Optical and Raman spectroscopy of carbon nanotube-based hybrid materials

Ph.D. dissertation

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Abstract

In this dissertation I present Raman, optical absorption and photoluminescence spectroscopy results on carbon nanotube-based hybrid materials formed by noncovalent interactions. Three types of structures are discussed: nanotubes wrapped with conductive polymers, C_{60}@SWCNT and coronene@CNT hybrids. i) I investigated the wrapping of nanotubes by various conducting polymers, and showed how the strength and nature of the interaction between the constituents of the hybrids can be estimated by observing the surface attenuated infrared absorption (SAIRA) effect. ii) I followed the synthesis of double-walled nanotubes via C_{60}@SWCNT systems to probe the host-guest interactions. iii) I applied the collected knowledge from wrapped and encapsulated systems to the synthesis and characterization of a coronene-nanotube hybrid material. I investigated the application of nanotubes as protective containers for luminophore storage, and as nanosize reactor vessels for templated graphene nanoribbon growth.
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List of notations and acronyms

The following notations are used in the thesis:

\[(n, m)\] chiral vector of the nanotubes
\[E_{ii}\] energy difference between the \(i\)-th Van Hove singularities
\[M_{ii}\] transition between the \(i\)-th Van Hove singularities of metallic nanotubes
\[S_{ii}\] transition between the \(i\)-th Van Hove singularities of semiconducting nanotubes
\[\tilde{\nu}_{\text{RBM}}\] Raman shift of the radial breathing mode
\[\text{guest}@\text{host}\] guest molecules encapsulated in the specified host nanotubes

The following acronyms are used in the thesis:

AGNR armchair graphene nanoribbon
ATR attenuated total reflection
CCD charge coupled device
CNT carbon nanotube
DOS density of states
DWCNT double-walled carbon nanotube
FIR far infrared
FT Fourier transformation
GNR graphene nanoribbon
IR infrared
JDOS joint density of states
MIR mid-infrared
MWCNT multi-walled carbon nanotube
NIR near infrared
NMR nuclear magnetic resonance
PAH polycyclic aromatic hydrocarbon
PANI polyaniline
PCz polycarbazole
PL photoluminescence
RBM radial breathing mode
SAIRA surface attenuated infrared absorption
sc-CO\(_2\) supercritical CO\(_2\)
SDS sodium dodecyl sulfate
SEM scanning electron microscopy
SWCNT single-walled carbon nanotube
(HR-)TEM (high-resolution) transmission electron microscopy
ZGNR zigzag graphene nanoribbon
Foreword

The electronic structure of carbon allows the formation of numerous allotropes. A majority of these, such as graphite or diamond, are well known and have been used for a long time in our everyday life. However, in the last few decades various new forms of carbon have been synthesized, and have had a crucial impact on the current nanotechnology research. The discovery of fullerenes [1] opened a new area of chemistry, and consequently lead to the identification of carbon nanotubes [2] and various other tubular structures such as nanobuds and nanocones. The next breakthrough was the isolation of graphene [3], which has long been used as a model material for theoretical studies. Research interest grew rapidly for these new forms of carbon due to their remarkable structural, electronic, thermal, and magnetic properties. These properties make them ideal candidates for various applications in electronics, composite materials, biological engineering, etc. One of the promising application perspectives of carbon nanotubes is that, owing to their rigid structure and one-dimensional hollow cavity, they can be used as "nanocontainers" or "nanoreactors".

This dissertation focuses on carbon nanotube-based hybrid materials formed by non-covalent interactions. First, I will give a broad overview about the properties of carbon nanotubes, which is followed by an introduction to their chemistry. In Chapter 2, I will introduce the theoretical background of the experimental methods and their application for the characterization of nanotube-based hybrid materials, followed by the description of arrangements and the devices that were used for the experiments.

Chapters 3 to 5 summarize the results regarding the carbon nanotube-based hybrid materials. The structures can be divided into two main categories: nanotubes having molecules attached to their outer surface, and having molecules encapsulated into their hollow inner cavity. Chapter 3 discusses hybrids formed by conducting polymers and carbon nanotubes, which represent the first category. Here I showed how the interaction strength between the investigated polymers and the nanotubes can be estimated based on their vibrational spectra. The following two chapters discuss hybrid structures of the second category. In Chapter 4, I will present wide-range optical and Raman studies on C_60@SWCNT systems and the double-walled carbon nanotubes prepared from them, and investigate the interaction between the host tube and the encapsulated species. Chapter 5 discusses a complex work on coronene-carbon nanotube hybrid materials. Two main topics are examined: the application of carbon nanotubes as protective containers for dye storage
and as nanoreactors for templated nanoribbon growth. Based on the knowledge gathered about the encapsulated and wrapped systems in the case of the other hybrid structures, I was able to distinguish between the encapsulated and adsorbed molecules, and found ideal conditions to produce well defined coronene@CNT heterostructures. I characterized the optical properties of the nanocontainers, and followed the polymerization reactions of coronene molecules inside the confined environment.
1. Introduction

In this chapter I will give an overview of the structural, electronic and vibrational properties of carbon nanotubes (CNTs). Properties of the other constituents of the hybrid materials, such as conductive polymers, fullerene, coronene and its oligomers, will be described in the corresponding chapters and their appendices for easier understanding. I will discuss the basic concepts of the chemistry of carbon nanotubes with an emphasis on the noncovalent interactions.

1.1 Carbon nanotubes

There is a wide range of hollow nanocontainers available, such as calixarenes, cyclodextrins, cucurbiturils, supramolecular or coordination cages, and bilayer vesicles. [4] The key feature that, in certain applications, makes carbon nanotubes superior to these, is the significantly higher mechanical stability and robustness. Carbon nanotubes can be used as protective packaging, as these hybrid systems are able to preserve the properties of the individual constituents, while the encapsulated species become more processable and mechanically stable in the cavity of the nanotubes. For instance, functional molecules such as fluorophores or pharmaceuticals can be encapsulated while the outer surface of the nanocontainer can be functionalized with specialized targeting agents according to the needs of application (e.g. targeted drug delivery, biomedical imaging). [5–8] The concave interior of the carbon nanotube has very low chemical reactivity, providing a good environment for chemical processes. Structure and size of the final products can be tuned via the adjustable diameter of the CNTs. These properties open a wide range of applications of CNTs from containers to active nanoreactors. [9]

1.1.1 Structural properties

A single-walled carbon nanotube (SWCNT) is conceptually built up by folding a graphene sheet into a cylinder. The microscopic structure of the nanotube is controlled by the diameter and chiral angle, which are uniquely determined by the folding vector, also called chiral vector. Nanotubes are described by the coordinates of this vector (given in units of the graphene base vector), generally referred to by using the \((n,m)\) chiral indices. [10]

\[
\mathbf{C} = n\mathbf{a}_1 + m\mathbf{a}_2
\]
1. Introduction

The diameter of single-walled carbon nanotubes is usually between 0.6 and 2 nm, but today’s production methods can reach almost the theoretical limit of the largest diameter of free standing nanotubes with up to 6 nm [11–13]. Double-walled carbon nanotubes (DWCNTs) consist of two concentric SWCNTs with interlayer separation close to the distance between graphene layers in graphite ($\approx 3.4 \, \text{Å}$). The number of walls in multiwalled carbon nanotubes (MWCNTs) varies in a wide range from approximately 3 to 200, depending on the preparation method. Different manufacturers offer tubes usually in the diameter range from 5 to 80 nm.

Depending on the requirements of the specific application, both single- and multiwalled carbon nanotubes can be used as nanocontainers or nanoreactors, but from the spectroscopic characterization point of view MWCNTs are very hard to investigate. Since this work will mainly focus on single- or double-walled carbon nanotubes, I will discuss their properties in more detail.

1.1.2 Electronic properties

The electronic structure of nanotubes shows unique features typical of low dimensional nanomaterials. As a result of quantum confinement the band structure shows levels comparable to those of molecules. The electronic structure of an SWCNT (Fig. 1.2) can be deduced from that of graphene by the zone folding approach. [10] Corresponding to the direction along the nanotube axis ($k_\parallel$) the wave vectors are quasi-continuous, but around the circumference of the nanotube ($k_\perp$) they are quantized.
1.1. Carbon nanotubes

Fig. 1.2: Zone folding of the 2D Brillouin zone of graphene. a) Tight binding band structure of graphene and the corresponding zone folding scheme that generates states satisfying the periodic boundary conditions for nanotubes. \( k_1, k_2, k_{\perp}, k_{\parallel} \) are the reciprocal unit vectors of graphene and nanotubes, respectively. The white lines indicate the allowed \( k_{\perp} \) values. b) The resulting states: metallic and semiconducting nanotubes and c) their density of states. The band gap energy is the difference between the energy of the bottom of the conduction band and the top of the valence band. The latter is indicated by blue / red filling.

\[
k_{\perp} = \frac{2\pi}{C} l
\]  
\hspace{1cm} (1.2)

where \( l \) has integer values from \(-q/2 + 1\) to \(q/2\). \( q \) represents the number of hexagonal cells in the unit cell of the carbon nanotube, and its value can be calculated by:

\[
q = \frac{2(n^2 + m^2 + nm)}{NR}
\]  
\hspace{1cm} (1.3)

\( N \) is the greatest common divisor for \( n \) and \( m \). \( R = 3 \) if \((n-m)/N\) is an integer, otherwise \( R = 1 \).  

Plotting the allowed wave vectors on the Brillouin zone of the graphene results in a set of parallel lines, which are defined by the chiral indices \((n,m)\). The electronic band structure of the nanotubes is given by the energies along the lines formed by the allowed wave vectors. Graphene is a zero-gap semiconductor, meaning that the conduction band and valence bands only intersect at the \( K \) point of the Brillouin zone. Whenever the \( K \) point is among the allowed states:

\[
\mathbf{K} \cdot \mathbf{C} = \frac{1}{3} (k_1 - k_2)(na_1 + ma_2) = 2\pi l \Rightarrow (n - m) = 3l
\]  
\hspace{1cm} (1.4)
1. Introduction

Fig. 1.3: Kataura plot shows the optical transition energy as a function of the diameter calculated in the tight binding approximation. Black dots belong to semiconducting, red dots to metallic nanotubes. [16,17]

the zone-folding approximation predicts metallic properties. If curvature is taken into account in more precise calculations, a small secondary gap exists in the case of non-armchair (n ≠ m) nanotubes. The energy of the curvature-induced band gap is inversely proportional to the nanotube diameter. [14]

The density of states (DOS) strongly depends on the dimension of a system. For nearly free electrons in parabolic bands in three dimensional materials the DOS is proportional to the square root of the energy, while it is constant in two dimensions. For one dimension it diverges as the inverse of the square root of the energy for \( k = 0 \), and for 0 dimension it is a \( \delta \)-function. In general, divergencies in the DOS always occur if the velocity of the electrons vanishes (flat part in the dispersion). These divergencies are called Van Hove singularities. These occur in the nanotubes at the bottom of the essentially parabolic bands. The optical absorption of nanotubes depends on the joint density of states (JDOS) and the selection rules determined by the nanotube symmetry (Sec. 2.2). The selection rules for light polarized parallel to the nanotube axis allow transitions symmetric to the Fermi level. These transitions are referred to as \( M_{11}, M_{22} \), etc. in metallic, and \( S_{11}, S_{22} \) etc. in semiconducting tubes. The numbers refer to indices of the Van Hove singularities participating in the transitions. Perpendicular to the tube axis the oscillator strength of the symmetry allowed transitions is negligible due to the antenna effect. [15] The energy separation of the Van Hove singularities (\( E_{ii} \)) depends on the chiral indices, which allows the identification of nanotubes. The Kataura plot (Fig. 1.3) shows the energy of the absorption maxima (\( E_{ii} \)) as a function of the tube diameter \( d \). The energies follow roughly \( 1/d \). The deviations from this trend reflect the chiral angle dependence. [16]
1.1. Carbon nanotubes

Tab. 1.1: The infrared- and Raman-active vibrational modes of SWCNTs. The number of modes and their symmetry are given.

<table>
<thead>
<tr>
<th></th>
<th>infrared-active modes</th>
<th>Raman-active modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>zigzag</td>
<td>1 $A_{2u}$</td>
<td>2 $A_{1g}$</td>
</tr>
<tr>
<td></td>
<td>2 $E_{1u}$</td>
<td>3 $E_{1g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 $E_{2g}$</td>
</tr>
<tr>
<td>armchair</td>
<td>3 $E_{1u}$</td>
<td>2 $A_{1g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 $E_{1g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 $E_{2g}$</td>
</tr>
<tr>
<td>chiral</td>
<td>1 $A_{2}$</td>
<td>3 $A_{1}$</td>
</tr>
<tr>
<td></td>
<td>5 $E_{1}$</td>
<td>5 $E_{1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6 $E_{2}$</td>
</tr>
</tbody>
</table>

1.1.3 Vibrational properties [18]

To first approximation the phonon modes of carbon nanotubes can be found by folding the Brillouin zone of graphene. The phonon dispersion relations depend on the chiral vector of the carbon nanotubes. The unit cells of the tubes having the same diameter but different chirality are very different in size, and, accordingly, the number of phonon modes varies greatly, so even tubes having similar diameters are expected to have very different vibrational properties. The number of modes can be predicted by group theory. The Raman-active modes are those transforming like the quadratic forms of the spatial coordinates ($xx$, $yy$, $zz$, $xy$, $yz$, $zx$), and the infrared-active modes are the ones whose irreducible representations transform like the vectors ($x, y, z$). The infrared- and Raman-active vibrational modes of carbon nanotubes are summarized in Table 1.1. The infrared and Raman frequencies depend on the tube diameter, the larger the tube the closer it approaches the graphene modes. A more accurate calculation based on line group symmetries can be found in Ref. [19].

1.1.4 Real carbon nanotube samples

Real CNT samples are a mixture of tubes with different length, diameter, and chirality. Depending on the production method they may contain catalyst residues, graphite, and amorphous carbon. Even though the preparation methods have improved significantly in the last decade, there is still no method for a large scale, cost-effective production of carbon nanotubes with well-defined, uniform structural properties. Chirality or semiconducting/metallic separated samples are available, but at very high cost.
1. Introduction

Growth methods

The traditional methods for CNT synthesis include laser ablation, arc discharge, and chemical vapor deposition (CVD). [2, 20–25] All growth processes have in common that they start from a carbon plasma which is formed by heating or chemical decomposition. By controlling the growth conditions (such as temperature, type of catalyst) single-, double- or multi-walled carbon nanotubes can be grown. In this work we used nanotubes produced by both arc discharge, P2-SWCNT (Carbon Solutions), and CVD method, CoMoCat CG SWCNT (SouthWest NanoTechnologies) and NC3100 MWCNT (Nanocyl). The growth process of the nanotubes does not influence the final properties of the hybrids discussed in this work, the different types of nanotubes were chosen based on their diameter distribution.

Samples are cleaned after production to remove the catalysts and other contaminants. The products obtained after cleaning and filtering are called buckypapers, containing bundles of carbon nanotubes. It should be considered when comparing samples that each batch of nanotubes even of the same brand is slightly different.

Toxicity

Many reports on endohedrally modified carbon nanotubes emphasize their importance in biological applications, such as pharmaceutical carriers in targeted delivery, imaging, diagnosis, and treatment tools. [6, 7, 26] Their long quasi-one-dimensional character enables them to enter the cells, while the hollow inner cavity is ideal for storage. However, it is very important to mention that the interactions between the cells and the nanotubes are not well understood yet, and there are several contradictory studies about CNT toxicity. The reason behind this contradiction is that carbon nanotubes exist in great variety, and their toxicity depends on the length, diameter, surface area, tendency to agglomerate, dispersibility in solution or presence and nature of catalyst residues. Chemical functionalization is used to make the nanotubes more biocompatible. The type, number, size, and bonding of functional groups all play a role in the interaction with the living environment. [27, 28] To produce biocompatible CNT-based hybrids, it is required to be able to characterize their structure in great detail, especially the interaction between the nanotubes and the functional groups, which can help to understand the differences occurring in the biocompatibility of these hybrids.

1.2 Chemistry of carbon nanotubes

Similar to graphene, nanotubes consist of $sp^2$ hybridized carbon atoms, although the curvature adds some perturbation (see below). A carbon atom has six electrons in the $(1s)^2(2s)^2(2p)^2$ configuration. In the ground state the two unpaired electrons in the outer
shell have the ability to bond, but since the energy difference between the 2s and 2p orbitals is less than the energy gain through C–C bonding, the 2s and 2p orbitals mix with one another in hybridized orbitals. In $sp^3$ configuration the carbon atom forms four bonds, arranged in a tetrahedral configuration (such as diamond). In $sp^2$ hybridization state (such as graphene) the s orbital combines with two p orbitals ($p_x, p_y$) forming three $\sigma$-bonds. The resulting structure is planar, having a characteristic bonding angle of 120°. The additional $p_z$ electrons form a planar delocalized $\pi$-electron system parallel to the plane of $\sigma$-bonds on both of its sides. Due to the delocalized $\pi$-electron system the strong van der Waals interaction between the CNTs renders them into bundles, and makes them virtually insoluble in common organic solvents and water. In order to harvest the full potential of the remarkable properties of carbon nanotubes, two major obstacles need to be overcome: separation, according to diameter or chirality, and uniform dispersibility in a solvent or matrix. To increase the processability of carbon nanotubes, chemical functionalization is needed.

