Raman spectroscopy, as well as AFM. Moreover, peptide cross linking by the formation of amide bonds between amino acid side chains increases the stability of the nanotube dispersions and facilitates

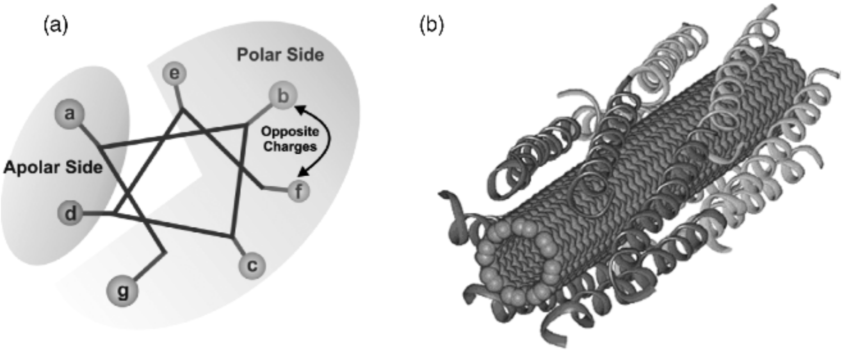


*Figure 1.13 (a) Schematic representation of the designed helical peptide **nano-1**. The residues in positions a and d are hydrophobic in nature thus creating an apolar side of the peptide presumably interacting with the nanotube; (b) model of the peptide wrapping of **nano-1** on the nanotube with head to tail alignment of helices in two adjacent layers. Reprinted with permission from reference [90]*

self-assembly into fiber-like structures [95]. Further investigations have demonstrated the importance of the aromatic content in the apolar side of the designed peptide, as it has been shown that the degree of nanotube exfoliation increases with an increasing amount of aromatic moieties indicating that π-π-stacking interaction plays an important role [96, 97]. Nanotubes are also spontaneously debundled by the artificial peptide **nano-1** similar to DNA-based dispersions [98]. However, the number fraction of individual nanotubes even surmounts that of the DNA-based dispersions, as the maximum reaches 95 %.

Apart from the designed peptides constructed by Dieckmann's group, other peptides have been studied with respect to nanotube adsorption and solubilization. A series of branched anionic and cationic amphiphilic peptides has also been discovered to efficiently solubilize SWCNTs in aqueous media as demonstrated by the aid of TEM and optical absorption spectroscopy [99]. A multifunctional peptide has further been used to disperse nanotubes and to direct the precipitation of silica and titania onto the nanotube sidewall at room temperature [100]. Highly exfoliated SWCNTs in water have also been obtained by noncovalent functionalization with designed peptides combining a combinatorial library sequence to bind to nanotubes with a rationally designed section to yield controllable solubility characteristics as evidenced by optical absorption and emission spectroscopy, as well as cryo-TEM imaging [101]. In contrast to previous works on nanotube solubilization by the aid of peptides having focused on maximizing the interaction of the peptide with the nanotubes, recent investigations have probed the fluorescence properties of SWCNTs dispersed in various custom-designed peptides [102]. It has been revealed that self-assembling properties of the peptide onto the nanotube scaffold are beneficial for the degree of dispersion on the one hand and for the preservation of the SWCNT emission features on the other hand. The brightest nanotube emission has been found for peptides that uniformly coat the nanotube which has been attributed to nanotubes templated self-assembly of the peptide dispersants.

Similarly to natural and artificial peptides, some proteins also interact with nanotubes and can thus be considered as promising candidates for nanotube solubilization. In an attempt to

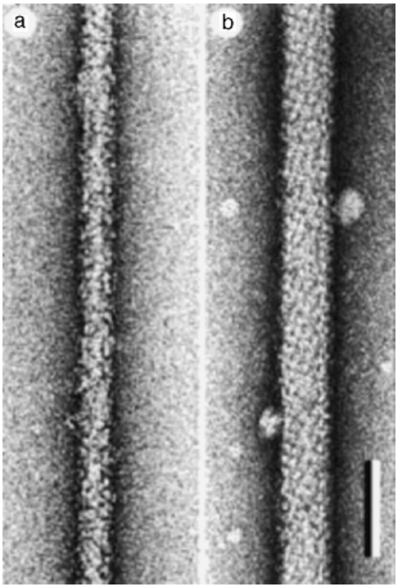


Figure 1.14 *TEM images of streptavidin immobilized on MWCNTs: (a) stochastic binding of streptavidin molecules on a MWCNT with a diameter smaller than 15 nm; (b) helical organization of streptavidin molecules on a carbon nanotube with a suitable diameter of 16 nm. The bar represents 50 nm. Reprinted with permission from reference [103]*

trace crystallization of proteins by electron microscopy, it was found that upon incubation of streptavidin in the presence of MWCNTs, the nanotubes are almost completely covered by the protein molecules under ideal conditions [103]. In some instances, the nanotubes showed lateral striations regularly spaced at 6.4 nm along with perpendicular striations suggesting that the streptavidin molecules were organized in a square lattice along the nanotube backbone (Figure 1.14).

In order to elucidate the adsorption mechanism of proteins on the nanotube sidewall, the structure and function of enzymes was probed [104], as the catalytic activity of enzymes requires the near complete retention of their native structure. The structure and therefore function of the enzymes is strongly influenced by the hydrophobic, nanoscale environment of a SWCNT, however with varying extend. As revealed by IR and circular dichroism (CD) spectroscopy, as well as AFM, α-chymotrypsin unfolds upon adsorption on the nanotube leading to a loss of its native activity. In contrast, soybean peroxidase retains 30 % of its activity due to the preservation of its three-dimensional shape underlining the complexity of the adsorption process of proteins on nanotubes.

It has further been shown that proteins do not only adsorb onto the nanotube backbone, but are also capable of acting as nanotube solubilizers in water as demonstrated by UV/Vis/nIR absorption, Raman spectroscopy and AFM [105]. Removal of the unbound proteins by dialysis leads to flocculation of the nanotubes indicating the presence of an adsorption-desorption equilibrium. Due to the rich functionality of proteins with respect to functional groups and biorecognition abilities, a protein based dispersion approach is highly versatile for the preparation of self-assembled nanostructures and nanobioconjugates.

Among nanotube biosurfactants, lysozyme, a well-studied antibactierial cationic protein, holds great promise for applications of nanotubes as optical pH sensors and in biomedical research, as nanotube exfoliation by lysozyme has been revealed to be highly pH sensitive [106]. Thus, the aggregation state of the nanotube can be reversibly tuned by varying the pH: the SWCNTs are highly debundled below a pH of 8 and above a pH of 11, while being aggregated in the pH range of 8–11. Furthermore, the secondary structure of the protein remains largely intact as indicated by CD spectroscopy.

Since the structural properties of proteins are highly complex compared to the well-defined characteristics of detergents, it is reasonable that the task of exploring the protein adsorption mechanism onto the nanotube backbone is tedious to resolve. One approach towards this topic was presented by a cryo-TEM investigation of the nanotube dispersion by bovine serum albumin (BSA) labeled with gold nanoparticles (GNP) to yield a high density contrast [107]. The TEM analysis has unveiled that the majority of the BSA-GNP complexes are distributed at distances of 20–80 nm from each other along the individually dispersed nanotube. Based on the cryo-TEM study in combination with AFM and CD techniques, it has been proposed that the BSA molecules are adsorbed on the SWCNT with their hydrophobic domains resulting in partial unfolding. Thus the majority of the ionized residues interact with the solvent.

In analogy to monomeric carbohydrates that have been introduced as nanotube surfactants as outlined in Section 1.3.1.2, oligomeric and polymeric carbohydrates also induce nanotube exfoliation to achieve solubilization in aqueous media. The first report was presented by Star *et al.* who have shown that SWCNTs are effectively solubilized by common starch, provided starch is activitated towards complexation by wrapping itself helically around small molecules [108]. This is nicely reflected by the observation that SWCNTs are insoluble in an aqueous solution of starch, while being dispersed and individualized in an aqueous solution of a starch-iodine complex due to the preorganization of the amylose in starch into a helical conformation by iodine. The solubilization process is reversible at high temperatures and preferred for nanotubes compared to amorphous carbon and catalyst particle impurities. Since addition of glucosidase to the starched nanotubes results in precipitation of the SWCNTs, starch wrapping gives access to a completely nondestructive purification route.

SWCNTs are also solubilized by the aid of amylose in a DMSO-water mixture [109]. In an optimal procedure, SWCNTs are presonicated in water to partly exfoliate the nanotube bundles, followed by addition of amylose in a DMSO-water mixture to maximize cooperative interactions between the nanotubes and amylose leading to solubilization. The ideal solvent condition is 10–20 % DMSO, in which amylose is characterized by an interrupted loose helix indicating that the helical organization of amylose is not a prerequisite for nanotube solubilization.

Among carbohydrates, β-1,3-glucans such as single-chain schizophyllan and curdlan, also effectively disperse as grown and cut SWCNTs [110, 111]. In the case of cut SWCNTs, mainly nanotube bundles are dispersed, while exfoliation occurs for as-grown nanotubes. Upon adsorption of the β-1,3-glucans, a right-handed helical superstructure is formed on the nanotube backbone with two carbohydrate chains twining one nanotube.

Sodium carboxymethylcellulose, an etherified derivative of cellulose, is a promising candidate for increasing nanotube processability, as it does not merely highly exfoliate nanotubes in solution, but also retains the individualized state upon film formation.

Significantly, the nanotubes in the films tend to align as demonstrated by considerable dichroism in their absorption spectra. These homogeneous thin films of high quality constitute a further step towards the development of nanotube based optical devices with wavelength tuning capability.

Another example of a carbohydrate nanotube dispersing additive is presented in chitosan and its derivatives [33, 112–116]. The great value of chitosan and its derivatives lies in the biocompability and their use as biosensors. The dispersion state of the nanotubes can be controlled by applying pH changes as stimulus: chitosan disperses nanotubes in acidic aqueous media, while an inverse dispersion behavior is observed for N-succinyl chitosan, as nanotube precipitate below a pH of 4.66. Carboxymethyl chitosan allows dispersion below a pH value of 6.7 and above 7.3 and 2-hydroxypropyltrimethylammonium chloride chitosan allows nanotube dispersion in the pH range of 2-12 [115]. Furthermore, *o*-carboxymethyl chitosan (OC) and OC modified by poly(ethyleneglycol) at the COOH terminus are effectively exfoliating SWCNTs in neutral pH solutions completing the picture of pH sensitive dispersion of nanotubes [116].

Among natural polymers, gum arabic, a natural, highly branched polysaccharide with a small amount of arabinogalactan-protein complexes, has also been unveiled as excellent additive for nanotube dispersion and exfoliation as shown by cryo-TEM and HRTEM [117].

Owing to their amphiphilic nature, lipids can be used for the solubilization of carbon nanotubes. Based on solubility and TEM investigations, a half-cylindrical binding mode has been suggested for lysophospholipids such as lysophosphatidylcholine LPC 18:0 and lysophosphatidylglycerol LPG 16:0 [118]. In the TEM study, a periodic wrapping in the lipid phase has been observed with the size and regularity of the striations being dependent on the polarity of the lysophospholipid as denoted by Figure 1.15.

After performing molecular dynamics simulations, the same authors have concluded that the adsorption of the lipids on the SWCNT varies from the proposed hemimicellar adsorption mechanism, as this organization requires the lipid micelles to break from the middle and to reassemble in tandem onto the nanotube backbone. They have pointed out that the lipids are organized into ‘crests’ consisting of several lipid layers shifted along the tube axis and packed in parallel and antiparallel directions that wrap the nanotube spirally [119].

Recently, it has been discovered that SWCNTs are also debundled by natural polyelectrolytes like sodium lignosulfonate, humic acid, fulvic acid and tannic acid [120]. This does not appear to be surprising, as natural polyelectrolytes are generally amphiphilic in nature comprising a mixture of amorphous, polydispersed organic polyelectrolytes of mixed aliphatic and aromatic constituents in which the aromatic moieties are known to interact *via* π-π-stacking interactions, as demonstrated for the solubilization of C_{60}-fullerene [121]. Most remarkably, SWCNTs are exfoliated at polyelectrolyte concentrations as low as 0.15 g/l as demonstrated by various spectroscopic and microscopic techniques.