Besides the functionalization of the outer wall, the hollow inner cavity presents an additional possibility for chemical modification of the nanotubes. It provides ideal environment for the encapsulated molecules either as a protective container or a nano-sized reaction vessel.

Interactions of CNTs with other atoms or molecules can be divided into five main groups: intercalation with ions, covalent attachment of sidegroups either directly to the sidewall or to defects, and noncovalent attachment either inside the tubes (encapsulation) or outside (wrapping or adsorption). Covalent functionalization allows attachment of a great variety of functional groups, to modify the surface properties of nanotubes. The curvature of carbon nanotubes induces rehybridization of the bonds (mixing of the $sp^2$ and $p_z$ orbitals) yielding a higher reactivity of carbon nanotubes than that of graphene. As carbon atoms bond covalently to functional groups, fewer electrons can participate in the delocalized $\pi$-electron system, changing the electronic properties of the nanotubes. The great advantage of noncovalent methods is that they do not alter the intrinsic properties of CNTs. The structures produced by noncovalent methods are called hybrids. Hybrid structures are defined as mixtures of an organic and an inorganic material; in this case the nanotube, built up of elemental carbon, is the inorganic part. (I will keep this notation even when talking about nanotubes filled with metals.)

I investigated various CNT hybrids prepared by noncovalent functionalization to examine how the interaction between the constituents is reflected in their vibrational spectra. Since the main focus of the present work is on the characterization of such samples, I only give a broad overview of the chemistry of these systems. For those interested in further details, several excellent review articles are available about the chemistry of CNTs. [9, 18, 29–32]
1. Introduction

Fig. 1.4: Overview of nanotube functionalization methods: covalent functionalization on the sidewall (A), on defects (B), and noncovalent functionalization by aromatic small molecules (C), polymer wrapping (D), and encapsulation (E). [32]

1.2.1 Noncovalent exohedral hybrids: adsorption and wrapping [30]

Various organic and inorganic molecules can be attached to the nanotube sidewall by noncovalent interactions like $\pi-\pi$ stacking, van der Waals interaction or charge transfer. Main application areas of noncovalent hybrids range from solubility tuning, composite reinforcement, purification, and separation of different tube species by gradient ultracentrifugation or selective interaction.

The most widespread application is the preparation of nanotube dispersions, where the nanotubes are enclosed in surfactant micelles in aqueous media. For example dispersions containing individual nanotubes are necessary for photoluminescence spectroscopy measurements (Sec. 2.3). Surfactants used for dispersing CNTs can be divided into three main groups: anionic surfactants, such as sodium dodecyl benzene sulfonate (SDBS), sodium dodecyl sulfate (SDS), sodium cholate (SC); cationic surfactants such as dodecyl trimethyl ammonium bromide (DTAB), tetradecyl trimethyl ammonium bromide (TTAB), hexadecyl trimethyl ammonium bromide (HTAB); non-ionic surfactants such as Triton X-100 (4-(1,1,3,3-tetramethyl butyl)-phenyl polyethylene glycol), Tween-20/40/60 (polysorbate). In ionic surfactants the non-polar head groups attach to the tubes, while the polar tails face toward the solvent. Molecules with aromatic groups tend to form stronger interactions with CNTs, which explains the efficiency of Triton X and SDBS in exfoliating nanotubes. In this work we used Triton X-100 and SDS to disperse nanotubes.

Besides micelles formed by surfactants, the other large group of noncovalent hybrids are polymers wrapped around nanotubes. Among natural polymers DNA, peptides, proteins, lipids show great potential in the exfoliation of nanotubes. Synthetic polymers are often
produced in situ in the presence of nanotubes. Polyaromatic molecules, such as pyrene, perylene, porphyrin, form strong secondary interactions with the nanotubes, as discussed in Chapter 5. Therefore such molecules are efficient units to attach longer molecules to the surface of CNTs. Aromatic units in longer polymers are believed to assist the wrapping by enhancing the attachment of the polymers. In Chapter 3 I will discuss how the type and strength of interaction between conducting polymers and carbon nanotubes can be estimated based on their vibrational spectra.

1.2.2 Encapsulation

The quasi one-dimensional hollow inner cavity of carbon nanotubes is able to encapsulate and retain molecules. I will present results on fullerene and coronene-filled nanotubes in Chapters 4 and 5, respectively. After introducing the different encapsulation methods, I give an overview of CNT hybrid systems, and present some examples of chemical reactions that are specific for these nano-reaction vessels. Encapsulated systems will be referred to as guest@host.

Encapsulation methods [33]

The encapsulation methods can be divided into three major groups: (1) vapor-phase encapsulation, (2) liquid-phase extraction from the solution of compounds or (3) from molten neat compounds. The molten-phase method is mostly used for the insertion of metal nanoparticles to serve as catalysts for further reactions. Since this latter method is not applicable for molecules presented in this work, I only discuss the first two techniques of encapsulation in detail. (A detailed description of the molten-phase method can be found in Ref. [29].)

The prerequisite for all encapsulation methods is the opening of the CNTs. This is usually achieved by oxidative treatment, such as annealing in air. This annealing results in the destruction of the fullerene caps on the tube ends and larger defects on the sidewall, providing the molecules with more entry sites into the nanotubes. After annealing, the encapsulation should be started immediately. The tube ends and the sidewall defects are very reactive and are rapidly functionalized in air. The newly attached functional groups block the holes and prevent the entry of guest molecules.

Choosing the appropriate nanotube diameter is a key factor for efficient encapsulation. The diameter of the hollow inner space of the nanotube capable to encapsulate molecules is approximately its diameter reduced by the van der Waals thickness of the walls ($\approx d_{\text{CNT}} - 2 \cdot 0.34 \text{ nm}$). For example, in the case of $C_{60}$ ($d = 0.69 \text{ nm}$) the ideal diameter of nanotubes suitable as hosts is approximately 1.37 nm. Though slightly smaller tubes can be filled as well, this formula gives a good estimate of the ideal host size.
1. Introduction

The **vapor-phase method** is the most efficient one. The open tubes are sealed together with the guest compound in a quartz tube under vacuum. By heating the mixture above the sublimation point of the filling molecules the encapsulation takes place [34]. This method was used to prepare C$_{60}$ and coronene-filled nanotubes. Though very high filling ratios can be achieved, the obvious drawback of the method is that it can only be applied to molecules that are capable of sublimation. Attention needs to be paid to side reactions that might occur during the sublimation, as will be discussed in Chapter 5.

To facilitate the encapsulation of sensitive molecules, several solution-based methods were developed. The most widely applied one is **nanoextraction**, where the opened nanotubes are dispersed in the solution of the guest molecules. Fluids that have surface tension less than 200 mN/m can spontaneously enter the SWCNTs. [35, 36] Generally the solvent used is a weak solvent of the guest molecule. The driving force behind the encapsulation is that the guest molecules have a stronger interaction with the nanotube than with the solvent, therefore they enter the protective inner cavity, where they are surrounded by fewer solvent molecules. This explains the drawback of all solvent-based filling methods: the solvent molecules enter together with the guest molecules into the nanotube, occupying part of the cavity, and leading to lower encapsulation ratios for guest molecules. The ability of solvent molecules to leave the nanotube afterward depends on the size of the molecules with respect to the nanotube diameter, and the number of defects on the nanotube walls. General solvents used for the encapsulation of apolar molecules are ethanol, n-hexane or supercritical CO$_2$. [37–39] The main advantage of the latter is that the solvent molecules are small, which allows them to leave the host tubes easier, resulting in higher filling ratios. Furthermore, once the encapsulation is finished CO$_2$ rapidly evaporates at ambient conditions, leaving clean hybrids behind. Nanoextraction can be used for a wide range of guest molecules, as long as the proper solvent is found. We used nanoextraction in supercritical CO$_2$ to encapsulate coronene molecules into CNTs, because the low temperature helped to eliminate the formation of unwanted by-products.

Independent of the filling method, the guest molecules do not only enter the interior of the tubes. Rather, a significant amount gets adsorbed onto the sidewall. Before characterizing the hybrid materials these molecules need to be removed, especially in cases of spectroscopic characterization, where they might lead to misinterpreted results, as discussed in Chapter 5. The surface of the nanotubes can be cleaned by sonication in a good solvent of the guest molecules or annealing under dynamic vacuum.

**Hybrid systems prepared by encapsulation in carbon nanotubes**

Fullerene molecules (C$_{60}$ and higher fullerenes) were among the first molecules which were filled into carbon nanotubes, forming so-called peapods (Fig. 1.4 E). [40] Due to their spherical shape and π-electron system, they build up a very strong van der Waals interaction with the inner walls of nanotubes. The alignment of the encapsulated fullerenes de-
1.2. Chemistry of carbon nanotubes

...pends on the size of the host. By increasing the diameter of the CNT, the one-dimensional chain of fullerenes turns into zigzag and then bilayer alignment. Encapsulation of various metallofullerenes [33] allowed the investigation of the rotational motion of the molecules inside the nanotubes by transmission electron microscopy (TEM). Due to the strong interaction of fullerenes with the inside of CNTs, they can act as a carrier to facilitate the encapsulation of other molecular segments attached to them. [41]

Several organic molecules, such as various types of polyaromatic hydrocarbons (PAHs) or metalloorganic systems, such as ferrocene, were filled into SWCNTs. The aim of the encapsulation of aromatic hydrocarbons in most of these experiments was to study their reactions in the confined environment, leading to growth of inner nanotubes or graphene nanoribbons. [26,42–45]

Combining carbon nanotubes with fluorophores is compelling, while it would allow the synthesis of robust materials with tunable luminescent properties. Though several attempts have been made to produce such structures, only few types of luminescent hybrids were successfully prepared. [5–7, 46–49] In Chapter 5, I will investigate how the encapsulation affects the luminescent properties of coronene.

In certain cases, the hybrids possess new, interesting properties that are not present in the individual constituents. Organic dyes, such as β-carotene [46] and oligothiophenes [47–49] were successfully encapsulated into carbon nanotubes. β-carotene and α-sexithiophene molecules inside the nanocontainer were recently shown to produce giant Raman scattering, with cross sections high enough to detect even only a few molecules. [7]

It was shown that the strong second-order nonlinear optical response of asymmetric dye molecules (such as p,p’-dimethylaminonitrostilbene), that cancels out in the bulk form, can be harvested when these molecules are encapsulated in SWCNTs. The coherent alignment inside the tubes results in extremely large total dipole moment and static hyperpolarizability. [8] Furthermore, as a crucial step towards the application of these hybrids, it was demonstrated that the outside of the SWCNT nanocontainer can be functionalized without affecting the encapsulated species. The covalent functionalization of the host helps to solubilize the SWCNTs or allows the attachment of targeting molecules for biological applications. [7,8]

Reactions inside carbon nanotubes

Inside carbon nanotubes the confinement can dramatically change the pathways of chemical reactions and can lead to unexpected products. Shortly after the discovery that molecules can be encapsulated into carbon nanotubes, it was demonstrated that fullerene guest molecules can oligomerize, coalesce, and merge into tubular structures nested inside the host CNT under high temperature annealing or irradiation by the electron beam. [40,50,51] We used this method in Chapter 4 for the synthesis of DWCNTs.
1. Introduction

**Fig. 1.5:** Formation of inner nanotubes. The non-catalytic transformation of the filled precursors into a well-defined CNT may proceed via two different routes of reaction, that is, (1) the conventional deformed fullerene path and (2) the twisted GNR path. The latter allows selective synthesis of inner tubes with predetermined chiralities. [42].

The quasi one-dimensional cavity facilitates special, oriented polymerization reactions. For example, regardless of the reaction conditions, fullerene dimers, oligomers, and polymers formed inside SWCNTs having typical diameters between 1.3 and 1.5 nm, are always linear. [33] Small aromatic hydrocarbons such as perylene, coronene, pentacene, picene form graphene nanoribbons (GNR) upon polymerization inside the nanoreactor. As illustrated in Fig. 1.5, these GNRs can wrap up to form inner carbon nanotubes by further thermal activation. [42] At sufficiently high temperatures, especially in the presence of catalysts, most carbon containing guest molecules can be turned into inner nanotubes. Sulphur-terminated GNRs were produced by encapsulation of C_{60} molecules having side groups containing sulphur [52] and from tetrathiafulvalene [53]. In Chapter 5, I will investigate how the interaction with the surface or inner cavity of carbon nanotubes influences the polymerization of coronene molecules.

MWCNTs have promising possibilities as nanoreactors for catalytic reactions. The catalyst is inserted into the nanotubes in the form of metal-containing molecules or metal nanoparticles. The confinement inside the carbon nanotubes appears to enhance their stability against sintering and coalescence, which prolongs their activity [9]. The high encapsulation rate of certain molecules can create special environments inside the nanoreactor, resulting in a higher concentration of reactants inside the carbon nanotubes than in the surrounding liquid or gas phase, which is beneficial for higher reaction rates. [29]
2. Experimental methods

Owing to the complexity of nanotube samples, there is no ideal characterization technique, the different techniques all have their benefits and drawbacks, and the combination of various methods has to be properly chosen for each specific problem. This section gives an overview about the spectroscopic and microscopic characterization methods used in this work. To study noncovalent functionalization and reactions inside and on the surface of nanotubes, I used Raman, optical absorption, and photoluminescence spectroscopy. In the case of coronene-nanotube hybrid structures the work was supported by high resolution transmission electron microscopy investigations. After giving a short summary about the theory behind each method, their application to carbon nanotube-based hybrid materials is described. I focus on the vibrational and electronic transitions of CNTs, and discuss how the hybrid formation is reflected in the spectral features. The spectroscopy of the conducting polymers and the guest molecules used for the endohedral functionalization will be detailed in the corresponding chapters and their appendices. Finally, I describe the experimental arrangements used for the measurements. The sample preparation will be described in the corresponding chapters for easier understanding.

2.1 Raman spectroscopy

Raman spectroscopy is one of the most powerful tools to study carbon-based hybrid systems, and it is widely used in nanotube research. It is non-destructive, the samples need no additional preparation before measurement. A broad range of information can be gathered about the sample, such as the diameter distribution of the nanotubes or the presence of attached or encapsulated molecules.

2.1.1 Theory [10]

Fig. 2.1 shows the lowest order Raman process for light scattering of phonons, molecular vibrations or spin excitations. The incoming photon with energy \( h\omega_1 \) creates an electron-hole pair, which scatters inelastically emitting a phonon with energy \( h\omega_{ph} \) and then recombines emitting a scattered photon, \( h\omega_2 \). The energy and the momentum are conserved in the process:

\[
    h\omega_1 = h\omega_2 \pm h\omega_{ph}
\]  

(2.1)
2. Experimental methods

\[ q_1 = q_2 \pm q_{ph} \] (2.2)

The ± refers to the Stokes and anti-Stokes process. The Raman spectrum is the plot of the intensity versus the Raman shift (usually in \( \text{cm}^{-1} \)) that is the energy difference of the incoming and scattered photon (\( \hbar \omega_{ph} \) in the case of excitation of phonons).

The calculation of the probability of the two optical transitions can be done in second order perturbation theory. The Raman efficiency of a bulk material for Stokes scattering is [54,55]:

\[
\frac{dS}{d\Omega} = \frac{1}{V} \frac{d\sigma}{d\Omega} = \frac{\omega_1 \omega_2^2 n_1 n_2^3 V_c N}{4\pi^2 c^4 (\hbar \omega_1)^2} \sum_f |K_{2f,10}|^2 \left[ N(\omega_{ph}) + 1 \right] \tag{2.3}
\]

where \( dS/d\Omega \) is the the number of photons per incident photon per unit length and solid angle \( d\Omega \), \( d\sigma/d\Omega \) is the energy integrated differential Raman cross section, \( V = V_c N \) is the scattering volume and \( V_c \) is the volume of the unit cell. \( n_{1(2)} \) is the index of refraction at \( \omega_{1(2)} \). \( N(\omega_{ph}) = f_{BE}(\omega_{ph}) = [\exp(\hbar \omega_{ph}/k_b T) - 1]^{-1} \) is the Bose-Einstein occupation factor and \( c \) is the speed of light in vacuum. A representative transition matrix element with the final state \( f \) and energy \( \hbar \omega_{ph} \) is given by [55]:

\[
K_{2f,10} = \sum_{a,b} \frac{\langle \omega_2, f, i | H_{eR,\rho} | 0, f, b \rangle \langle 0, f, b | H_{eR} | 0, 0, a \rangle \langle 0, 0, a | H_{eR,e} | \omega_1, 0, i \rangle}{(E_1 - E_{ai}^e - i\Gamma)(E_1 - \hbar \omega_{ph} - E_{bi}^e - i\Gamma)} \tag{2.4}
\]

where \( \omega_1, 0, i \) denotes the state with incoming photon energy of \( E_1 = \hbar \omega_1 \), the ground state 0 of the phonon and the ground electronic state \( i \). The other states are labeled accordingly, \( f \) denotes the final state. The initial and final electronic states are assumed to be the same.