In general, dispersion of CNTs in synthetic polymers is highly desirable, as it enhances the intrinsic properties of the polymer due to the outstanding electronic and mechanical properties ascribed to the nanotubes. To fully exploit the potential of the reinforcing procedure, nanotubes need to be individualized in order to be homogeneously distributed in the polymer matrix. Commonly, exfoliation is aided by the presence of aromatic moieties in the polymer (Fig. 1.16). The reports on dispersion of nanotubes in polymers are numerous and merely some can be considered here.

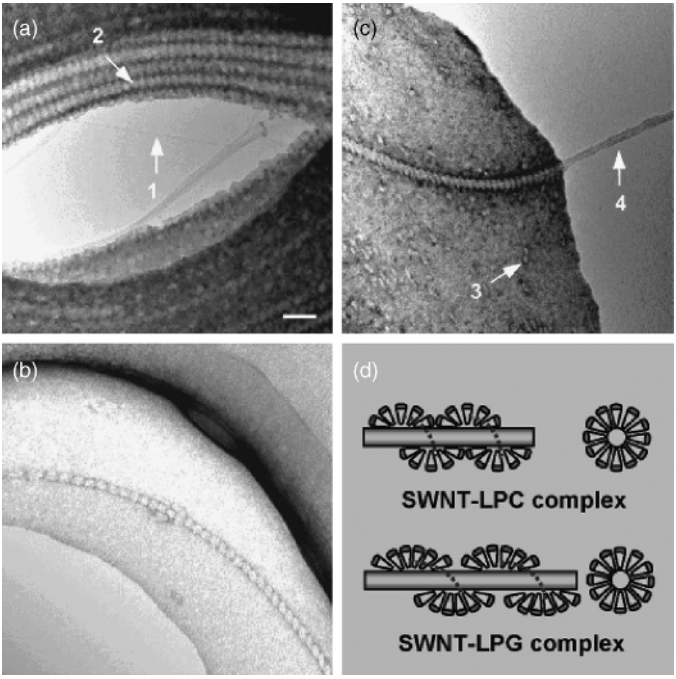


__Figure 1.15__ TEM images of SWCNT-LPC (a and c) and SWCNT-LPG (b) complexes. Numbers in a and c correspond to (1) an isolated SWCNT in the vacuum phase, (2) an LPC striation on an SWCNT/SWCNT bundle, (3) possibly an LPC micelle on the substrate in the lipid phase, and (4) an uncoated SWCNT bundle in the vacuum phase. Note the less organized and wider striations of SWCNT-LPG complexes in (b), as compared to those in (a) and (c) for SWCNT-LPC. Scale bar: 20 nm (same for a–c). (d) Hypothesized microscopic binding modes of LPC and LPG with SWCNTs. The lysophospholipids are shown as truncated triangles, their headgroups are shown in black, and the SWCNTs as gray bar. The left section of (d) illustrates the proposed lipid spiral wrapping along the tube axis, while the right section shows their possible binding along the circumference of the tubes. Reprinted with permission from reference [118]

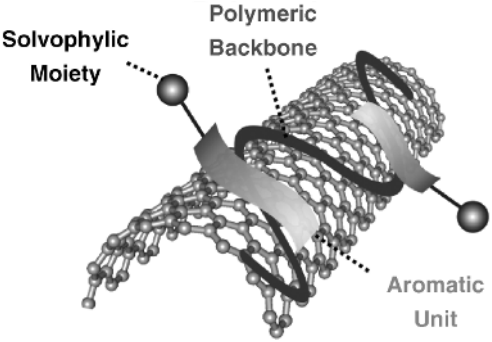


__Figure 1.16__ Solubilization concept for the dispersion of SWCNTs by aromatic polymers

Early reports have focused on nanotube composites with PPV (*p*-phenylenevinylene) [122], as PPVs exhibit interesting optoelectronic properties and may be applied as light-emitting semiconductor in organic light emitting devices [123]. Especially the structural analogue PmPV (poly-*m*-phenylenevinylene-*co*-2,5-dioctoxy-*p*-phenylenevinylene) can be used as additive to form stable nanotube dispersions in organic solvents such as chloroform. The SWCNT/PmPV hybrids increase the conductivity of undoped PmPV by eight times while maintaining the luminescence properties [124–126] which allowed production of photovoltaic devices [126] and the application as electron transport layers in organic light emitting devices [127]. For further details on this subject the reader is referred to several review articles concerned with this topic [6, 11, 12, 25, 128].

By using polymers carrying polar side chains such as PVP (polyvinylpyrrolidone), PSS (polystyrenesulfonate) or bovine serum albumin, stable aqueous SWCNT dispersions are obtained [129]. The wrapping of the polymer around the nanotube has been shown to be robust not being dependent on the presence of free bulk polymer giving access to stable nanotube dispersions with concentrations up to 1.4 g/l. The wrapping and solubilization of the SWCNTs associated with the SWCNT-polymer interaction can be reversed by addition of an organic solvent such as THF. The addition of PVP also stabilizes nanotube dispersion in NMP allowing higher concentrations of nanotubes to be homogeneously distributed [130, 131]. Furthermore, especially oxidatively purified SWCNTs are efficiently dispersed in an aqueous solution of diamine-terminated oligomeric poly(ethylene glycol) [132].

Noncovalent functionalization of SWCNTs by designed conducting polymers essentially being based on PAmPV (poly{(5-alkoxy-m-phenylenevinylene)-co-[(2,5-dioctyloxy-p-phenylene)-vinylene]}) disperse nanotube bundles in organic solvents [133]. The formation of pseudorotaxanes has been achieved by PAmPV derivatives bearing tethers and rings, respectively, to yield threaded complexes which might be of interest for the development of molecular actuators and switches.

In contrast to polymer wrapping, SWCNTs are also dispersed in organic solvents by conjugated PPEs (poly(aryleneethynylene)s) which cannot wrap around the nanotube due to their rigid backbone [134]. Thus, dispersion has been attributed to π-π-stacking interactions. Advantageously, various neutral and ionic groups can be introduced onto the nanotube surface. The versatility of the π-π-stacking approach is also reflected in the dispersion of both SWCNTs and MWCNTs by a series of polymers containing a pyrene moiety to increase the interaction with the nanotube surface [135–140].

A very efficient route towards nanotube polymer composites based on polyimide has been presented by *in situ* polymerization in the presence of nanotubes [141–144]. In the case of a polyimide derivative equipped with sulfonic acid groups, exfoliated nanotubes in organic solvents have been obtained as revealed by fluorescence spectroscopy, as well as microscopic investigations [144].