**Fig. 2.1:** Feynman diagram of the lowest order process of phonon Raman scattering. An incoming photon with energy \( \hbar \omega_1 \) and wavenumber \( q_1 \) excites an electron-hole pair. The electron scatters inelastically, emitting a phonon with energy \( \hbar \omega_{ph} \) and wavenumber \( q_{ph} \), then recombines with the hole, emitting a photon with energy \( \hbar \omega_2 \) and wavenumber \( q_2 \). The Feynman diagram can also be read from the right to the left. This order of time represents the anti-Stokes process. A phonon is annihilated, and its energy is added to the energy of the incoming photon. (After Ref. [10].)
2.1. Raman spectroscopy

Fig. 2.2: (a) non-resonant, (b) single-resonant, (c) double-resonant Raman scattering. The solid lines indicate real electronic states, the dashed lines are virtual states (not eigen-energies of the system). The incoming photon excites an electron (1), the excited electron is scattered by emitting a phonon with energy $\hbar \omega_{\text{ph}}$ (2), and the electron recombines with a hole emitting a photon (3). (After Ref. [10].)

in the process, and the sum runs over all possible virtual intermediate electronic states $(a, b)$. $H_{eR,\sigma}$ ($H_{eR,\rho}$) is the Hamiltonian for the electron-radiation interaction with light polarization of $\sigma$ ($\rho$), $H_{ep}$ is the Hamiltonian for the electron-phonon interaction. The $E^{e}_{ai}$ are the energy differences between the electronic states $a$ and $i$. The lifetimes ($\Gamma$) of the various excited states are taken to be the same. If the electronic states $a$ or $b$ are real in the process, the transition is called resonant. The Raman cross section diverges around these states, the denominator vanishes, only the lifetime keeps the intensity finite.

Most Raman experiments are performed in the UV-visible or near-infrared energy range, and are therefore restricted to the $\Gamma$-point in the Brillouin zone due to the small wave vector of the light. For example, using laser light at 488 nm and backscattering geometry the momentum transfer in a material with $n = 4$ is \( q_{\text{max}} = 4n\pi/\lambda \approx 0.01 \text{ \AA}^{-1} \), while the Brillouin zone is \( k_{\text{max}} = \pi/a_0 \approx 1.3 \text{ \AA}^{-1} \), using the lattice vector of graphite \( a_0 = 2.46 \text{ \AA}^{-1} \). However, in the case of multiple scattering events, such as defect induced scattering, where the defect elastically scatters the electron, or second-order processes, where two phonons are excited at the same time, large $q$ scattering can be observed, since the momenta of the two excitations have to fulfill the conservation rule, $|q_{\text{max}}| = |q_{\text{ph,1}} - q_{\text{ph,2}}|$. The Raman cross section of two-phonon processes is usually about two orders of magnitude weaker than that of the first order processes [56], but if resonance occurs, specific large wavenumber modes can be selectively enhanced.

The matrix elements are usually not known numerically, but the symmetry of the system determines the selection rules that yield the processes having nonzero transition matrix elements. For Raman scattering those excitations are allowed that transform like a symmetric combination of the quadratic functions of the spatial coordinates. The measurement of the polarization dependence of the spectra allows the classification of the symmetry properties of the excitations through group theory.
2. Experimental methods

![Graph of Raman spectra](image)

**Fig. 2.3:** Raman spectra of single-walled carbon nanotubes with the main modes indicated. The insets show (a) the radial (RBM) and (b) the tangential (G mode) movement of the carbon atoms [57], and (c) a schematic illustration of the double-resonance process (D mode) with the green arrow corresponding to the phonon and blue to the defect scattering [58]. The illustrated double-resonant Raman scattering shows the following process: (1) the incoming photon creates an electron-hole pair near the \( \mathbf{K} \)-point of the Brillouin zone, (2) the electron is scattered to a state on the second band by a phonon, then (3) elastically scattered back by a defect and (4) recombines, conserving the momentum of the process.

2.1.2 Raman spectroscopy of CNT-based hybrid materials [10]

Raman spectroscopy performed on conventional SWCNT samples, which are a mixture of tubes with different chiralities, is always enhanced by resonance process. If the laser energy is close enough to the optically allowed electronic transitions of some tubes, the Raman cross section of the related excitation is increased significantly. By taking a look at the Kataura plot (Fig. 1.3) it can be seen which chiralities are selected by certain laser lines. Resonance effects are very useful while measuring CNTs, since a high signal-to-noise ratio can be obtained allowing even the detection of single SWCNTs and the investigation of certain selected subgroups of the mixture. On the other hand, the resonance enhancement has its drawbacks. To properly gather information of the sample as a whole, the use of multiple laser lines is needed. Hybrid materials made of carbon nanotubes are sometimes very hard to characterize, because the strong nanotube Raman signal obscures the rest of the spectrum. Most of the phonon modes of carbon nanotubes can be derived from graphene by zone folding as has been discussed in Section 1.1.3. The main regions of the CNT Raman spectra are the radial breathing modes (RBMs), the disorder induced mode, the high energy modes, and the second order 2D mode (Fig. 2.3).
Radial breathing mode  The radial breathing mode (RBM) is a unique mode that only exists in nanotubes, usually located between 100 and 400 cm$^{-1}$. It is the breathing like expansion and contraction of the nanotubes in the radial direction. Consequently its Raman shift is approximately inversely proportional to the tube diameter:

$$\tilde{\nu}_{\text{RBM}} = C/d_t + \Delta \tilde{\nu}_{\text{RBM}}$$  (2.5)

There are several models yielding slightly different constants. $\Delta \tilde{\nu}_{\text{RBM}}$ is a correction, where the environmental effects can be taken into account such as tube-tube interaction in the case of bundling, or tube-environment interaction by wrapping agents, surfactant micelles surrounding the nanotubes. A summary of different experimental and theoretical values can be found in Table 8.2 of Ref. [10]. In the case of isolated tubes the value of $C = 248$ cm$^{-1}$ nm [59] is generally used, while for bundles $C = 234$ cm$^{-1}$ nm and $\Delta \tilde{\nu}_{\text{RBM}} = 10$ cm$^{-1}$ [60]. For CNTs having a diameter of less than 1 nm the chirality has to be taken into account for precise assignment [61]. In the diameter range of nanotubes analyzed in this work (0.7–1.6 nm) the differences resulting from using the various formulas are of the order of 0.04 nm if the diameters are derived from $\tilde{\nu}_{\text{RBM}}$. In this work we measured nanotubes in bundled form.

Double-walled carbon nanotubes exhibit radial breathing-like modes (BLMs). The interaction between the outer and inner tube modifies the low energy phonons of the isolated layers. The changes are diameter dependent. The layers can be imagined as coupled oscillators. In the case of larger nanotubes, where the frequencies of the separate oscillators are nearly equal to each other, the interactions between them lead to a strongly mixed vibrational mode, the collective motion of the tubes. Whereas in smaller tubes, where the RBM frequency of the inner and outer tube is well separated, the mixing of the modes is negligible, and the in-phase and counterphase BLM frequency is very close to the RBM frequency of the individual SWCNTs. [62] Samples investigated in Chapter 4 have an average outer diameter of 1.4 nm, therefore the shifts caused by the coupling are negligible.

High energy modes  The high energy modes are tangential vibrations parallel to the tube surface, corresponding to the optical mode at 1580 cm$^{-1}$ of graphene, therefore also referred to as G band. As a consequence of confinement in SWCNTs, the doubly degenerate $\Gamma-E_{2g}$ phonon of graphene splits for both metallic and semiconducting tubes into longitudinal (LO) and transverse optical (TO) modes. These modes are characteristically different in metallic and semiconducting nanotubes. In semiconducting nanotubes the peaks in the G band have Lorentzian line shape. In metallic nanotubes the lower energy part exhibits a Breit-Wigner-Fano (BWF) lineshape, but the underlying effect is not well understood. [63–65]
2. Experimental methods

**Disorder-induced band and its overtone** Generally the frequency of Raman lines is independent of the excitation energy, but in graphite, graphene, and carbon nanotubes dispersive modes were observed. The D mode, located between 1300 and 1400 cm\(^{-1}\) is the result of disorder-induced double-resonant Raman scattering. [58,66] One of the possible double-resonant processes is illustrated in the inset of Fig. 2.3. In graphite the Raman shift of the D mode increases with laser energy by about 50 cm\(^{-1}/eV\), in carbon nanotubes at a rate of 38–65 cm\(^{-1}/eV\). [67] The origin of the excitation energy dependence is that the resonance condition projects out different parts of the phonon dispersion. It is activated in all forms of carbon consisting of \(sp^2\) sites due to the presence of disorder such as heteroatoms, vacancies, grain boundaries, and other defects lowering the crystal symmetry. Its intensity, line width, and position carry information about the electronic properties, strain, and degree of disorder in CNTs.

The 2D (also referred as D* or G’) band, located around 2700 cm\(^{-1}\), is a D-band like overtone, but originates from second order Raman scattering, not necessarily requiring disorder to be present, since if two phonons are excited simultaneously the momentum conservation can be fulfilled. The dispersion of these modes is even stronger than for the D mode.

What can we learn from the Raman spectra of carbon nanotubes?

**Presence of carbon nanotubes** The presence of the radial breathing modes together with the graphite-type tangential G band is a clear sign that there are carbon nanotubes in the sample. The intensity is usually high due to the resonance effect.

**Diameter distribution** It is crucial for all encapsulation methods to determine the diameter distribution of the nanotube sample, which can be calculated from the energy of the RBMs. Since the inner tube diameter is approx. 0.69 nm smaller than that of the host tubes, the RBMs of inner and outer tubes in narrow DWCNT samples are well separated in energy. We used the RBM modes to detect the presence of DWCNTs prepared from \(C_{60}\) and coronene-filled SWCNTs.

**Defect concentration** The ratio between the D and the 2D peak is suggested to be related to the defect concentration. However, the dependence is not linear, and it can only be used to compare samples containing the same type of nanotubes, for example functionalized nanotubes and their control sample, because several other factors can influence the intensity of the D peak. [68]

**Environmental effects** Interactions between the delocalized \(\pi\)-orbitals and the environment strongly affect the electronic structures of the nanotubes and consequently their optical properties. Wrapping agents were reported to modify the width of the Raman
2.1. Raman spectroscopy

As a result of the strong intertube interactions the electronic structures near the Fermi level of bundled tubes are strongly perturbed. Several experimental works were done comparing the Raman spectra of individualized carbon nanotubes and the same tubes in bundles. The observed shifts of $\tilde{\nu}_{\text{RBM}}$ were explained to originate from the red shift of the excitation profile, resulting in the excitation of different nanotubes for the same laser energy. Nanotubes were measured in bundled form in this work.

Doping

As a result of intercalation with dopants or charge transfer in an electrochemical cell, it is possible to deplete (fill) the SWCNTs valence (conduction) band. Since the optical transitions strongly depend on the occupation of these states, radical changes occur in both the optical and Raman spectra. Doping is reflected in the position and line shape of the G band. RBMs are affected due to the change in the resonance conditions.

Chemical modification

The strong resonant contribution of CNTs often obscures the spectral features of the attached or encapsulated molecules. However, chemical modification is also reflected in changes in the nanotube vibrations. Covalent functionalization of carbon nanotubes results in an increased D band intensity, since the conjugated electron system of the nanotube wall is perturbed. Excessive covalent functionalization of the sidewall can significantly modify the electronic structure of the nanotubes. Depleting the Van Hove singularities results in the loss of the resonance, consequently weakening or quenching nanotube modes. Noncovalent surface modification can result in debundling of the tubes, causing changes in the resonant window resulting in the shift of $\tilde{\nu}_{\text{RBM}}$. Encapsulated molecules can also shift the position of the radial breathing mode, as discussed in Chapters 4 and 5.

2.1.3 Experimental arrangements

Raman spectroscopy was used to characterize both wrapped and filled carbon nanotubes. No further sample preparation was done for the Raman measurements, samples in all cases were measured as prepared, in powder, buckypaper or film form. Data were acquired in backscattering geometry under ambient conditions. Since carbon nanotube samples are slightly inhomogeneous, spectra were typically collected on 10 different points of each sample. To find the optimal resonance conditions and avoid luminescence of certain samples various laser lines were used. Since not all excitation energies were available with one instrument, three different types of spectrometers were used for the measurements.
2. Experimental methods

**Horiba Jobin-Yvon T64000**  This dispersive, triple stage spectrometer, connected to an Olympus microscope is equipped with two lasers, a krypton ion laser (Coherent Innova 400, 14 available laser lines between 406.7 and 799.3 nm) and a Nd-YAG diode-pumped solid state laser (Klastech Scherzo, 532 nm wavelength). For the measurements lines at 482.5 nm, 520.8 nm, 530.9 nm, and 532 nm were used. Most of the measurements were performed with an objective lens with ultra-large working distance with a magnification of 50 and a numerical aperture (N.A.) of 0.55 allowing the light to be focused to a spot of approximately 2 µm on the sample. To avoid overheating, the laser power on the sample surface was kept below 100 µW. ¹

**Renishaw System 1000**  The system is a dispersive single stage spectrometer equipped with a holographic notch filter connected to a Leica DM/LM microscope. For excitation a solid state laser (Renishaw, 785 nm wavelength) is used. The samples were measured with an objective lens having a magnification of 50. The laser power on the sample surface was kept under 200 µW. ²

**Bruker FRA 106/S FT-Raman module connected with an IFS 55 spectrometer**  This spectrometer uses Fourier transformation technique to separate the spectral components of the scattered light. It is equipped with a Nd-YAG diode-pumped solid state laser (1064 nm wavelength). The low excitation energy enabled the measurement of samples which produced a high luminescent background in the visible range, such as coronene and dicoronylene. ³

Fig. 2.4 shows the setup of the Horiba Jobin-Yvon T64000 spectrometer and the related optics. After leaving the laser the light passes through a pinhole system, consisting of a microscope objective lens, a circular aperture, and an achromatic lens, which expands the beam diameter and spatially filters it. This is followed by a prism monochromator combined with a slit, which filters out the laser plasma lines, and allows only monochromatic light to pass through. The next stage is a λ/2 plate combined with a polarizer, which is used to control the beam intensity. The final polarization state is achieved with a set of additional polarizers and phase shifters. In the current work, since no polarization dependence was measured, the polarizers were set to maximize the intensity when measuring through the microscope. The spectrum is analyzed by a triple stage spectrometer combined with a liquid nitrogen-cooled charge coupled device (CCD) detector. The spectrometer was used in a subtractive mode during the measurements, meaning that the

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¹ The instrument is located at the Walther Meissner Institute, Garching, Germany. Annealed coronene samples were measured on the same type of spectrometer but at the Eötvös Loránd University, Institute of Geography and Earth Sciences in Budapest, Hungary.

² The instrument is located in the Wigner Research Centre for Physics, in Budapest, Hungary.

³ The instrument is located at the Eötvös Loránd University, Department of Inorganic Chemistry in the Laboratory of Molecular Spectroscopy in Budapest, Hungary.
2.1. Raman spectroscopy

![Raman microscopy setup](image)

**Fig. 2.4:** Raman microscopy setup for the T64000 spectrometer. M: mirror, PH: pinhole system, P: polarizer, S: slit, G: grating.

The first two stages were used to disperse and recombine the scattered light, while filtering out the elastically reflected laser light. The third stage is used for dispersing the light for spectral analysis. The 2400 gr/mm gratings in the spectrometer have a dispersion of 0.5 nm/mm for light of 500 nm wavelength corresponding to 0.44 cm\(^{-1}\) per pixel (25 µm) of the CCD detector. The spectral resolution is determined by the width of the 3rd stage’s entrance slit and the binning factor in the dispersion direction, which is the number of pixels on the CCD. The measurements were generally performed using a width of 100 µm of the entrance slit and binning 2 resulting in resolution of approx. 1 cm\(^{-1}\). The frequency position of the spectrometer was calibrated by measuring the spectrum of a neon lamp before each set of measurements.

The main difference between the system described above and the Renishaw spectrometer is that the latter is a single stage spectrometer, therefore a holographic notch filter is used to block the elastically reflected laser line (±100 cm\(^{-1}\) from the original line) combined with one monochromator to disperse the light.

The FRA 106 FT-Raman instrument conceptually differs from the dispersive systems. Since I used this instrument in collaboration, and it was not part of our equipment I do not discuss the details here. The working principle of the Fourier transform technique is explained in the next chapter for the IR spectrometer.
2. Experimental methods

2.2 Optical absorption spectroscopy

2.2.1 Theory [86]

The strength of an optical absorption is determined by the quantum mechanical probability of the transition between the initial \((i)\) and final states \((f)\). Such transitions can happen across the energy gap, from excitons or from impurity states (found generally in the visible or infrared spectral range), and IR-active vibrational modes.