As already previously indicated, amphiphilicity of the dispersing agent is beneficial. Accordingly, numerous block copolymers have been presented for nanotube dissolution [145–157]. A highly interesting nanotube dispersing blockpolymer is polystyrene-*block*-poly(4-vinylpyridine), as SWCNTs can be exfoliated both in polar and apolar solvents [158]. In the case of dissolution in toluene and other apolar solvents, the polystyrene block is exposed to the solution phase, while the poly(vinylpyridine) forms a micellar shell incorporating the nanotube when polar solvents are used as revealed by transmission electron microscopy.

As summarized above, systematic research has shed light into the dispersion and exfoliation of SWCNTs. However, dissolution of the nanotubes merely constitutes one step towards the realization of nanotube-based applications. An obstacle even greater to overcome is the polydisperse nature of the raw material. Thus, the following section is devoted to the separation of SWCNTs according to diameter and/or chirality.

1.3.2 The Role of Noncovalent Functionalization in Nanotube Separation

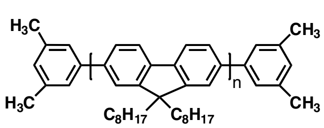
Even though the extraordinary potential of carbon nanotubes as new super materials especially in CNT-based electronics had been recognized soon after their discovery, integration of millions of nanotubes in functional circuits can thus far be merely considered a vision, as nanotube samples with defined electronic classification, or preferably single chirality with defined length are a prerequisite. Despite recent progresses in the field of controlled nanotube production [8], it is reasonable that this goal may not be achieved by controlled synthesis alone by considering the following aspects: SWCNTs are grown from metal catalyst particles widely defining their diameter. However, the futility of the exact chirality control by predefined catalyst particle size during synthesis can be imagined by recognizing that the diameter difference between a (10,10) metallic and a [9, 11] semiconducting SWCNTs is merely 0.03 Å. Furthermore, the high temperatures during nanotube production presumably induce thermal vibrations allowing variations in the SWCNT diameters even for identically sized catalyst particles. Thus, the development of post-synthetic separation techniques such as chromatography, electrophoresis and density gradient ultracentrifugation is deemed necessary and has received considerable attention in nanotube research [20, 159, 160]. Since exfoliation of the nanotube bundles is a precondition for efficient separation, noncovalent functionalization is highly versatile, as shall be discussed in the following sections on a variety of examples.

1.3.2.1 Selective Carbon Nanotube Interaction

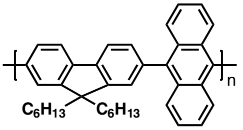
Additionally to the design of separation techniques, focus has been laid on the exploration of selective interaction of various molecules with SWCNTs according to electronic type, diameter and/or chirality, as differences between (n,m)-SWCNTs can thus be amplified aiding the separation process. Therefore, they shall be discussed first.

Based on preliminary works revealing that adsorption of linear alkylamines induces significant changes in the electrical conductance of oxidized semiconducting SWCNTs, while retaining the conductance behavior of metallic SWCNTs [161, 162], a separation method according to electronic type with the aid of octadecylamine has been proposed [163, 164]. The method relies on additional stabilization of oxidized semiconducting SWCNTs in THF by amines as opposed to their metallic counterparts allowing for the precipitation of the metallic SWCNTs. Most importantly, SWCNTs dispersed in THF/(octyl)amine solutions show the characteristic photoluminescence signals of individualized (semiconducting) nanotubes [165]. A multilaser Raman analysis of the enrichment process has shown that larger diameter metallic SWCNTs (above 1 nm) can be detected along with semiconducting nanotubes in the supernatant rendering separation less effective for laser ablation nanotubes with a higher average diameter as opposed to HiPco SWCNTs [164]. This behavior is related to amine assisted dedoping of the oxidized nanotubes and therefore the redox characteristics of the nanotubes. The reduction removes physisorbed counterions being accompanied with an increased organization of ODA in the case of the nanotube species remaining in the supernatant [166]. Conversely, enrichment of metallic SWCNTs in the supernatant has been achieved by a dispersion-centrifugation experiment of pristine SWCNTs in THF by the aid of propylamine and isopropylamine unveiling that amines preferentially interact with metallic SWCNTs, as long as they are not carboxy-functionalized [167, 168]. After five iterative dispersion-centrifugation steps, metallic nanotubes have been estimated to be enriched from 41% in the as produced mixture to 72% in the THF/propylamine supernatant solution.

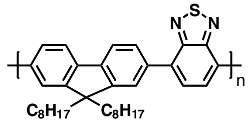
Selective interaction of SWCNTs produced by different techniques with fluorene based polymers has also been under investigation [169–172]. Hereby, different polymers have been shown to discriminate between nanotube species either by diameter or chiral angle. Upon dispersion of the nanotubes in toluene/polymer solutions, significant alterations of the nanotube photoluminescence features have been observed reflecting selective interaction depending on the polymer structure. Based on the optical properties of the nanotube dispersions, it has been concluded that PFO (poly(9,9-dioctylfluorenyl-2,7-diyl **21**) [169–172], and PFH-A (poly[(9,9-dihexylfluorenyl-2,7-diyl)-*co*-(9,19-anthracence)] **22**) [170] preferentially individualize SWCNTs with high chiral angle (> 24.5°), while PFO-BT (poly[9,9-dioctylfluorenyl-2,7-diyl)-co-1,4-benzo-{2,1′-3}-thiadiazole)] **23**) [169, 170, 172] exhibits diameter selective exfoliation in the range of 1.02–1.06 nm. However, the selective interaction is dependent on the solvent used for the dispersion. It has furthermore been revealed that overall solubilization follows the opposite trend to selective interaction, as more flexible conformations of the polymers allow more nanotubes to be dispersed, while at the same time reducing the selectivity [172]. Additionally, PFO **21** has been used as extracting agent for semiconducting SWCNTs in toluene assisted by ultracentrifugation allowing the fabrication of improved nanotube based field-effect transistors (FET) [173].



21
PFO



22
PFH-A



23
PFO-BT

Among biomolecules, a variety of additives have been suggested to promote selective interaction with specific SWCNTs. For example, SWCNTs can be threaded by large-ring cyclodextrins providing water solubility on the one hand and partial discrimination with respect to diameter on the other hand [174]. In a similar approach, diameter sorting has been achieved by reversible cyclization of designed peptides [94]. Artificial peptides containing thiol groups on the N and C terminus are capable of solubilizing and encircling SWCNTs within a certain diameter range (depending on the size of the peptide) by controlled formation of disulfide bonds on the termini with the advantage of avoiding dissociation of the peptide by the introduction of a covalent bond. Furthermore, individually suspended SWCNTs in aqueous media by adsorption of phosphatidylcholine are enriched in smaller diameter nanotubes as indicated by Raman spectroscopy [175].

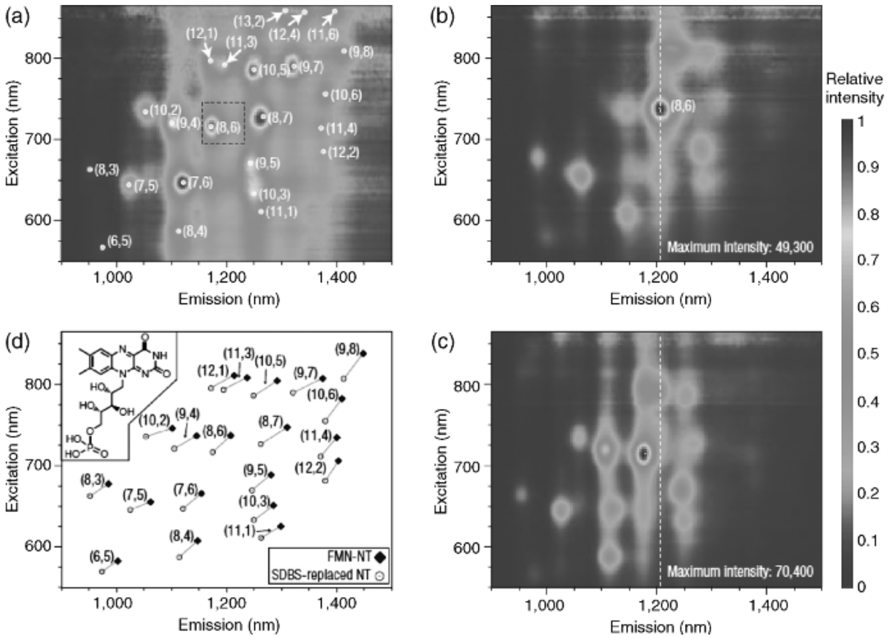


Figure 1.17 Photoluminescence emission maps of HiPco-SWCNTs dispersed in (a) SDBS, (b) flavin mononucleotide and (c) flavin mononucleotide after replacement with SDBS; (d) Plot of transitions for flavin dispersed SWCNTs (diamonds) and SDBS dispersed SWCNTs (circles). The inset in (d) represents the chemical structure of flavin mononucleotide. Reprinted with permission from reference [176]

Recently, the interaction of the common redox cofactor flavin mononucleotide with SWCNTs has been investigated [176, 177]. Due to cooperative hydrogen bonding between adjacent flavin moieties adsorbed on the SWCNT *via* π-π-stacking interaction, a helical ribbon organizes around the nanotube backbone, as demonstrated by HRTEM. Most interestingly, a strong chirality dependency in the interaction has been unveiled by replacing the flavin dispersant with SDBS. The replacement could be mapped by fluorescence spectroscopy, as π-π-stacking of the flavin induces a red-shift of the nanotube photoluminescence features, as demonstrated by Figure 1.16. The PLE map after complete replacement of the flavin from the nanotube sidewall (Figure 1.17c) reveals an enrichment of the (8,6)-SWCNT indicating that the (8,6)-SWCNT exhibits a profound affinity for the flavin helix. This strongly selective interaction can be exploited for enrichment of the (8,6) nanotubes (85 % enrichment value). For this purpose, an appropriate amount of SDBS was added to nanotubes dispersed in a solution of flavin mononucleotide to yield replacement of the flavin moieties on all chiralities except for the (8,6) nanotube. Since it has previously been reported that SDS suspended SWCNTs can be precipitated out of solution by addition of NaCl [178], all nanotubes being enclosed in SDBS micelles could be flocculated by the addition of NaCl to yield a nanotube sample highly enriched in a single chirality to remain in suspension.

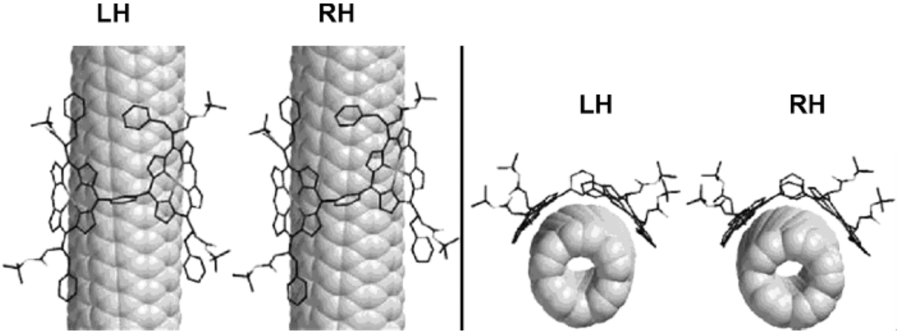


Figure 1.18 Schematic representation of the separation of left-handed (LH) and right-handed (RH) SWCNTs with a chiral diporphyrin derivative. Reprinted with permission from reference [182]

Another approach to achieve diameter selective enrichment of SWCNTs is presented in the concept of selective dispersion of the nanotube material by nanotweezers consisting of an anchor moiety shaped like a folded ribbon which adsorbs onto the nanotube sidewall and furthermore a solvophyilc moiety, as schematically depicted in Figure 1.2. This concept has been realized in the separation according to diameter in toluene by noncovalent functionalization with a pentacene-based molecular tweezer [179]. This nanotweezer principle has been expanded to the extraction of optically pure SWCNTs with the aid of chiral diporphyrins [180–182]. Figure 1.18 schematically illustrates complexation of a chiral diporphyrin preferentially solubilizing SWCNTs of a specific chirality. Thus, left and right-handed mirror images of chiral nanotubes can be separated. The resulting nanotube suspensions are distinguishable by circular dichroism after removal of the chiral extracting agents. The composition and the optical purity of the nanotubes can be tuned by varying the bridging moiety of the dispersing additives.