The interaction of electrons in solids with weak electromagnetic fields can be treated by perturbation theory. The transition probability is proportional to \(|H'_{fi}(0)|^2\), where \(H'\) is the Hamiltonian of the perturbation driving the transition. Using Fermi’s golden rule, the absorption can be calculated:

\[
\alpha(\omega) = \frac{2\pi}{V} \frac{i e m \omega_{fi} |M_{fi}|^2}{m^2 \epsilon_0 c n \omega} \delta(\hbar \omega_{fi} - \hbar \omega)
\] (2.6)

where \(|M_{fi}|\) is the matrix element for the dipole moment. (The other notations are the same as earlier, in Sec. 2.1). If there are several states in the vicinity of the initial and final states, that have \(\hbar \omega\) energy difference, all of them have to be taken into account, therefore the \(\delta\) function in equation 2.6 has to be substituted by a summation, called the joint density of states (JDOS):

\[
\sigma_{CV}(\omega) = \frac{V}{4\pi^3} \int \delta [\hbar \omega_C(k) - \hbar \omega_V(k) - \hbar \omega] d^3k
\] (2.7)

where \(C\) denotes the conduction, \(V\) the valence band. In the second equation the k-space integral has been replaced by an integral over the constant-energy surface \((S_E)\). In carbon nanotubes, for transitions between the Van Hove singularities the denominator in equation 2.7 vanishes, resulting in a high joint density of states, therefore strong absorption.

The absorption curve is mainly determined by the JDOS, since the dipole matrix elements \((M_{i,j})\) have week energy dependences. However, \(M_{i,j}\) plays an important role, since only those transitions are allowed that have nonzero transition matrix element. For example in nanotubes, according to the selection rules based on their symmetry properties, only symmetric transitions between the Van Hove singularities are allowed (see Sec. 1.1.2).

For molecular vibrations the IR absorption is given by the dipole moment induced by a vibration along a normal coordinate \(Q_k\).

\[
\alpha_k \approx \left| \frac{\partial \mu}{\partial Q_k} \right| \frac{\hbar}{2\Omega_k} (N_k + 1)
\] (2.8)
where \( \mu \) is the molecular dipole moment, \( \Omega_k \) is the angular frequency, \( Q_k \) is the coordinate of the normal mode, and \( N_k \) is given by the Bose-Einstein distribution \( N_k = f_{BE}(\Omega_k) \). The allowed transitions are determined by the selection rules, thus those vibrations are infrared-active that transform like the coordinates \((x, y, z)\).

### 2.2.2 Optical absorption spectroscopy of CNT-based hybrid materials

**Electronic transitions**  On free-standing transparent nanotube films wide-range optical measurements can be performed, allowing the calculation of the optical constants by Kramers-Kronig analysis. [87] The optical transitions between the symmetric Van Hove singularities appear as broad peaks in the near-infrared (NIR) and visible (Vis) region. Generally the \( S_{11} \) transition has the lowest energy, followed by the \( S_{22} \) and the \( M_{11} \) transition (Fig. 2.5). The far-infrared (FIR) region is dominated by the absorption of the free carriers. By investigating these transitions we can get information about the sample purity. [88] Since changes in the number of electrons available for excitation close to specific Van Hove levels strongly affect the optical spectra, the doping or covalent functionalization of the nanotube sidewall can also be investigated. [89] [P7] Since the position of the peaks depends on the tube radius, and the metallic and semiconducting transitions can be well separated, the selectivity of the functionalization method can be studied. [90,91] As optical absorption spectroscopy is a sensitive tool to detect charge transfer, it was used to investigate the interactions between the inner and outer tubes of DWCNTs (Chapter 4).

**Vibrations**  Though optical spectroscopy is actively used for the characterization of carbon nanotubes, there is not much known about the IR-active vibrations of SWCNTs. Since the transition dipole moment is small for these modes, they are only detectable with very careful measurements on clean samples. [92–96]

Even though the nanotube vibrations are not well detectable, infrared spectroscopy is widely used to probe the nanotube sidewall chemistry, the presence and type of functional groups can be detected. The combined use of Raman and infrared spectroscopy can probe changes of both the nanotube and the functional groups.

Molecules encapsulated in carbon nanotubes cannot be seen by IR spectroscopy, but the ones adsorbed to the surface are well detectable, therefore the efficiency of the cleaning process can be investigated after molecule encapsulation. [P6].

### 2.2.3 Experimental arrangements

Optical absorption spectroscopy was used to characterize the noncovalent sidewall functionalization of CNTs with conductive polymers and to investigate the interaction between
2. Experimental methods

Fig. 2.5: Wide-range optical conductivity spectra of arc produced SWCNTs. The FIR range is dominated by the Drude peak, also noted as $M_{00}$, belonging to the absorption of the free carriers. The NIR region shows broad peaks around 5400 cm$^{-1}$, 9600 cm$^{-1}$, and 14000 cm$^{-1}$ corresponding to the symmetric transitions between the Van Hove singularities ($S_{ii}, M_{ii}$). The higher energy part is dominated by the $\pi-\pi^*$ absorption of SWCNTs and carbonaceous impurities.

the host tube and the encapsulated species in $C_{60}@$SWCNT and DWCNT systems. Conducting polymer-CNT hybrid materials were measured as prepared, on gold substrates. $C_{60}@$SWCNT and DWCNT samples were measured in a wide energy range, therefore self-supporting films were used. Details of film preparation will be discussed in Sec. 4.3.1. In addition, UV-Vis spectroscopy was used to monitor the efficiency of the cleaning processes after encapsulation, by measuring the guest molecule content of the washing solutions. In the infrared region Fourier transform spectrometers, in the UV-Vis range grating spectrometers were used, therefore I discuss the working principles separately.

Infrared spectroscopy

The infrared measurements were performed on a Bruker IFS 66v/S Fourier transform spectrometer in the far-infrared and mid-infrared (MIR) region, and, in the mid-infrared and near-infrared region, on a Bruker Tensor 37 spectrometer equipped with a Bruker infrared microscope in reflection mode. In the MIR region spectra could also be recorded using a single-bounce diamond attenuated total reflection (ATR) accessory. 

Fourier transform infrared spectroscopy (FTIR) [86] The Fourier transformation technique was invented to overcome the technical difficulties in dispersing light, arising

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4 The instruments are located at the Wigner Research Centre for Physics, in Budapest, Hungary.
towards longer wavelengths. To disperse light properly in the infrared region large gratings are needed to provide the necessary resolution. Additionally the filters that are used to eliminate the contribution of the second-order diffraction can cover a very narrow bandwidth towards the far-infrared region. Since the use of several filters is necessary, the measurements are very complicated and laborious in this range. While in a dispersive spectrometer the intensities are observed sequentially at different wavelengths as the grating is scanned, the entire spectrum is observed from one scan in an FTIR spectrometer (multiplex or Fellgett advantage). Array detectors (such as CCDs and photodiode arrays (PDAs)) can be used in dispersive spectrometers, but the optimal spectral range is at higher energies than that of the FTIR spectrometers, therefore these techniques are complementary. Additionally, FTIR instruments do not require slits to achieve resolution, resulting in a much higher throughput than dispersive spectrometers (Jacquinot advantage), which is favorable especially in the FIR region, where the sources are generally weak. Besides, the wavenumber calibration of an FTIR is more accurate and stable than the calibration of a dispersive instrument (Connes advantage), because the wavenumber scale of an interferometer is derived from a HeNe laser that acts as an internal reference for each scan.

The Fourier transform spectrometers are based on an interferometer as shown in Fig. 2.6. Light from a broadband source (mercury lamp (FIR), glowbar (MIR), tungsten lamp (NIR)) is separated into two parts by a beamsplitter (BS). One part is reflected from a stationary mirror (M1), and the other part is reflected from a moveable mirror (M2), which glides continuously back and forth between its end positions, and the recombined beam is focused on the detector. The actual mirror position \(x\) is determined
interferometrically by a red laser. The transmission of the sample and the reference is measured separately, and the spectrum of the sample is corrected through the division by the corresponding reference spectrum. For the MIR the Tensor 37 is equipped with a mercury cadmium telluride (MCT) photoconductive detector cooled with liquid nitrogen, and a deuterium tryglycine sulphate (DTGS) pyroelectric detector. An InGaAs photodiode is used for the NIR region. The IFS 66v/S is equipped with a deuterated L-alanine-doped triglycine sulfate (DLaTGS) pyroelectric detector.

The detected intensity $I(x)$ (interferogram function) depends on the position $x$ of M2.

$$I(x) = \frac{1}{2} \int_{0}^{\infty} I(\nu) \cos(4\pi\nu x) d\nu$$

(2.9)

This equation demonstrates that the spectral components of the light can be directly obtained from the interferogram by Fourier transformation, without any spectral dispersion. There are two main factors that determine the operating conditions of the FT spectrometers: the finite length of the mirror path ending at $x_{\text{max}}$ instead of $\infty$ and the discrete sampling of the interferograms. The finite scan width ($\Delta x = 2x_{\text{max}}$) causes that the spectrum is convolved with a $\sin x/x$ function instead of a $\delta$ function, resulting in a resolution of

$$\delta\nu \approx \frac{0.7}{\Delta x}$$

(2.10)

The side lobe of the $\sin x/x$ function can be decreased by smoothing the abrupt cut-off caused by the finite mirror path. The smoothing is achieved by multiplying the interferogram with a so called apodization function before the Fourier transformation. This reduces the resolution, but the side lobe can be significantly decreased. Discrete sampling in practice means that the spectrum is detected at equal optical path difference steps (mirror shifts). According to the Nyquist criterion any waveform that is a sinusoidal function of time or distance can be sampled unambiguously with a sampling frequency greater than or equal to twice the bandpass of the system. [97] If the sampling frequency is lower than required by the Nyquist criterion aliasing of the signal occurs, meaning that frequencies greater than the folding frequency ($\nu_f = \nu_{\text{sampling}}/2$) appear additionally on the spectra at a frequency lower than $\nu_F$.

**Attenuated total reflection**  ATR is a sampling technique used to study surface properties of materials. As the ATR crystal with high refractive index is pressed onto the sample surface, total internal reflection occurs at the boundary between the crystal and the sample. An evanescent wave is formed that extends usually up to 0.5–2 $\mu$m into the sample surface (Fig. 2.7). The penetration depth can be calculated using:

$$d_p = \frac{\lambda}{2\pi(n_e^2 \sin^2(\Theta) - n_s^2)^{1/2}}$$

(2.11)
2.2. Optical absorption spectroscopy

Fig. 2.7: Schematic drawing of a single bounce attenuated total reflection (ATR) setup. If $\Theta \geq \Theta_{\text{critical}}$ total internal reflection occurs. The evanescent wave reaches the surface layer of the sample.

where $n_c$ and $n_s$ are the refractive indices of the crystal and the sample, respectively, $\Theta$ is the angle of incidence, and $\lambda$ is the wavelength. The ATR accessory is placed in the sample compartment of an infrared spectrometer. The material of the ATR crystal determines the detectable spectral range. A diamond crystal, used for the experiments here has strong absorbance between 1650 and 2500 cm$^{-1}$, therefore it is only applicable outside this range.

UV-visible spectroscopy

The measurements in the visible and UV range were performed on a JASCO V550 and an Ocean Optics QE65000 grating spectrometer. The JASCO V550 spectrometer, shown in Fig. 2.8, is equipped with deuterium lamp (UV) or halogen lamp (Vis) light sources and a photomultiplier detector. It has two light paths, the reference and the sample can be measured simultaneously, and the transmission can be calculated as the ratio of the sample and reference intensities for every position of the grating. The Ocean Optics QE65000 spectrometer operates with a mercury-argon lamp and a CCD detector. It has a single light path, the reference data are needed to be remeasured regularly and updated in between the measurements of the samples.

For wide-range optical measurements on self-supporting nanotube films the JASCO V550 spectrometer was used. The washing process of filled nanotube samples was monitored on the Ocean Optics QE65000 device.

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5 The instruments are located at the Wigner Research Centre for Physics, in Budapest, Hungary.
2. Experimental methods

![Diagram of a double-beam dispersive spectrometer](image)

**Fig. 2.8:** Schematic drawing of a double-beam dispersive spectrometer. LS: light source (deuterium and halogen lamp), F: filter wheel, BS: beamsplitter, M: mirror, PM: photomultiplier.

2.3 Photoluminescence spectroscopy

2.3.1 Theory

Luminescence is a consequence of the radiative relaxation of the excited electrons with holes, therefore it can be thought of as the inverse of the absorption process. In competition with luminescence other, non-radiative recombination processes may occur, therefore, for luminescence to be efficient, the radiative recombinations must dominate over the non-radiative pathway. A non-equilibrium carrier concentration of the electronic bands or electronic states of a defect structure required for luminescence can be achieved by optical excitation (photoluminescence, PL) or by electronic excitation (electroluminescence).

2.3.2 Photoluminescence spectroscopy of CNT-based hybrid materials [18]

The majority of the semiconducting SWCNTs (s-SWCNTs) has direct band gaps. In the diameter range of 0.5–1.5 nm s-SWCNTs emit light in the near-infrared range (800–1800 nm). The key to observe this photoluminescence is to efficiently exfoliate the tubes, because intertube interactions are quenching the PL, since the metallic nanotubes in the bundles facilitate other, non-radiative decay mechanisms. This exfoliation is usually realized by surfactants, and PL is measured in aqueous suspensions. After sonicating the nanotubes with the surfactants, the bundles are removed by ultracentrifugation from the
2.3. Photoluminescence spectroscopy

Fig. 2.9: Left: photoluminescence of SWCNTs with excitation energy $E_{22}^S$ and emission energy $E_{11}^S$. ($e^-$: electron, h: hole) Right: Typical PL map of SWCNTs, with assignment of the chiral vector $(n,m)$. [98]

Similar to Raman spectroscopy, in a PL measurement resonance plays an important role. If the excitation light is in resonance with an allowed optical transition of the system, the probability of the generation of an electron-hole pair is greatly enhanced. Fig. 2.9 shows the mechanism of the photoluminescence process. The photoluminescence is generated by the radiative recombination of the correlated electron-hole pairs (excitons). [102]

By measuring the PL intensity for varying excitation wavelengths the energy separation between allowed optical transitions, the Van Hove singularities symmetric to the Fermi level, can be mapped. Since the $E_{11}^S$ values are characteristic of the structure of SWCNTs, identification of the chiralities is possible based on the PL map. The technique is therefore routinely used for monitoring SWCNT separation processes. PL spectroscopy can be used to analyze the population of a specific chirality $(n,m)$, since the optical intensities depend on the number of scatterers.

Attempts have been made to use PL spectroscopy to investigate the luminescence of molecules encapsulated in SWCNTs. In principle, most molecules emit in the visible, therefore their emission is well separated in energy from the NIR emission of the nanotubes. When interpreting the PL spectra, attention should be paid to the fact that the preparation of the dispersions might alter the structure of the hybrids. For example, Muramatsu et al. [103,104] reported strong luminescence from the inner tubes of peapod-derived DWCNTs, but later results [105,106] showed that this luminescence may result from extracted inner tubes produced by sonication when preparing the suspension for PL measurements. The luminescence of the inner tube is quenched due to the interaction with the host tube. The host-guest interaction does not necessarily quench the fluoresc-
2. Experimental methods

Fig. 2.10: Schematic drawing of the Nanolog fluorimeter with main parts indicated.

cence of the encapsulated species though, for example in the case of small oligothiophenes the emission spectrum changes little upon encapsulation. [47, 107] Here, PL spectroscopy was used to investigate how the hybrid formation of coronene with carbon nanotubes influences the luminescent properties of the molecule (Chapter 5).

2.3.3 Experimental arrangement

Photoluminescence spectroscopy was used to characterize the luminescent properties of the coronene@CNT hybrids, and to analyze the washing process after the encapsulation of coronene. In the latter case, the guest molecule content of the filtrate was estimated by comparing the PL emission spectra of the filtrates to the spectra of reference solutions with known concentrations. The coronene-filled nanotubes were analyzed in dispersion form. PL emission was measured in a wide energy range to detect both the nanotube (NIR) and the guest molecule (Vis) emission. Therefore dispersions were prepared in D$_2$O to avoid the high absorption of water in the NIR range. Sodium dodecyl sulfate was used as surfactant to disperse the nanotubes. Typically 1 mg of CNTs was added to 25 ml of 1wt% SDS-D$_2$O solution, followed by 60 minutes of sonication. After letting the dispersions settle for a day, they were centrifuged at 8500 rpm for two times 30 minutes with a 15 minutes break in between the centrifugations.
Photoluminescence spectra were recorded with a **Horiba Jobin Yvon NanoLog Fluorometer**\(^6\) (Fig. 2.10). The excitation wavelength is chosen from a broadband (UV to NIR) xenon lamp by a double grating monochromator. The sample is excited with the monochromatic light, and the emitted light is analyzed by iHR320 type grating spectrometer unit. The fluorometer has a photomultiplier detector (200–850 nm) and a liquid nitrogen-cooled InGaAs array detector (800–1550 nm). The former was used to measure the luminescence originating from coronene and its oligomers, the latter for detecting the nanotube transitions. Spectra were recorded with a resolution of typically 5 nm on the excitation and 3 nm on the emission side.