Furthermore, enrichment of metallic and semiconducting SWCNTs can be achieved on the foundation of the stronger interaction of bromine with metallic SWCNTs [183]. For this purpose, cut nanotubes dispersed in Triton X-100 have been treated with bromine which resulted in the formation of charge transfer complexes, preferentially with the metallic species. Due to the increased density of the complexes, the metallic nanotubes can be separated from the semiconducting counterparts by centrifugation.

Selective noncovalent functionalization of semiconducting nanotubes has been realized by porphyrin chemistry involving 5,10,15,20-tetrakis(hexadecyloxyphenyl)-21*H*,23*H*-porphyrin (THPP) [184]. Upon redispersing noncovalently functionalized SWCNTs in THF, it has been shown that the suspended nanotubes are enriched in semiconducting species, while the precipitate is enchriched in metallic SWCNTs after repeated extractions.

The concept of solubilizing SWCNTs by π-π-stacking additives has already been outlined as versatile approach for noncovalent functionalization of nanotubes. It is reasonable to assume that chirality recognition of nanotubes is possible, when a large enough aromatic moiety is chosen, as the π-π-stacking interaction may lead to preferred orientations along the nanotube backbone to ensure maximum p-orbital overlap. The fertility of this concept has recently been indicated by fluorescence spectroscopic investigations on the selective interaction of two aromatic amphiphiles with a pentacenic moiety and a quaterrylene moiety, respectively [185]. Upon adsorption of the pentacene-based amphiphile, the fluorescence of nanotubes with small to medium helicity angles is quenched, while it is retained for the quaterrylene-based additive.

Even though separation of nanotubes according to diameter and chirality by the supramolecular approaches described here is highly desirable, it suffers from the drawback that the nanotube complexes are not readily separated, as selective interaction does not necessarily result in enrichment of certain nanotube species without the additional use of well established separation techniques which shall be summarized in the following.

1.3.2.2 Chromatography

Chromatographic techniques are well established in chemistry and biology to separate materials on the molecular scale. Thus, it is not surprising that evaluating the suitability of chromatographic techniques for the separation and purification of nanotubes has commenced soon after their discovery. Focus has been laid on size exclusion chromatography (SEC), gel permeation chromatography (GPC), field flow fractionation (FFF) and ion exchange chromatography (IEC).

Size exclusion chromatography has shown to be effective in purification and length sorting of both MWCNT and SWCNT material. A prerequisite for SEC to be effective is the dispersion of nanotubes either by covalent [192] or noncovalent functionalization methods, e.g. encapsulation in surfactant micelles [186–189], or DNA wrapping [190, 191]. Length separation of SWCNTs has shown to be highly effective, when nanotubes are cut prior to injection in the SEC column [193]. Furthermore, purification and length sorting on oxidatively shortened SWCNTs was achieved without the addition of dispersing additives [194]. SEC can also be used to remove the unbound dispersing additives, e.g. DNA, yielding information about the stability of the noncovalently functionalized nanotubes in the absence of bulk dispersing agent [195].

In addition to SEC, length separation of zwitterionic functionalized SWCNTs has been achieved by GPC [196]. It has also been revealed that the purification efficiency of oxidatively shortened SWCNTs in THF could be improved by GPC [197]. Field flow fractionation, a separation technique where a field is applied to the mixtures flow allowing fractionation due to different mobilities of the various components in the electrical field, has also been successful in purification and length sorting of shortened SWCNTs [198–200].

Among chromatographic techniques, ion exchange chromatography is most promising, as it allows for the separation of SWCNTs according to diameter and/or electronic type. As previously described, SWCNTs can be efficiently individualized by DNA. After ion-exchange chromatography, nanotubes are separated by electronic type and diameter, as revealed by optical absorption, fluorescence and Raman spectroscopy [80, 83]. The differences in the optical properties are reflected by the distinguishable color of the fractions. Further investigations demonstrated that the sorting quality is strongly dependent on the DNA sequence [81], as the effective charge density of the DNA-SWCNT hybrid governs the separation process [201]. A major obstacle in the IEC separation of DNA-wrapped SWCNTs is presented in the broad length distribution of the SWCNTs, as separation is achieved by differential movement of the nanotubes stimulated by an external field. This problem has been overcome by combining SEC to obtain length separation with

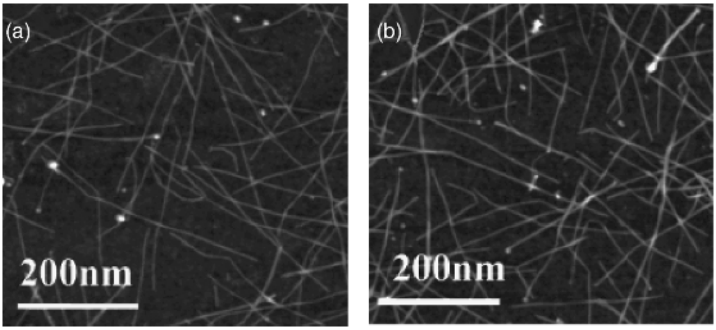


Figure 1.19 AFM images of DNA-wrapped SWCNTs sorted first by length in a SEC column, followed by diameter sorting by IEC. The AFM images are taken from different fractions after the IEC with an average diameter of 1.20 ± 0.11 nm (a) and 1.37 ± 0.14 nm (b). Reprinted with permission from reference [203]

IEC to refine the sorting by diameter and/or chirality [202, 203]. Thus, nanotubes with defined lengths and diameters are accessible, as exemplarily depicted by the atomic force micrographs in Figure 1.19. The versatility of this approach is particularly reflected by the successful separation of two nanotube species with the same diameter, but different chirality, namely the (9,1) and the (6,5) SWCNTs.

1.3.2.3 Electrophoresis

Since carbon nanotubes are similar in dimension to biomolecules, attempts to adopt separation techniques from life sciences such as electrophoresis have been undertaken. Electrophoretic separation approaches can be classified in conventional direct current (dc) electrophoresis on the one hand which is based on sorting nanotubes according to their different mobilities through a gel, capillary or solution upon applying an external electrical field and alternating current (ac) dielectrophoresis on the other hand which exploits the different polarizabilities of metallic and semiconducting SWCNTs. Apart from separation of nanotubes, dc electrophoresis [204–206] and ac dielectrophoresis [207–214] has been applied to align and deposit nanotubes in a controlled fashion – a crucial aspect for the fabrication of nanotube-based electronic devices.