### 2.4 Transmission electron microscopy

Transmission electron microscopy (TEM) was used to visualize the structure of coronene@CNT hybrids (Chapter 5). The measurements were done by Andrei Khlobystov\(^7\), therefore I do not discuss the theory and the experimental arrangement of TEM in detail here. The working principle of a transmission electron microscope is similar to an optical microscope but uses electrons instead of light, guided by electromagnetic lenses. Since the wavelengths of the electrons are inversely proportional to their velocities, the resolution is controlled by the acceleration voltage applied on the source electrons.

Transmission electron microscopy (TEM) is the most important characterization tool besides optical and Raman spectroscopy to investigate endohedrally functionalized CNT hybrids. Since SWCNTs are atomically thin, the guest molecules can be studied directly at an atomic level by high resolution TEM (HR-TEM). \[9, 43, 52\] In the case of smaller organic molecules, such as coronene, the stability under the electron beam can be a major problem, since the molecules are constantly bombarded by electrons during imaging, and some of the kinetic energy of the electron beam can trigger chemical transformations. To investigate these molecules the use of low acceleration voltage is needed. On the other hand, the modification caused by the electrons can also be an advantage, if the reactions inside the CNTs are to be studied. \[108\] Besides the investigation of encapsulated species, TEM is widely used to study sidewall functionalization, though generally only larger molecules or metals can be detected, and to gain direct structural information further spectroscopic investigation is needed.

Transmission electron microscopy was performed using a JEOL 2100F TEM (field emission gun source, information limit \(< 0.19\) nm) at room temperature and an accelerating voltage of 100 kV. The image processing and analysis was conducted using Gatan Digital Micrograph software.

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\(^6\) The instrument is located at the Wigner Research Centre for Physics, in Budapest, Hungary.

\(^7\) University of Nottingham, University Park, Nottingham, United Kingdom
3. Conducting polymer-nanotube hybrids

3.1 Aim

Hybrid materials made from two types of carbon-based conductors, carbon nanotubes and conducting polymers, are of considerable interest, because it is hoped that the interaction can improve the electrical conductivity, the mechanical stability, and the biocompatibility of the resulting system. Due to the complexity of these hybrids, generally little is known about their structure. Hybrid formation of nanotubes with three different polymers: polyaniline (PANI), polycarbazole (PCz), and melanin were investigated. I examined how surface attenuated infrared adsorption can be used to determine the structure and type of bonding in these systems.

3.2 Introduction

The polymer-nanotube hybrids in this work were prepared to investigate their potential to be used for neuronal growth and repair. \[109, 110\] The main problems with reconnecting brain pathways after neural injury are the poor adhesion of neurons to the surface and the solution-derived shunting noise. \[111\] CNTs can be good candidates, since their diameters are very close to those of neural dendrites and resemble extracellular components, and studies on chemically modified MWCNTs have already suggested their potential to guide neurite outgrowth in vitro, by influencing neuronal extracellular or molecular interactions \[112\]. Coating the nanotubes with conductive polymers results in the increase of their conductivity and enhanced electron transfer from the electrolyte to the composite electrode. (Fig. 3.1) To better understand the improved properties of the hybrid systems it is important to investigate the interaction between the nanotubes and the polymers.

Various carbon nanotube-polymer hybrids were prepared earlier and tested for practical applications. However, fundamental questions about the structure and type of bonding in these systems often remain unanswered. Baibarac et al. suggested that both polyaniline and poly(N-vinyl carbazole) bonds covalently to the nanotube wall when the polymerization of the monomers is performed in the presence of nanotubes. \[113, 114\] On the other hand, if nanotubes are mixed with PANI in solution phase, two main structures were observed: polymer-functionalized nanotubes and nanotube-doped polymers. Other aromatic polymers, such as polyvinil pyrrolidone (PVP), polystyrene sulfonate (PSS),
3. Conducting polymer-nanotube hybrids

![Graphs showing AC impedance spectroscopy](image)

**Fig. 3.1:** AC impedance spectroscopy, Nyquist plot ($Z''$ versus $Z'$), of the conductive polymer-nanotube hybrids (PANI, PCz, and melanin-SWCNT on ITO) and the respective references (pure polymers and SWCNT on ITO). Hybrid formation with PANI and PCz results in increased conductivity. [P1]

dextran, were reported to helically wrap nanotubes when the constituents are mixed in water. [115] More rigid aromatic-based systems, such as poly(aryleneethynylene)s, form a $\pi-\pi$ complex without wrapping. [116]

Due to the complex vibrational pattern, the investigation of the hybrid formation by vibrational spectroscopy is rather complicated. However, Setyowati et al. showed that when a molecule is in strong contact with the nanotube, certain infrared-active modes are attenuated. The underlying effect is the surface attenuated infrared absorption (SAIRA). [117] The vibrations of molecules adsorbed on a conducting surface interact with the evanescent field induced during reflection. As discussed in Section 2.2, a criterion for IR absorption is a net change in the dipole moment of the molecule as it vibrates. However, because image charges are formed on the conductive surface, the dipole change of the original molecular vibrations is canceled out, and the corresponding IR modes are attenuated. (Fig. 3.2) Because of the extensive delocalized $\pi$-electron system, the CNT surface is highly polarizable. Therefore, those IR vibrations of the adsorbed molecules that give rise to dipole changes parallel to the CNT surface become diminished considerably in intensity. Dipole changes perpendicular to the surface are unable to create an image dipole on a CNT due to its thin surface. The authors used this effect to investigate the wrapping of poly(p-phenyleneethynylene)s (PPEs) onto various types of nanotubes. Since the distance between the molecule and the surface affects the magnitude of the attenuation, by investigating the strength of the SAIRA effect, the tightness of PPE wrapping can be estimated, which can be correlated with the surface quality of the nanotubes.
Fig. 3.2: SAIRA effect. The vibration of the dipole moment and its image charge parallel to the surface of the CNT.

Here, I investigated how the SAIRA effect can be used to study the strength of the interaction between the nanotube and the different polymers. The nanotubes are the same in all three hybrids, therefore the property responsible for the changes in the attenuation is the distance of the polymer from the nanotube surface.

3.3 Experimental

3.3.1 Samples

The materials have been prepared by electrochemical polymerization of the respective monomers using gold working electrodes coated by purified nanotubes. CVD grown single-walled carbon nanotubes, having diameters between 1 and 2 nm were purchased from Sigma-Aldrich. Electrochemical polymerization has been performed by cyclic voltammetry (CV) on gold coated by SWCNT serving as the working electrode, Pt wire as counter electrode and Ag/AgCl as reference electrode. Table 3.1 describes the electrolytes used. Fig. 3.3 summarizes the structure of the polymers. Samples were prepared by Shoshana Ben-Valid¹.

Tab. 3.1: Electrolytes used for the polymerization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>polycarbazole (PCz)</td>
<td>0.1 M NaClO₄ in acetonitrile saturated with carbazole</td>
</tr>
<tr>
<td>polyaniline (PANI)</td>
<td>0.1 M aniline in triple distilled water solution at pH 3.5</td>
</tr>
<tr>
<td>melanin</td>
<td>4 mM dopamine in 0.1 M PO₄³⁻ buffer solution and 0.5 M KCl at the solution of pH 7</td>
</tr>
</tbody>
</table>

¹ Institute of Chemistry and Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem.
3. Conducting polymer-nanotube hybrids

Fig. 3.3: a) Aniline $\Rightarrow$ polyaniline (PANI) base form. Structure: $\left( (-B-NH-B-NH-) \right)_y \left( (-B-N=N-) \right)_{(1-y)}^x$, where B and Q stands for benzenoid and quinoid structure respectively. $y$ can be varied continuously from one to zero (from completely reduced form to the completely oxidized form). The terms leucoemeraldine, emeraldine, and pernigraniline refer to the different oxidation states of the polymer where $y=1, 0.5, and 0$, respectively. b) Carbazole $\Rightarrow$ polycarbazole (PCz). c) Dopamine $\Rightarrow$ melanin. The polymer contains building blocks presented as the intermediate reaction state. However, the exact bonding pattern, therefore the final structure of synthetic melanin cannot be assigned based on the literature.

3.3.2 Measurements

The polymer-nanotube hybrid coated gold electrodes were investigated in reflectance mode in the mid-infrared region by the Bruker Tensor 37 spectrometer connected to a microscope and an ATR accessory. Raman spectroscopy was measured with a 785 nm laser excitation on the Renishaw 1000 spectrometer. Since both the ATR crystal and the Raman microscope probes only a small sample area, multiple measurements were performed on each sample to check the homogeneity. MIR-NIR absorption measurements (except the ATR measurements) were done by Katalin Kamarás. UV-Vis-NIR absorption was measured by Shoshana Ben-Valid.

Besides spectroscopy, samples were analyzed by impedance measurements, high resolution scanning electron microscopy, and atomic force microscopy by Shoshana Ben-Valid, Aiping Zeng, and Shlomo Yitzchaik.

Impedance measurements with alternating voltage amplitude of 5 mV between 20 and 250 MHz were conducted by using AUTOLAB PGSTAT12 (Eco Chemie B.V.). Measurements for all samples were performed in aqueous solution of 5.0 mM ferric cyanate.

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2 Wigner Research Centre for Physics, Budapest, Hungary.
3 Institute of Chemistry and Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem.
(K₃Fe(CN)₆), 5.0 mM ferrous cyanate (K₄Fe(CN)₆), and 100 mM potassium chloride at a constant potential of 0.17 V, and with a Pt counter electrode and an Ag/AgCl reference electrode. The electron transfer resistance is the difference between the low and high frequency intercept of the impedance curve with the real axis of the Nyquist plot.

The present discussion will focus on the spectroscopic characterization. SEM pictures and UV-Vis-NIR absorption results are presented in App. A. These measurements were used to confirm the success of the polymerization reaction. Impedance results, presented on Fig. 3.1, are compared to the results obtained from the vibrational analysis but are not part of the current discussion. Details of these measurements can be found in Ref. [P1].

3.4 Results

3.4.1 Infrared spectra

The infrared spectra, shown in Fig. 3.4, recorded in the mid- and near-infrared range demonstrate the presence of both the polymers and the nanotubes in the samples. The S₁₁ nanotube transitions occur around 5300 cm⁻¹, and some vibrational peaks originating in the polymers are present. In the infrared spectra of the melanin hybrid the polymer bands show no appreciable change. However, in the case of PANI and PCz hybrids distinct changes occur compared to the spectra of the pure polymers. Several peaks corresponding to the polymers appear with lower intensity or are not present at all.

Changes can be investigated in more detail in the ATR spectra, shown in Fig. 3.5. Polycarbazole is present in an oxidized form, therefore ClO₄⁻ ions from the electrolyte are intercalated into the sample, providing the electric neutrality of the system. [118] ClO₄⁻ vibrations appear at 1090 cm⁻¹ and 630 cm⁻¹ on the spectra of both the pure polymer and the hybrids. On the other hand, most of the vibrations originating from the polycarbazole are considerably weaker or completely disappear from the spectra. The peaks observed at 804 cm⁻¹ and 884 cm⁻¹ are vibrations of the trisubstituted benzene rings, at 1205 cm⁻¹ and 1235 cm⁻¹ are C-H in-plane deformations of the aromatic rings. The pattern between 1300 and 1500 cm⁻¹ consists of C-H and N-H in-plane bending vibrations and ring deformations, and the one at 1552 cm⁻¹ of C-H in-plane bending vibrations and ring deformations. The 1600 cm⁻¹ mode belongs to the C-C stretching vibration. [119, 120] All the attenuated modes have in common that they belong to in-plane vibrations.

Similar effect can be observed in the case of polyaniline. The spectrum of pure PANI suggests that both the emeraldine base and salt form is present in the sample. (Fig. 3.3) In the case of salt form, ionic bond is formed between a proton and the non-bonding electrons of the nitrogen, and the counterion provides the electric neutrality of the system. The peak at 1149 cm⁻¹ is the vibration of the B-(NH)⁺=Q structure, characteristic of the salt form, while the peak at 1375 cm⁻¹, corresponding to the C-N stretching in the
3. Conducting polymer-nanotube hybrids

![Infrared spectra](image)

**Fig. 3.4:** Infrared spectra in the mid- and near-infrared range of the different conducting polymer-nanotube hybrids. Asterisks indicate extrinsic peaks (water, CO$_2$). Both nanotube transitions ($S_{11}$ around 5300 cm$^{-1}$) and some vibrational peaks originating from the polymers appear in all the hybrids.

...neighborhood of the quinoid ring, is characteristic of the base form of the polymer. The polyaniline peaks attenuated in the presence of nanotubes are located: at 1149 cm$^{-1}$, between 1300 and 1400 cm$^{-1}$, corresponding to C-N stretching modes, and at 1509 cm$^{-1}$ and 1590 cm$^{-1}$, corresponding to the stretching vibration of the benzooid and quinoid ring, respectively. [121,122] The attenuation of these vibrational modes in the case of the PCz-CNT and the PANI-CNT hybrid can be explained by the SAIRA effect. The vibrations that are parallel to the nanotube surface are attenuated due to the formation of image charges.

### 3.4.2 Raman spectra

The polycarbazole-CNT and melanin-CNT hybrids show Raman spectra typical of nanotubes, with only the RBM, D, and G bands present (Fig. 3.6 a). In covalently functionalized nanotubes, in most cases sidegroups are not detectable due to the resonant enhancement of the nanotubes. No increase in the intensity of the D mode was observed with respect to the G mode, which suggest non-covalent interaction between all three investigated polymers and the nanotubes.

In the polyaniline hybrid (Fig. 3.6 b), however, the vibrational modes of both the nanotubes and the polymer are present. This can be explained by the resonance of the emeral-
3.4. Results

### Fig. 3.5:
ATR spectra of the polycarbazole (PCz), polyaniline (PANI), and the respective hybrids. The assigned in-plane vibrations of the polymers are marked with arrows.

![ATR spectra of the polycarbazole (PCz), polyaniline (PANI), and the respective hybrids](image)

### Fig. 3.6:
a) Raman spectra of the polycarbazole-CNT and melanin-CNT hybrid compared to the spectra of pristine nanotubes coated on gold substrate. b) Raman spectra of polyaniline-CNT hybrid compared to pure polyaniline and CNT reference. Peaks belonging to PANI are marked with arrows on the spectra of the hybrid. Spectra are offset vertically for clarity.

![Raman spectra of the polycarbazole-CNT and melanin-CNT hybrid](image) ![Raman spectra of polyaniline-CNT hybrid](image)
3. Conducting polymer-nanotube hybrids

dine salt with the 785 nm laser excitation. The Raman spectrum of the PANI-CNT hybrid is approximately the superposition of the spectra of the constituents. A minor shift occurs in the position of the mode at 1338 cm$^{-1}$, and the shoulder of the peak at 1170 cm$^{-1}$ disappears. The former corresponds to the C-N$^+$ vibration of delocalized polaronic structures, the latter to the C-H bending vibration of the semiquinoid ring.

3.5 Discussion

The presence of the SAIRA effect in the IR spectra in the case of polycarbazole and polyaniline, suggests a strong interaction of the aromatic rings with the surface. Earlier results on aniline-, polyaniline-, and poly(N-vinylcarbazole)-CNT hybrids indicated covalent bonding induced by proton transfer. [113,114,123] The electrochemical polymerization, presented here, results in the attachment of the polymers to the nanotube surface through $\pi$-$\pi$ interactions. Based on the results wrapping and rigid coating cannot be distinguished. It is hard to identify if protonation occurred due to the presence of nanotubes. PANI was present both in the emeraldine salt and base form in the polymer prepared on gold surface. The characteristic IR-active modes are both in-plane vibrations and therefore are attenuated, and the Raman spectra is dominated by the salt form, both for the pure polymer and the hybrid due to resonance effects.

The factors governing the changes in the vibrational spectra are the distance of the organic molecule from the nanotube surface and the quality of the surface, respectively. Based on the attenuation of the infrared peaks, among the three polymers investigated, polyaniline and polycarbazole develop stronger interaction with the nanotubes than the melanin, resulting in tight coating. This is in good agreement with the observed changes in the electrode impedance: polyaniline gives the most pronounced decrease in the impedance of the hybrid electrode, followed by polycarbazole and melanin.

3.6 Conclusion

I have shown that based on the SAIRA effect observed in the vibrational spectra of carbon nanotube-conducting polymer hybrid systems, the strength and type of the interaction between the constituents can be estimated. The results suggest that polycarbazole and polyaniline strongly interact with the nanotube surface, in agreement with the observed changes of the conductivity due to hybrid formation. These polymers are tightly attached to the nanotubes by noncovalent interactions.
3.6. Conclusion

Theses:

1. I have investigated the hybrid structures formed by polymerization of aniline, carbazole, and dopamine in the presence of carbon nanotubes. The conductivity of the polyaniline-nanotube and polycarbazole-nanotube hybrid electrodes was observed to improve significantly compared to the pristine carbon nanotube electrodes.