In direct current electrophoretic separation, the mobility of the objects in the electrical field is regarded as a main driving force for separation. However, the charge-density differences between the nanotubes of different geometry dispersed in a surfactant solution is also expected to influence the movement in the external field. Since the total charge on the nanotube is defined by the surface area, the charge density differences are diameter dependent so that dc electrophoretic separation is theoretically capable of sorting SWCNTs by diameter. Thus far, separation of nanotubes according to diameter has not yet been realized by dc electrophoresis, even though length separation, separation of bundled and individualized SWCNTs, as well as purification of nanotubes dispersed in an aqueous solution has been achieved by capillary electrophoresis [215, 216]. The reproducibility of the experiments could be improved by adding small amounts of hydroxypropyl methyl cellulose during the dispersion process allowing to precisely evaluate nanotube size distributions which is valuable for the optimization of nanotube synthesis [217]. Similar results have been obtained when nanotubes are dispersed in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate prior to encapsulation in SDS micelles [218]. In analogy to capillary electrophoresis, length sorting of SWCNTs dispersed in sodium cholate [219] or RNA and DNA [220], as well as purification [221] is permitted by gel electrophoresis. Interestingly, the separation by length occurs alongside with some diameter selection, as the scission process during ultrasonication is diameter dependent, e.g. smaller diameter nanotubes tend to be cut to a higher degree.

Among electrophoretic techniques, alternating current dielectrophoresis holds most promise, as nanotube separation by electronic type may be accomplished. Based on the preliminary work on the deposition of nanotube bundles containing at least one metallic tube [222], Krupke and coworkers have been able to demonstrate that metallic nanotubes are selectively deposited between the electrodes in ac field, when a nanotube dispersion with a high degree of individualization is dropped onto the [223]. Upon subjecting nanotubes to an external electric field, a dipole moment is induced resulting in a translational motion along the field gradient which depends both on the dielectric constant of the nanotubes ε_{p} and solvent medium ε_{S}. The static dielectric constant for semiconducting HiPco nanotubes has been calculated to be less than 5, while that of metallic SWCNTs has been estimated to be around 1000 [224]. Since the dielectric constant of the solvent, in this case an aqueous solution of sodium dodecyl sulfate, is around 80, semiconducting nanotubes exhibit a negative dielectrophoretic force, e.g. they move towards the low electric field region, while the electrophoretic force in the case of metallic nanotubes is positive so that they move towards the high field region. Upon investigation of the deposited material by incident-light dark-field microscopy it has been shown that the Rayleigh scattered light is polarized perpendicular to the electrode revealing the alignment of the nanotubes.

The characterization by Raman spectroscopy indicates that up to 80 % of the deposited nanotubes are metallic. However, the Raman characterization of the deposited material has been questioned, as the resonant conditions may change due to bundling upon deposition [225–228]. Meanwhile, the enrichment of semiconducting nanotubes in the leftover suspension has been ascertained by repeated dielectrophoretic filtering of the metallic species, strongly supporting the proof of principle experiments [229].

Further experiments on ac dielectrophoresis on SWCNTS have demonstrated that the electrophoretic mobility of sidewall functionalized SWCNTs is strongly decreased suggesting that the dielectric function of the functionalized material is strongly altered [227]. Subsequent work has furthermore been able to show that the sorting efficiency is increased by increasing the frequency of the electrical field [230, 231] even though numerical calculations have suggested the use of low frequency fields [232], or by using a surfactant system composed of anionic (SDS) and cationic (HTAB) additives, as the surface charge on the semiconducting nanotubes is neutralized by this procedure [233]. It has also been demonstrated that metallic and semiconducting SWCNTs can be simultaneously separated and assembled in a multigap nanoelectrode setup to yield a sequential metallic-semiconducting-metallic multiarray structure [234].

Even though dielectrophoretic separation is highly promising in sorting SWCNTs by electronic properties, the method suffers from the disadvantage of limited throughput. In any case, dielectric spectroscopy on SWCNT suspensions allows rapid and accurate determination of both the dielectric properties of the SWCNTs, as well as the proportions of metallic and semiconducting nanotubes [235]. Nonetheless, several attempts have focused on upscaling the original setup by using larger electrodes [236] or making use of dielectrophoretic field flow-fractionation [237]. Furthermore, by the use of a radio frequency dielectrophoresis setup, nanotube films with a thickness of 100 nm can be constructed [238]. The carbon network at very large electrical fields is composed of aligned metallic and randomly oriented semiconducting SWCNTs as revealed by polarization dependent absorption measurements. The deposition of the semiconducting SWCNTs has been explained by a refined model which takes into account the longitudinal and transversal polarizability of the nanotubes.

1.3.2.4 Density Gradient Ultracentrifugation

The last postsynthetic separation technique to be discussed in this chapter is density gradient ultracentrifugation (DGU). The method exploits subtle differences in the buoyant density of the material to be separated. In principle, the sample is loaded into an aqueous solution with a known density gradient established by a gradient medium such as iodixanol, nycodenz or sucrose. Upon applying a centrifugal force, the species travel towards their respective isopycnic points, e.g. the position where their density is equal to that of the gradient. The spatially separated bands can then be fractionated.

If differences in the buoyant density were merely related to the diameter of the nanotube, larger diameter SWCNTs would have smaller density than smaller diameter nanotubes. However, as described by a hydrodynamic model [239], the thickness and hydration of the surfactant coating, as well as the eventual filling of the nanotubes with water [240], strongly alters the buoyant density. The choice of the surfactant is a crucial aspect for the nanotube sorting criteria by DGU. When a surfactant is chosen which uniformly coats all nanotubes equally, the sorting is related to the diameter. In this case, the density increases with increasing diameter (Figure 1.20a). If nanotubes are dispersed in a surfactant, or a combination of surfactants that exhibits preferences for some (n,m)-species, separation by properties beyond geometrical aspects, e.g. sorting by electronic structure may be achieved.