   (a) I observed the attenuation of the in-plane infrared-active vibrations of polyaniline and polycarbazole upon hybrid formation with carbon nanotubes. I showed that the attenuation can be explained by the surface attenuated infrared absorption (SAIRA) effect, caused by the interaction between the polarizable \( \pi \)-electron network of the nanotubes and the vibrations of the molecules. Based on the observed changes I suggested that polyaniline and polycarbazole develop stronger interaction with the nanotubes than the melanin, resulting in a tight coating.

   (b) I showed that the strength of the SAIRA effect correlates with the conductivity results: hybrids where the nanotubes are more tightly wrapped by the polymer show larger increase in electrical conductivity upon hybrid formation.

Related publications:


4. Peapods and DWCNTs

4.1 Aim

In this chapter, I show an example of encapsulated species in nanotubes and the investigation of the host-guest interactions by vibrational spectroscopy. $C_{60}@$SWCNT hybrids (peapods) and their transformation to double-walled carbon nanotubes constitute a widely studied topic. I investigated the preparation process, and applied the obtained results to optimize our characterization protocol of other endohedrally functionalized hybrids. The controlled synthesis of double-walled carbon nanotubes allowed the investigation of the interactions between the inner and outer nanotubes in DWCNTs, which were reported to cause changes in the electronic structure of both tubes, and were suggested to lead to a semiconducting-to-metal transition. [124]

4.2 Introduction

As discussed in Sec. 1.2.2, the filling process results in both the encapsulation of molecules inside the CNTs and their adsorption onto the outer surface of the walls. To remove the adsorbed species, the nanotubes are either treated under dynamic vacuum, which facilitates the desorption of the molecules, or sonicated in a good solvent of the guest molecules. I investigated the second method, because it can be applied for a wider range of guest species. Since both the filling and the washing steps can result in changes of the sample morphology, which can influence the Raman spectra, the preparation of a control line is recommended. These samples undergo similar treatments but without the addition of guest molecules. It is important to note that even after repeated washing steps, some adsorbed residue can remain on the sample. As Botos et al. showed, the combination of infrared and Raman spectroscopy can be used to identify if the molecules are encapsulated or adsorbed inside the tubes. [P6] Encapsulation of molecules inside the SWCNTs were reported to cause shifts of the RBMs. These shifts are generally attributed to two main factors: the strain imparted by molecules inside nanotubes and the interaction of the electronic states of the host and guest subsystems, which results in the change of the resonance conditions. [33, 85] The vibrational modes of the guest molecules can also be affected by the encapsulation. In the case of $C_{60}$, the splitting of the $A_g(2)$ mode was observed [85]. Since this mode is non-degenerate, it cannot split even if electric or
4. Peapods and DWCNTs

mechanical fields of the host tubes break the symmetry. Pfeiffer et al. suggest that the splitting is a result of the mechanical coupling between $C_{60}$ and the host tube. [125] The conversion of the encapsulated molecules to inner nanotubes can be used to unambiguously prove the efficiency of the filling process. [51]

DWCNTs are interacting systems consisting of inner and outer nanotubes. As discussed previously in Sec. 1.1.2, the electronic structure of a carbon nanotube is determined by its chirality. Approximately one third of the possible nanotube structures is metallic, the others are semiconducting. However, by addition or removal of electrons (doping) the metallicity of the nanotubes can be changed. In double-walled carbon nanotubes the interaction between the two concentric tubes can modify the electronic structure of both constituents. Nuclear magnetic resonance (NMR) experiments by Singer et al. on DWCNTs [124], which were prepared from peapods filled with $^{13}$C isotope enriched fullerene molecules [126], showed that there is no indication of a metal / semiconductor separation among the inner tubes. These results are very surprising, since the transformation of $C_{60}$ molecules into inner tubes results in a broad variety of chiralities, the diameter of the inner tubes is controlled by that of the host CNT. Since the average diameter of the host nanotubes is 1.4 nm, the inner tubes forming inside them are narrow enough that the presence of a secondary gap in the armchair nanotubes reduces further the number of possible metallic tubes. The authors suggested that the universal metallicity of the inner tubes could result from charge transfer between the inner and outer tubes. Zólyomi et al. investigated the inter-shell interactions in DWCNTs within an inter-molecular Hückel model and first principles density functional theory within the local density approximation. The authors confirmed that the interaction between the layers of DWCNTs can lead to a semiconductor-to metal transition but not necessarily to a universal metallicity. However, all semiconducting DWCNT systems showed significantly reduced band gaps compared to the band gaps of the corresponding individual SWCNTs. The interaction between the layers was found to consist of both charge transfer and orbital mixing. All inner tubes were found to be negatively charged, however the magnitude of charge transfer is small, around 0.005 e/Å to 0.035 e/Å (about 0.0005 to 0.0045 e/atom for the inner wall, and 0.0002 to 0.0024 e/atom for the outer wall) depending on the tube chiralities. As a consequence, the density of states at the Fermi level is predicted to be large according to the calculations, since the Fermi level is close to the Van Hove singularities. Orbital mixing was found to significantly reduce the band gap of semiconducting DWCNTs. All Van Hove transitions showed a red shift, compared to the transitions of the individual SWCNT subsystems, but the magnitude of the shift was predicted to be larger for low energy transitions. The authors point out that, since orbital mixing is present, the inner and outer tubes cannot be treated separately. [127,128]

As discussed in Chapter 2, optical and Raman spectroscopy are suitable tools to investigate changes in the electronic structure of CNTs. In the Raman spectra, the G band
4.3 Experimental

4.3.1 Samples

C\textsubscript{60} (99.5% purity, NANOS Research) was encapsulated into P2-type SWCNTs (Carbon Solutions) by the vapor phase method. With an average diameter of 1.4 nm these nanotubes are of ideal size to host C\textsubscript{60} molecules. The structure, Raman and infrared spectra of C\textsubscript{60} can be found in App. B. Table 4.1 summarizes the sample names. The samples were prepared by Ákos Botos\textsuperscript{1}.

Opening

The first step of all encapsulation processes is the opening of nanotubes, which was achieved by annealing them at 570 °C for 20 minutes in air. The open nanotubes were processed immediately after the annealing ended to prevent the closing of the holes. After opening the nanotubes, part of the sample was kept for reference (sample P2-O).

Encapsulation

The mixture of nanotubes and fullerene in 1:1 weight ratio was sealed into a quartz tube under dynamic vacuum of 10^{-5} mbar. The furnace was heated at a rate of 5 °C/min up

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4. Peapods and DWCNTs

Tab. 4.1: Summary of sample names and experimental conditions.

<table>
<thead>
<tr>
<th>treatment</th>
<th>sample</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>original</td>
<td>P2</td>
<td>P2-OF</td>
</tr>
<tr>
<td>opened</td>
<td>P2-O</td>
<td></td>
</tr>
<tr>
<td>filled</td>
<td>PP</td>
<td>P2-OF</td>
</tr>
<tr>
<td>washed</td>
<td>PP-W</td>
<td>P2-OFW</td>
</tr>
<tr>
<td>annealed</td>
<td>DWCNT</td>
<td>P2-OFWA</td>
</tr>
</tbody>
</table>

to 650 °C, where the temperature was kept constant for 2 hours, then allowed to cool at a rate of 5 °C/min (sample PP). The reference sample was prepared the same way without adding C$_{60}$ to the nanotubes (sample P2-OF).

**Washing**

After preparation each sample was sonicated in toluene, a good solvent of C$_{60}$, to remove the excess of the material adsorbed on the nanotube surface. After approximately 30 minutes of sonication the solution was vacuum filtered using a nylon filter paper with 0.2 µm pore size. The filtrate was analyzed by UV-Vis spectroscopy to estimate the concentration of guest molecules by comparing to reference solutions of known concentration. The washed samples are sample PP-W (peapod, Fig. 4.1) and sample P2-OFW (blank control sample).

**Annealing**

DWCNTs were prepared by annealing the sample at 1250 °C (with heating and cooling rate 1 °C/min) for 24 hours in vacuum (10$^{-4}$ mbar).

**Self-supporting films**

Nanotubes were dispersed in Triton X-100 solutions by ultrasonication, and the supernatant of the solution was filtered through a cellulose-based filter membrane. The filter paper was then dissolved in acetone, and the nanotube film was placed over a hole on a graphite support. Mild annealing was used to evaporate the solvent residues. This technique allows one to measure transmission from FIR to UV range on the same sample. [129]

**4.3.2 Measurements**

Raman measurements were performed on the Jobin-Yvon T64000 Raman spectrometer using excitation lines at 482.5 and 530.9 nm at room temperature. Spectra were recorded on the nanotube films to allow direct comparison to the optical measurements. Each sample was measured at three different positions.
4.4 Results

4.4.1 Peapods

Fullerene-related vibrations are hard to detect in the Raman spectra of C_{60}@SWCNT, because, in contrast to the nanotubes, C_{60} molecules are not in resonance with any of the laser lines that were available for the measurements. They can be best detected using blue laser excitation. [85] With 482.5 nm excitation we observed the splitting of the A_g(2) line of C_{60} (Fig. 4.2 b, App. B Fig. B.2) belonging to the encapsulated fullerene molecules. The radial breathing modes of the nanotubes are shifted, as observed before. [51, 85, 130, 131] In the case of powder samples these changes are masked by the general inhomogeneity of the sample, thus they are hard to detect. By using Triton X-100 dispersed films we obtained more homogeneous samples, therefore the shifts can be unambiguously detected.

Fig. 4.2: Raman spectra measured with a) 530.9 nm and b) 482.5 nm laser excitation. All spectra have been normalized to the G mode of the nanotube. Spectra are offset vertically for clarity. On panel a) the D and 2D area is magnified 10 times for better visibility of the modes. In the spectra of DWCNTs the D mode increases with respect to the G mode, and all modes show features related to the inner tubes. On panel b) we can see the A_g(2) mode of the enclosed fullerene molecules in the case of peapods. The dips marked with asterisks are artifacts of the CCD.

Wide-range optical spectra were measured on free-standing nanotube films on the Bruker IFS 66v/S (FIR: 30–700 cm\(^{-1}\) and MIR: 500–7000 cm\(^{-1}\)), the Bruker Tensor 37 (NIR: 4000–15000 cm\(^{-1}\)), and the JASCO V550 spectrometer (UV-Vis: 11100–52500 cm\(^{-1}\)) by Áron Pekker².

² Wigner Research Centre for Physics, Budapest, Hungary
4. Peapods and DWCNTs

**Fig. 4.3:** Raman spectra measured with 530.9 nm laser excitation a) for comparing the RBM range. The intensities of all spectra are normalized to the G mode of the nanotubes, and offset vertically for clarity. No changes occur on the reference series upon the different treatments. In the spectra of peapods the position and the line width of the breathing modes change. In the case of DWCNTs new peaks appear at higher energies belonging to the inner tubes. b) Lorentzian fit of the radial breathing modes for peapods and the reference sample. Each Lorentzian curve represents the contribution of nanotubes with different diameter to the RBM. The results of the fit are summarized in Table 4.2.

**Tab. 4.2:** Peak positions and shift observed on C\textsubscript{60}@SWCNT compared to the reference SWCNT.

<table>
<thead>
<tr>
<th>center $\tilde{\nu}_{\text{RBM}}$ (cm\textsuperscript{-1})</th>
<th>host diameter $d$ (nm)</th>
<th>shift (cm\textsuperscript{-1})</th>
<th>line width (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2</td>
<td>PP-W</td>
<td>160.7</td>
<td>159.3</td>
</tr>
<tr>
<td>175.7</td>
<td>171.9</td>
<td>1.45</td>
<td>-3.8</td>
</tr>
<tr>
<td>182.0</td>
<td>179.1</td>
<td>1.38</td>
<td>-2.9</td>
</tr>
<tr>
<td>187.9</td>
<td>186.5</td>
<td>1.33</td>
<td>-1.5</td>
</tr>
</tbody>
</table>
4.4. Results

Slight inhomogeneity was found only in the case of the peapod sample. The diameter of the host nanotubes was calculated using the formula:

\[ \tilde{\nu}_{\text{RBM}} = \frac{234}{d} + 10 \]  

(4.1)

RBM shifts upon the encapsulation of C\(_{60}\) molecules depending on the diameter of the SWCNT. Joung et al. reported an upward shift in the case of nanotubes with diameter smaller than 1.32 nm and a downshift of the RBMs in the case of larger diameter tubes. Ohno et al. reported similar behaviour. Our results, shown in Fig. 4.3, are summarized in Table 4.2. In the investigated diameter range the RBMs of the peapods shift to lower energies, and the size of the shift depends on the diameter of the host nanotubes. For diameters smaller than 1.45 nm our results are in accordance with Joung et al. and Ohno et al., however, for larger diameters the shift of the RBM decreases again in contrast to their results. Besides the shift, the narrowing of the lines was also observed. The decrease in the line width could be indicative of weaker interaction between the tubes.

In the optical spectra of the films prepared from the reference series, no prominent changes were detected due to opening, annealing, and washing. In the optical spectra of the fullerene peapods a peak appears in the UV region [132] at 342 nm which corresponds to the \(h_g + g_g \rightarrow t_{1u}\) transition of the encapsulated C\(_{60}\) molecules (Fig. 4.4 c, App. B). [133] The position is downshifted by 11 nm compared to outside fullerene molecules. Though vibrations of the encapsulated C\(_{60}\) molecules can be detected by Raman spectroscopy, in the optical absorption spectra no vibrational features appear. [P6]

4.4.2 DWCNTs

The Raman intensities of the outer tube modes of the DWCNT are smaller compared to that in all the other samples. The RBMs of the outer tubes shift back to almost the same position as in pristine tubes (Fig. 4.3). Small shifts were reported before in the case of DWCNTs [135] and explained by the interaction between the walls of the inner and outer tube. As discussed in Sec. 2.1.2, the breathing-like modes of the DWCNTs in this diameter range are very close to the RBMs of the individual SWCNTs. The small shifts caused by the coupling can be masked by the effect of bundling. The downshift observed in the RBM of DWCNTs is not larger than 1 cm\(^{-1}\) in our case. Between 260 and 300 cm\(^{-1}\) new modes appear which belong to the inner tubes. The defect ratio (I\(_{D}/I_{G}\)) increased in DWCNTs, and the D, G, and 2D modes have components shifted to lower energies, corresponding to the inner tubes (Fig. 4.2 a).

As the peapods are converted to DWCNTs, notable changes occur in the optical spectra (Fig. 4.4). All the peaks lose their fine structure, but they do not get broader overall. The intensity of the Drude peak (Fig. 4.4 a) and also the other peaks decreases. Though transitions from the encapsulated C\(_{60}\) are detectable, we could not identify the electronic
transitions of the inner tubes in the spectra. The mean diameter of the inner tubes that grow inside P2-type SWCNTs is approximately 0.7 nm. It is very close to the diameter of the CoMoCat SG-type SWCNTs, of which wide-range optical absorption data are available in Ref. [134] (shown in App. B Fig. B.4). The $S_{11}$ transition of these narrow SWCNTs fall into the same energy range as the $S_{22}$ transitions of the host tubes, but their higher energy transitions would be distinguishable from the ones of the outer SWCNT.
4.5 Discussion

The lack of inner tube transitions in the optical spectra results from the interaction between the inner and outer tubes. As Piao et al. have shown, by heavy diazonium functionalization, it is possible to deplete the electronic levels of the outer tubes until their electronic transitions fully disappear and detect the transitions of the inner tubes. [136]

Charge transfer between the inner and outer tubes would result in their doping. Moderate doping causes the depletion or filling of the nanotube electronic levels the effect of hole doping is demonstrated in Fig. 4.5. This, on one hand, results in the decrease of the intensity of the optical absorption, since the depleted electronic states cannot participate any further in the absorption. The electronic transitions disappear sequentially in the order of increasing energy with the increasing doping level. On the other hand, as the Fermi level shifts, the number of free carriers increases, thus the intensity of the Drude peak increases. Our results do not indicate the presence of charge transfer between the tubes, since all transitions decrease in intensity. (Wide-range optical transmission data are available in

Fig. 4.5: The effect of different degree of hole doping on the electronic levels of a semi-conducting (a) and a metallic SWCNT (b). a) In s-SWCNTs the Fermi level with no doping is in the middle of the band gap. Upon hole doping the Fermi level shifts into the first singularity, the s-SWCNT behaves like a metal. Upon further doping the first Van Hove singularity becomes depleted and cannot contribute to the optical absorption. b) In metallic nanotubes the DOS is initially finite at the Fermi level. Slight doping does not change the number of free carriers considerably. Upon heavy doping the Van Hove singularities contain no more available electrons to participate in the optical absorption.
4. Peapods and DWCNTs

App. B Fig. B.5.) The observed pattern in the case of DWCNTs is similar to the effect observed in functionalized nanotube samples. [84,134] Covalent chemistry introduces saturated bonds on the nanotube. These $sp^3$ hybridized atoms function as defect sites in the extended $\pi$-electron network, which destroy the electronic band structure yielding to the weakening the strength of all of the interband transitions. Based on the similarity to this process, in the case of DWCNTs most likely the localization of the electrons occurs rather than charge transfer as a result of the interaction between the tubes.

4.6 Conclusion

The preparation of peapod-based DWCNTs in a systematic way was followed by optical and Raman spectroscopy, and the spectral changes due to C$_{60}$ filling and subsequent DWCNT formation were summarized and analyzed. It can be concluded that these changes are more prominent if homogeneous nanotube films are used for the measurements. Fullerene features showed up in the peapod optical spectra, but the transitions of inner tubes were not observed in the DWCNT spectra. In the case of DWCNTs we observed no significant charge transfer between the inner and outer tube. The decrease in free carrier absorption and interband transitions and the increase in the defect ratio points to localization of the charge carriers.

Thesis:

2. I followed the process of C$_{60}@$SWCNT preparation and its transformation to DWCNT. I used Raman spectroscopy to confirm the successful encapsulation of C$_{60}$ molecules and the inner tube formation. Based on the simultaneous decrease of the intensity of the nanotube transitions in the optical conductivity spectra, I concluded that there is no significant charge transfer between the outer and inner nanotube in DWCNTs. The observed changes can be explained by the localization of the charges.

Related publication:

5. Coronene-nanotube hybrids

5.1 Aim

In this chapter I present a system, where both the surface and the inner cavity of the carbon nanotubes are involved in the hybrid formation. By exposing flat and curved carbon surfaces to coronene a variety of van der Waals hybrid heterostructures can be prepared. I used Raman and photoluminescence spectroscopy to investigate the different structures that were prepared by systematically changing both the temperature of the experiment and the curvature of the carbon surface.

Coronene@SWCNT can be an ideal candidate for various applications, if the durability of nanotubes can be combined with the strong PL emission of coronene. Finding optimal conditions to produce well-defined coronene-carbon nanotube heterostructures allowed me to examine how the enclosure of coronene inside carbon nanotubes affects the fluorescent properties of the guest molecules. Furthermore, the combination of polycyclic aromatic hydrocarbons (PAHs) with nanotubes, used as nanoreactors, offers the possibility for templated graphene nanoribbon (GNR) growth. I followed the polymerization of the coronene molecules in the confined one-dimensional environment of SWCNTs resulting in the possible formation of graphene nanoribbons and then inner nanotubes.

5.2 Introduction

5.2.1 Stacks or ribbons

Combining fluorophores with nanotubes could result in robust nanohybrids with variable emission in the visible spectral range, while keeping the merits of pristine single-walled carbon nanotubes, like superior durability. Using nanotubes as protective containers could be beneficial for various optoelectronic and biological applications. [107] However, only a few such hybrid materials have been successfully synthesized. Recently, Okazaki et al. reported the preparation of self-organized coronene stacks inside SWCNTs (Fig. 5.1b) using vapor-phase filling at 450 °C. [26] Samples were washed in toluene and annealed at approximately 300 °C under vacuum to remove excess coronene adhered to the outer wall. The authors used Raman and photoluminescence spectroscopy and transmission electron microscopy to characterize the structure. The hybrid system was expected to be
5. Coronene-nanotube hybrids

Fig. 5.1: a) Coronene. b)-c) TEM images and schematic drawings of coronene-nanotube hybrid structures observed in earlier works: b) stack [26] and c) ribbon [137] structure.

Fig. 5.2: Raman spectrum of coronene-nanotube hybrids by a) Okazaki et al. [26] and b) Talyzin et al. [137]. The latter also shows the spectra of coronene oligomers prepared by annealing of coronene in argon atmosphere.

a promising candidate for optical applications, based on the observation that as coronene is exposed to nanotubes, its blue fluorescence shifts to green, but still remains very intense.

A similar aggregated state consisting of coronene stacks in a face-to-face arrangement, called nanowires, can be prepared in SDS-water solution. [138] Coronene nanowires also emit green fluorescence, but the spectral shape is different from that of the coronene@SWCNT. Therefore the exact origin of the fluorescence shift of the coronene@SWCNT was still to be identified. The Raman spectrum of the hybrid (Fig. 5.2 a) also showed strong shifts and splittings compared to the spectra of the pristine materials, which the authors explained by the interaction between the coronene molecules in the stacked alignment. However, the observed pattern in the range of 1200–1400 cm\(^{-1}\) does not support this idea. Coronene has only two Raman-active modes in this range, at 1354 and 1369 cm\(^{-1}\), and both of them have non-degenerate \(A_g\) symmetry. [139,140]
Shortly after, Talyzin et al. reported that by applying similar filling conditions, they observed the formation of ribbon structures inside SWCNTs (Fig. 5.1 c). [137] They investigated the vapor-phase encapsulation of coronene between 450 °C and 530 °C at various temperatures under argon atmosphere, and analyzed the hybrids with TEM and Raman spectroscopy. Though the structures observed on the TEM images were markedly different from those observed by Okazaki et al., the Raman spectra (Fig. 5.2), which were attributed to originate from the encapsulated structures, were similar. The spectrum of the hybrid shows similar vibrational pattern as coronene oligomers, prepared by annealing of coronene. [43]

It is important to point out that while TEM images show only a few nanotubes, the Raman spectrum is measured on a macroscopic sample volume, therefore cannot be directly assigned to the visualized structure. Since both coronene and its oligomers possess extended π-electron network as the CNTs, their adsorption to the nanotube surface is very probable. Talyzin et al. observed oligomers adsorbed on the outer surface of the nanotubes at filling temperatures over 470 °C, and they mentioned that these by-products were neither soluble in toluene nor sublimed. This raises the question whether the observed spectroscopic data can be attributed to the encapsulated species.

Both the stacked and the ribbon hybrid structure has interesting properties worth investigating. The aim was to determine how the reaction conditions affect the final structure and synthesize the different heterostructures in a systematic way. Two parameters were found to play primary roles in the reactions of coronene in the presence of nanotubes: the reaction temperature and the diameter of the nanotubes. The coronene-carbon nanotube hybrid formation was studied by systematically varying these two parameters (Sec. 5.4.1, 5.4.2). The obtained structures allowed me to identify the molecules encapsulated and adsorbed to the nanotube surface.

Using the nanoextraction method with supercritical CO₂ as a solvent, hybrids having sidewalls free from adsorbed side products were successfully prepared, which is of utmost importance for reliable characterization of encapsulated molecules. These samples were used to investigate the luminescent properties of the coronene@SWCNT hybrids, and to follow the polymerization reaction of the molecules inside the nanotubes.

### 5.2.2 A road to graphene nanoribbons

Graphene has remarkable properties, such as supreme mechanical stiffness, strength, and elasticity, very high electrical and thermal conductivity. As discussed in Sec. 1.1.2, graphene is a semimetal. Though it is already used in flexible electronics, the absence of an electronic band gap in this material remains one of the main obstacles hindering its application in a broader range of electronic devices. Slicing the 2D structure into strips
of fixed width is an efficient solution for opening a band gap in the electronic structure of graphene, through lateral confinement.

It has been theoretically shown that the electronic properties of these graphene nanoribbons (Fig. 5.3) can be tuned from perfectly metallic, in the case of zigzag edge ribbons (ZGNR), to semiconducting for armchair ribbons (AGNR), where the engineered energy gap decreases as the function of increasing ribbon width. The production of narrow GNRs is of utmost interest, since these have band gap energies suitable for electronic applications.

Graphene nanoribbons can be prepared by both top-down and bottom-up methods. Top-down techniques are based on unzipping carbon nanotubes or cutting graphene sheets by lithographic or catalytic methods. Decreasing the ribbon width while maintaining well-defined edge structure in the case of top-down methods is a challenge, though recently 2 to 8 nm wide ribbons with well-defined edge structures were prepared by STM lithography. In larger scale production the 10 nm range has been reached using block copolymer lithography.

Bottom-up synthesis, on the other hand, provides access to GNRs having widths of few nanometers. Direct chemical synthesis was reported from polyphenylene molecules as precursors that are mediated by either solutions or metallic surfaces. Even though, the solution-based methods are promising, the number of available ribbon structures is limited at the moment, and the low solubility hampers the attempts to extend the length of these ribbons. Templated growth inside a long one-dimensional cavity can offer a solution to overcome these difficulties. Chamberlain et al. investigated the formation of sulphur-terminated GNRs from tetrathiafulvalene (TTF) by TEM, and found that the ideal host nanotube diameter for templated GNR growth is between 1 and 2 nm. Polycyclic aromatic hydrocarbons (PAHs), such as perylene or coronene were suggested to be ideal candidates for graphene nanoribbon growth.
Fig. 5.4: Routes for bottom-up synthesis of GNRs: a) from polyphenylene building blocks [156] and b) via templated growth in confined environment [53].

works on coronene-nanotube hybrids all used high temperature vapor-phase encapsulation [137,158] method, which does not result in well-defined hybrid structures, therefore makes the spectroscopic characterization unreliable. I followed the polymerization of coronene inside SWCNTs having outer surface clean of adsorbates (Sec. 5.4.3).

5.3 Experimental

5.3.1 Samples

For encapsulation carbon nanotubes were selected with as large a range of internal diameters as possible. For reference to study coronene adhesion without encapsulation, experiments were also performed on highly ordered pyrolytic graphite (sample GR). A sample of coronene nanowires (sample CW) [138] was also used as a reference. Details of the samples are given in Table 5.1, the structures of coronene and its oligomers are presented in App. C. Theoretical considerations by Okazaki et al. [26] give 1.32 nm as the minimum diameter for a carbon nanotube which can encapsulate coronene molecules. Based on these calculations, CoMoCat tubes were chosen as a reference to study sidewall adhesion, because coronene cannot fit inside the majority of them (sample CM). In contrast, the cavity of multi-walled carbon nanotubes (sample MW) is sufficiently large to allow any orientation, motion, and subsequent chemical reactions of coronene molecules to take place. However, the inner cavities of these nanotubes are too wide for GNR formation. [53] P2-SWCNT, a widely studied SWCNT type (samples SC, LT, and HT), are of ideal size to be filled with coronene molecules.
5. Coronene-nanotube hybrids

**Tab. 5.1:** Summary of the different carbon structures and experimental conditions to form coronene/carbon heterostructures.

<table>
<thead>
<tr>
<th>sample</th>
<th>carbon structure</th>
<th>manufacturer</th>
<th>$d_{av}$ [nm]</th>
<th>reaction type</th>
<th>$T$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>P2-SWCNT</td>
<td>Carbon Solutions</td>
<td>1.4</td>
<td>sc-CO$_2$</td>
<td>50</td>
</tr>
<tr>
<td>LT</td>
<td>P2-SWCNT</td>
<td>Carbon Solutions</td>
<td>1.4</td>
<td>vapor</td>
<td>385</td>
</tr>
<tr>
<td>HT</td>
<td>P2-SWCNT</td>
<td>Carbon Solutions</td>
<td>1.4</td>
<td>vapor</td>
<td>450</td>
</tr>
<tr>
<td>CM</td>
<td>CoMoCat CG SWCNT</td>
<td>SouthWest NanoTechnologies</td>
<td>0.9</td>
<td>vapor</td>
<td>450</td>
</tr>
<tr>
<td>MW</td>
<td>ox-MWCNT</td>
<td>Nanocyl 4@9 nm$^1$</td>
<td></td>
<td>vapor</td>
<td>450</td>
</tr>
<tr>
<td>GR</td>
<td>graphite</td>
<td>Johnson Matthey</td>
<td>-</td>
<td>vapor</td>
<td>450</td>
</tr>
<tr>
<td>CW</td>
<td>coronene nanowire</td>
<td>Ref. [138]</td>
<td>-</td>
<td>solution</td>
<td>-</td>
</tr>
</tbody>
</table>

The effect of reaction temperature was studied for P2-SWCNT samples (Sec. 5.4.1). Three reaction temperatures were employed: i) 50 °C with nanoextraction from supercritical CO$_2$, ii) 385 °C, slightly above the sublimation temperature of coronene, and iii) 450 °C, to compare with results presented in Ref. [26] and [137]. Investigation of the curvature and diameter dependence was conducted using carbon surfaces with increasing curvature in the sequence graphite < MWCNT < P2-SWCNT < CoMoCat-SWCNT (Sec. 5.4.2). Polymerization reactions were investigated on both the sample prepared by nanoextraction and vapor-phase filling at 385 °C (Sec. 5.4.3).

**Encapsulation**

For opening the nanotubes we followed the same procedure as in the case of preparation of C$_{60}$@SWCNT in Sec. 4.3.1. Encapsulation was done by vapor-phase method and nanoextraction in supercritical CO$_2$ (sc-CO$_2$). Coronene was purchased from a commercial source (Sigma-Aldrich, 97%). For all encapsulation reactions carbon nanotubes and coronene were used in 2:1 weight ratio.

**Vapor-phase encapsulation** The procedure used was similar to that described in Sec. 4.3.1. For encapsulation into P2-SWCNT two different reaction temperatures were used: (i) 450 °C (sample HT), to prepare samples that can be compared with the previous results on such hybrids ([26, 137]), and (ii) 385 °C (sample LT) to minimize the chance for side reactions occurring during sublimation. To determine the ideal sublimation temperature for filling, the open nanotube and coronene mixture was sealed into a glass tube, and placed into the furnace in a way that the empty side of the vessel was kept at lower temperature than the side containing the host and guest mixture. The temperature was raised at a rate of 5 °C/min until a yellow condensate appeared on the lower temperature

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1 Smallest inner and largest outer diameter.
side of the vessel, indicating the sublimation of coronene molecules. At this temperature the furnace was fully closed, and the encapsulation reaction was continued for 24 hours as for the other samples.

CoMoCat-SWCNTs and MWCNTs were filled at 450 °C (CM, MW), and, as a reference, coronene was sublimed onto graphite (GR) under the same conditions as the encapsulation reactions were done. The HT, MW, and GR samples were prepared by Dorina Kocsis and Gyöngyi Klupp\(^2\).

**Nanoextraction** The nanoextraction was performed in a closed high pressure reactor [33] under supercritical CO\(_2\) at 50 °C and 150 bar for 96 hours. [P6] Sample SC was prepared by Melinda Emese Füstös\(^2\) and Edit Székely\(^3\).

**Washing**

To remove the excess of coronene molecules from the surface of nanotubes, repetitive washing in toluene was employed. The samples were sonicated for 10 minutes in toluene, then vacuum filtered using a nylon filter paper with 0.2\(\mu\)m pore size. Washing cycles were monitored by photoluminescence and UV-Vis absorption spectroscopy, and were repeated until the coronene concentration of the filtrate was less than 0.001 mg/ml. As the removal of excess adsorbed coronene constitutes an important part of the established protocol, toluene washing was performed for all samples, except for those specifically referred to as "as-prepared".

To remove the dicoronylene and other polymerized coronene forms adsorbed on the samples prepared at 450 °C, the hybrids were repeatedly washed in aqueous SDS solutions. This washing step was not applied as part of the protocol, since the aim was to visualize the effect of adsorbed species for samples prepared at high temperature. Samples where this washing step was applied are named HT-SDS, CM-SDS. Aromatic surfactants, such as sodium cholate are expected to remove the adsorbed molecules more efficiently, since they possess stronger interaction with the nanotube surface and the adsorbed aromatic species as well. The use of SDS was preferred in this work to allow the comparison with previous PL results by Okazaki et al. [26]

**Annealing**

Double-walled carbon nanotubes were prepared by annealing the samples prepared from P2-SWCNT in vacuum at 1250 °C for 24 hours. The process is similar to the one described in the case of fullerene (Sec. 4.3.1). To study the polymerization of coronene inside the

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nanoreactor environment, samples SC and LT were annealed at 500, 700, 900 °C for 24 hours each (Samples SC/LT-500, SC/LT-700, SC/LT-900).

5.3.2 Measurements

Raman spectroscopy

To avoid the strong fluorescence occurring for excitation in the visible spectral range, pure coronene and dicoronylene was measured by FT-Raman with 1064 nm excitation. The nanotube hybrids and the corresponding reference samples were measured with 482.5, 530.9 and 532 nm excitation on the Horiba Jobin Yvon T64000 and with 785 nm excitation on the Renishaw 1000 spectrometer. Measurements were performed under a microscope with objective lens with magnification of 50 to test the homogeneity of the hybrids, which was found satisfactory in all cases. The data presented are averages of spectra measured on 10 different points on each sample. The spectral resolution was better than 2 cm\(^{-1}\). Only on the T64000 the resolution was set at 1 cm\(^{-1}\). The laser power was carefully adjusted to avoid any type of change in the samples. Part of the Raman measurements was done by Gyöngyi Klupp and Tamás Váci\(^4\).

Photoluminescence

To test the coronene and dicoronylene content, filtrates and dispersions of the various hybrids were measured with the excitation set at 342, 356, and 468 nm. The PL map of the nanotube transitions of the CM sample was measured and compared to the blank CoMoCat reference sample. Part of the PL measurements was done by Hajnalka Mária Tóháti\(^5\).