In a first report, enrichment of DNA-wrapped HiPco and CoMoCAT SWCNTs by diameter has been described [241]. Further works focusing on SWCNTs dispersed in conventional detergent solutions have demonstrated the versatility of the DGU approach [242–251]. Multiple possibilities for sorting of CoMoCAT, laser ablation and arc discharge SWCNTs according to diameter or electronic properties exist up to now, so that merely a few shall be summarized here. For example, sodium cholate encapsulated CoMoCAT nanotubes can be sorted by diameter as evidenced by the evolution of visibly colored bands as illustrated in Figure 1.20b [242]. Due to the high optical purity of the fractions, investigations concerning the photoluminescence quantum yields could be carried out revealing that the quantum yields exceed 1 % which is by a factor of 5 higher than previously reported for aqueous nanotube dispersions [243, 244]. Electronic-type separation has been achieved by using surfactant mixtures of SC and SDS. Most remarkably the position of the metallic and semiconducting fractions, respectively can be tailored by changing the ratio of the two surfactants, e.g. semiconducting nanotubes have a lower density when sodium cholate is the main surfactant [242, 252], while metallic nanotubes

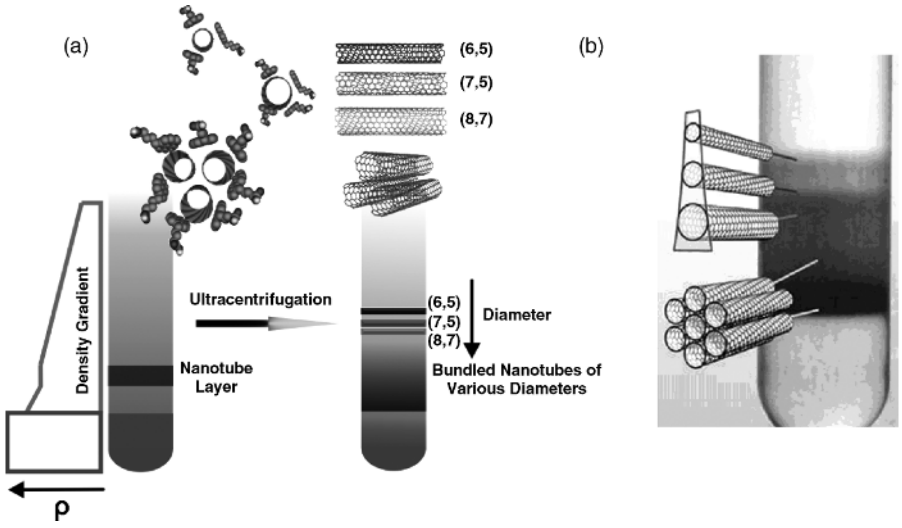


Figure 1.20 *Principle of density gradient ultracentrifugation on SNWTs. (a) Prior to ultracentrifugation surfactant encapsulated nanotubes are injected into an approximately linear density gradient. In the centrifugal field, the nanotubes move to the respective isopycninc points in the centrifuge vial resulting in separation according to diameter (or electronic properties). (b) The separation process is evidenced by the formation of colored bands. Reprinted with permission from reference [242]*

show a lower density with SDS as main surfactant and SC as cosurfactant [245, 249, 250, 253, 254]. The metallic fractions have been applied to the preparation of colored semi-transparent conductive coatings with colors varying between cyan, magenta and yellow, depending on the composition of the starting material [245, 249, 250, 253, 254]. The semiconducting counterparts allowed the fabrication of thin film nanotube transistors [252, 255]. Furthermore an assignment of the (n,m) indices is possible by the use of an aberration corrected transmission electron microscopic study [249].

As has been mentioned above, the sorting of SWCNTs according to electronic type in DGU has been attributed to inequivalent binding of two surfactants as a function of nanotube polarizability and therefore electronic type. This principle has been confirmed by electronic type sorting of narrowly distributed (n,m) SWCNTs by iterative centrifugation steps in a SDS-SC surfactant mixture without the aid of a density gradient [246].

The density gradient medium usually chosen for SWCNT-DGU is iodixanol which has the disadvantage of being equipped with iodine atoms potentially acting as electron acceptor. Furthmore, iodixanol is an expensive reagent and a rather large molecule causing problems when removing the gradient medium from the nanotube sample. Consequently, other gradient media deserve some attention. Recently, it has been demonstrated that electronic-type sorting also occurs in sucrose as gradient medium when temperature and surfactant concentration is adjusted [248].

Even though significant progress in DGU-based separations has been achieved, the sorting of HiPco SWCNTs has shown to be difficult due to the wide diameter distribution with small average diameters. Recently, two variations of the commonly used procedure have been reported which are potentially capable of overcoming this obstacle. One approach is based on a cosurfactant replacement DGU, where the initial perylene derivative surfactant **2** is replaced by SDS during the centrifugation procedure [256]. The second approach exploits the higher packing density of SDS on the nanotubes with increasing electrolyte concentration [251]. For this purpose, varying amounts of NaCl have been added prior to DGU which resulted in separation of HiPco SWCNTs according to electronic type, as SDS presumably preferentially adsorbs on metallic SWCNTs.

Finally, it is worthwhile mentioning that DGU on functionalized SWCNTs has revealed that the density of the covalently functionalized nanotubes is altered allowing separation of functionalized from nonfunctionalized SWCNTs which is an important step for precise reaction control [257]. Length sorting of nanotubes in DGU has also been reported by exploiting the transient motion regime, as opposed to the equilibrium regime which is approached for diameter and electronic-type sorting [258].

1.4 Conclusion

As indicated above, recent years have been affected by tangible progress in nanotube research, especially concerning their dispersion and separation according to diameter and/or chirality. This is nicely reflected by the number of publications in the vast field of nanotube research. Soon after the discovery of this novel super material by Ijima in 1991 [259], the number of publications about nanotube purification, production, functionalization, separation and application has risen exponentially reaching a number of approximately 10400 in 2008. Obviously the climax of this plot has not yet been reached and the progression resembles that of Moore's law.

It seems that the polydispersability problem which has been the major challenge so far will unambiguously be solved by the noncovalent approach in combination with selective growth and clever refinement techniques such as chromatography, electrophoresis and density gradient centrifugation. However, one should keep in mind that other obstacles still need to be overcome including the issue of scalability, alignment, process compability and economic aspects. Attention should furthermore be drawn towards establishing a standard for the precise determination of SWCNT purity. Thus, we are still somehow at the beginning so that following and participating in nanotube research will become even more exciting as time progresses.

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