Transmission electron microscopy

Transmission electron microscopy was performed using a JEOL 2100F TEM by Andrei Khlobystov\(^6\). Samples were measured at room temperature using an accelerating voltage of 100 kV. Samples were prepared via drop-drying methanolic solutions onto copper TEM grid mounted "lacey" carbon films. Coronene molecules are stable under these conditions for 5-10 s which was sufficient for capturing images of coronene stacks in nanotubes. Further exposure of the electron beam results in rapid transformations of coronene into amorphous carbon and internal nanotubes.

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\(^6\) University of Nottingham, University Park, Nottingham, United Kingdom
5.4 Results and discussion

5.4.1 Effect of the reaction temperature on the encapsulation

P2-SWCNTs having an average diameter of 1.4–1.6 nm are ideal to host coronene molecules. The Raman spectroscopy and TEM results show that all three different methods applied for filling them resulted in the encapsulation of coronene molecules.

TEM imaging of the P2-SWCNTs treated with coronene at different temperatures reveals different structures (Fig. 5.5). The nanotubes filled by nanoextraction at 50 °C (SC) or sublimation at 385 °C (LT) both show coronene stacks similar to those reported by Okazaki et al. [26] Surprisingly the nanoextraction method yielded well-ordered stacks of coronene even at the relatively low temperature. In contrast, sublimation filling at 450 °C (HT) results in considerably fewer coronene stacks with a larger proportion of other types of carbon structures formed inside the host nanotube, including nanotube within nanotube structures.

Raman spectra taken in the energy range of the radial breathing mode of the samples based on P2-SWCNT are shown in Fig. 5.6. The spectra of the reference material are shown in black. On all samples the energies of the RBMs are upshifted with respect to the reference material due to the encapsulation of coronene. On the HT sample the peak marked with an asterisk belongs to coronene dimers. (Further proof is provided in

Fig. 5.5: TEM images of P2-SWCNTs hybrids: sample SC (a,b), LT (e,f), and HT (h). Short black arrows indicate the positions of coronene stacks in nanotubes within bundles. The structural diagram (d) and corresponding simulated TEM image (c) show how the coronene molecules stack inside the nanotube, and are in good agreement with the experimental image (b). Stacks of coronene molecules are seen to extend through the nanotube interior, the structural diagram (g) corresponds to experimental image (f). Coronene molecules are unstable in the electron beam, and therefore quickly transform into amorphous carbon or internal nanotube (i and j). [P5]
5. Coronene-nanotube hybrids

Fig. 5.6: Raman spectra of the hybrids based on P2-SWCNT using various laser excitations. The vertical dotted line indicates $\tilde{\nu}_{\text{RBM}}$ equivalent to 1.36 nm nanotubes, which is theoretically reported to be the minimal size capable to encapsulate coronene molecules. [26]. The asterisk indicates a peak belonging to coronene dimers on the HT samples (see text).

Fig. 5.7: Raman spectra of the DWCNTs prepared from P2-SWCNT-based hybrids with 482.5 nm excitation. Arrows indicate the RBMs of the inner tubes. Data are offset vertically for clarity.

Fig. 5.12, in the MW samples, where the RBM range of the nanotubes does not overlap with the dicoronylene modes.) This mode, like other dicoronylene modes, is absent in the spectra recorded using 785 nm excitation for being off resonance.

As an even stronger proof for encapsulation the inner species can be turned into nanotubes, using the same method as in the case of peapods. The mechanism will be discussed in more detail in Sec. 5.4.3 together with the polymerization reactions. Even though the DWCNT conversion method cannot identify the exact molecular species filled into the
5.4. Results and discussion

Fig. 5.8: Raman spectra of hybrids based on P2-SWCNT in the high energy region compared to the reference materials. Coronene and dicoronylene was excited at 1064 nm to avoid fluorescence present for visible excitation. In panel c data are offset vertically for clarity.

nanotubes, it can unambiguously confirm the encapsulation on a macroscopic scale. After conversion, RBMs related to inner nanotubes were observed in all samples (Fig. 5.7), indicating successful encapsulation in all cases.

Fig. 5.8 shows the Raman spectra in the range of the high energy modes of the hybrids together with those of reference materials for comparison. Coronene (Fig. 5.8 a) and dicoronylene (Fig. 5.8 b) can be clearly distinguished. Measurements were performed with all available laser lines to test different resonance conditions. Coronene has transitions in the blue, while dicoronylene in the green. Comparing all three P2-SWCNT-based materials, neither coronene nor dicoronylene is detected in the samples prepared at 50 °C or 385 °C (SC and LT). High temperature treatment at 450 °C (HT), however, results in Raman bands of dicoronylene, but not coronene. Besides dicoronylene, longer oligomers might also be present in sample HT. Based on this spectral range, dicoronylene and oligomers containing few coronene units are not well distinguishable. [43,158] The absorption of the oligomers shifts towards the red as their length increases, therefore even in their presence the dicoronylene signals are expected to dominate the spectrum recorded with 530.9 nm excitation for being on resonance. These molecules are adsorbed to the nanotube surface, as will be discussed in Sec. 5.4.2. The absence of coronene vibrations in the case of 482.5 nm excitation is not unexpected, based on the results of Chapter 4 on C$_{60}$@SWCNT
5. Coronene-nanotube hybrids

Fig. 5.9: Photoluminescence spectra of coronene, dicoronylene in toluene, coronene nanowires (CW), and samples SC, LT, and HT in aqueous SDS solution at excitation wavelengths of 356 nm and 468 nm. P2-SWCNT samples which underwent identical treatment as samples SC and LT are marked as "ref". Data are offset vertically for clarity.

samples. While TEM results clearly confirm the presence of the encapsulated species, their Raman signals are generally expected to be weak.

Photoluminescence measurements were carried out in D$_2$O-SDS suspension. SDS was found to desorb dicoronylene and transfer it into solution, although the exterior of the nanotubes cannot be cleaned completely. Okazaki et al. attributed the green luminescence of the material prepared via high-temperature vapor filling to stacks of coronene inside the nanotubes. [26] The present results, summarized in Fig. 5.9, however, do not support this proposal. Sample SC possesses ordered stacks of coronene inside the nanotubes but exhibits no green luminescence. Sample HT, on the other hand, shows a luminescence spectrum identical to that of dicoronylene, markedly different from that of coronene. The spectrum also differs from that of coronene nanowires (CW), a model for the stacks of coronene without the nanotube. Though the luminescence of coronene shifts towards green when stacked [138], the spectral shape is clearly different from what is observed on the hybrids, indicating that coronene partially dimerized in vapor phase or on the nanotube surface upon filling at 450 °C. This is in agreement with the Raman spectra measured here. The suspension of sample LT shows fluorescence bands of both coronene
5.4. Results and discussion

Tab. 5.2: Summary of the observed structures at various filling temperatures.

<table>
<thead>
<tr>
<th>sample</th>
<th>T</th>
<th>inside</th>
<th>on the outer wall</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>50 °C</td>
<td>coronene stacks</td>
<td>-</td>
</tr>
<tr>
<td>LT</td>
<td>385 °C</td>
<td>coronene stacks</td>
<td>dicoronylene or short oligomers (small amount)</td>
</tr>
<tr>
<td>HT</td>
<td>450 °C</td>
<td>coronene and oligomers</td>
<td>dicoronylene or short oligomers</td>
</tr>
</tbody>
</table>

and dicoronylene, but the lack of dicoronylene Raman features in the solid (Fig. 5.7 d) suggests that the dicoronylene content is much lower than that of the HT sample.

Chernov et al. investigated the luminescent properties of hybrids prepared by vapor-phase filling at 450 °C under argon atmosphere. [159] Though some changes in the encapsulation process might occur when the filling is done under argon atmosphere instead of vacuum [160], the observed luminescence characteristically agrees with our results. The ratio of the coronene and dicoronylene peaks in the PL spectra obtained in the solid phase is slightly different, as the exact reaction conditions affect the dimerization rate, and the properties of the nanotubes used, such as the curvature or the sidewall contamination, can influence the ability of the dimer to adsorb onto the nanotube surface [117].

In conclusion, nanotubes were successfully filled with coronene at various temperatures. The observed structures are summarized in Table 5.2. The vapor-phase filling is feasible at lower temperature than previously reported [26, 43]. Increasing the reaction temperature results in dimerization and oligomerization of coronene. These larger aromatic side products adsorb on the nanotube surface during the filling process, and, since, they are not soluble in conventional organic solvents, cannot be removed by toluene washing. Therefore samples in Ref. [26, 137, 158, 161] are likely to contain both adsorbed and encapsulated molecules. On the other hand, SDS and other surfactants used for preparing dispersions for PL studies can solubilize some of the adsorbed dimers. To study the luminescence of the hybrids and reactions inside the nanotubes, coronene@SWCNT samples with surfaces free from contamination are highly desirable. Sample SC is ideal for further studies, as the nanoextraction from sc-CO₂ not only yields good filling ratios, but eliminates the formation of unwanted by-products.

5.4.2 Effect of carbon-surface curvature

To get more insight into the formation of the oligomerized side products, vapor-phase filling was repeated using carbon surfaces with various curvatures: CoMoCat-SWCNTs (Fig. 5.10) have narrower, MWCNTs (Fig. 5.11) larger internal diameters than P2-SWCNTs, and graphite. As expected, TEM images show that the cavities of the narrow CoMoCat nanotubes are empty and neither contain coronene nor other guest species
5. Coronene-nanotube hybrids

(Fig. 5.10). In the large cavities of MWCNTs, on the other hand, signs of dimerization and oligomerization of coronene are clearly observed (Fig. 5.11).

![TEM image of sample CM showing empty nanotubes](image1)

![Average diameter distribution](image2)

![Raman spectra](image3)

**Fig. 5.10:** a) TEM image of sample CM showing empty nanotubes, since the average diameter is too small for encapsulation. [P5] b) Tube distribution based on the manufacturers datasheet. [162] c) Raman spectra of CoMoCat-SWCNT measured with 785 nm excitation in the RBM area. The Raman shift \( \tilde{\nu}_{RBM} \) is converted to diameter using \( \tilde{\nu}_{RBM} = \frac{234}{d} + 10 \) cm\(^{-1} \) formula. The minimum diameter of tubes capable to encapsulate coronene is marked with a dotted line.

![TEM image of sample MW](image4)

**Fig. 5.11:** TEM image of sample MW. The hybrids are filled with coronene molecules, ordered stacks occur occasionally (marked with arrow), but overall a disordered structure is typical in this case, as the larger inner cavity allows molecules more orientational freedom. [P5]

**The role of the carbon surface in the oligomerization**

The Raman spectra of samples HT, CM, MW, and GR, along with those of the corresponding reference materials, are shown in Fig. 5.12. All samples prepared at high temperature (including the small-diameter CoMoCat nanotubes and graphite) exhibit dicoronylene spectra similar to those of sample HT. The presence of dicoronylene appears
5.4. Results and discussion

![Raman spectra](image)

**Fig. 5.12**: Raman spectra of samples HT, CM, MW, GR, and the corresponding reference materials. Data are offset vertically for clarity. Reference materials are carbon structures which underwent the same thermal treatment as the coronene-carbon heterostructures, without applying coronene. The dicoronylene spectrum (App. C Fig. C.3) appears in all samples.

The detected Raman signal in the sample MW presumably originates from molecules adhered to the surface, since it is very unlikely to excite inner species through several tube walls. CoMoCat samples, according to the manufacturers characterization data [162] and wide-range optical measurements [134], contain only a negligible amount of tubes having diameters suitable for coronene encapsulation. However, the presence of tubes with diameter up to 1.7 nm was detected by Raman spectroscopy (Fig. 5.10 c), as resonance effects enhance the contribution of these structures to the spectra.

The as-prepared material from high-temperature synthesis contains both coronene and dicoronylene adsorbed onto the CNT surface. As the molecules consist of aromatic rings,
they adsorb via strong $\pi$-$\pi$ interaction onto the sidewall of the nanotube. Coronene can be removed by toluene washing, whilst further SDS treatment removes mostly dicoronylene. The Raman spectrum of the as-prepared sample SC, which contains no dicoronylene, indicates the presence of coronene. After the toluene treatment (Fig. 5.14a) no coronene vibrations can be detected. In contrast, Fig. 5.14b illustrates that the intensity of the dicoronylene bands hardly changes after SDS washing on sample CM, although a high amount of dicoronylene was detected in the filtrate. The lack of intensity decrease upon washing can either be caused by resonance effects or the presence of higher oligomers. The Raman signal of dicoronylene molecules that are in close contact with the nanotubes, like encapsulated molecules or the first adsorbed layer can possess strong Raman scattering due to enhancement effects. Recently very strong signal from encapsulated dye molecule aggregates was reported. [7] The underlying enhancement mechanism is not fully understood, but it was suggested that the nanotubes are not directly responsible for it, their only role is to render the guest molecules in an aggregated state that has electronic transitions resonant with the applied excitation. Even though the encapsulation of coronene molecules into CoMoCat tubes is not likely, since the vast majority of the tubes are too small to accommodate coronene molecules, it cannot be completely ruled out. Resonance effects might enhance the contribution of the filled tubes to the spectra. On the other hand, a more likely explanation is that short oligomers can also be present in the sample, which might not be distinguishable from dicoronylene based on their Raman spectra, but are harder to exfoliate by SDS washing.

Based on the comparison of the different carbon materials, we can conclude that dicoronylene adsorbed on the surface (GR, MW samples) and, in the case of enhancement [7], encapsulated inside the nanotubes (HT, possibly CM) can be detected by Raman spectroscopy. The presence of a carbon surface triggers the dimerization even at temperatures lower than reported in case of vapor-phase dimerization. [43] The adsorbed and encapsulated species are not distinguishable based on the vibrational spectra, therefore the preparation of hybrids having outer walls free of contamination is of utmost importance.
5.4. Results and discussion

**Fig. 5.14**: a) Raman spectra of samples SC after toluene washing and b) CM after SDS washing. c) PL spectra of the toluene and SDS filtrate and the corresponding reference samples (coronene and dicoronylene). Data in panels (a) to (c) are offset vertically for clarity. d) Photos of the first and third SDS-washing filtrate under UV lamp (356 nm).

**Fig. 5.15**: Photoluminescence spectra measured on SDS dispersions of CM and HT sample compared to dicoronylene at 356 and 468 nm excitation. Data are offset vertically for clarity. The broad low energy band in the case of HT spectrum at 356 nm excitation and the band at 529 nm present at 468 nm excitation are nanotube features (see Fig. 5.9).
The origin of the green luminescence

Photoluminescence measurements were performed in aqueous surfactant suspensions in this study as well as in previously published work. [26, 137, 158, 161, 165, 166] These suspensions may contain, beside nanotube-centered micelles, dissolved excess dicoronylene from the external surface of the nanotubes. To determine the origin of the emission, photoluminescence spectra of the filtrate collected upon the washing procedure was measured. These solutions contained almost no nanotubes. The toluene filtrate contains only coronene, but a large amount of dicoronylene was found to be present in the SDS filtrate (Fig. 5.14 c). The green luminescence of the first few filtrates is intense enough to be easily seen by eye under UV light (356 nm). As the photos (Fig. 5.14 d) show, further washing steps with SDS result in a remarkable decrease of the luminescence intensity. The photoluminescence spectra of samples HT and CM suspended in aqueous SDS solution proved to be identical to each other and to that of dicoronylene (Fig. 5.15). These findings further
Results and discussion

5.4. Substantiate the claim that the fluorescence in SDS solution, observed previously, originates mainly from the excess adsorbed dicoronylene suspended by the surfactant rather than the encapsulated coronene.

To deduce whether this green photoluminescence comes from the molecules remaining in contact with the suspended nanotubes or those desorbed in the solution, the CoMoCat-SWCNT-coronene hybrid (CM) was suspended in aqueous SDS which was subsequently filtered. The photoluminescence spectra of both the original nanotube suspension and the filtrate were measured at various excitation wavelengths. Fig. 5.16 shows the photoluminescence results for the near-infrared and visible region in panels (a)–(d) and (e), respectively. The NIR luminescence excitation map is typical of the CoMoCat sample, with nanotubes of (6,5) chirality prevailing. In addition, dicoronylene emission is seen at 356 nm excitation. In the filtrate, the latter emission remains while the NIR luminescence almost completely disappears. These results demonstrate that the emission predominantly originates from the dissolved dicoronylene and not from the molecules in contact with the nanotubes.

In conclusion, exposing coronene molecules to carbon surfaces at high temperature results in dimerization of the molecules. Dimers are both encapsulated and adsorbed, oligomerization is favored in samples with a larger inner cavity. The green luminescence observed earlier by Okazaki et al. [26] originates from dicoronylene molecules detached from the nanotube surface and not from the hybrids.

5.4.3 Transformations of coronene inside nanotubes

As mentioned in Sec. 5.4.1, the presence of encapsulated coronene can be confirmed by annealing the hybrid structures to form DWCNTs and detecting the inner-nanotube RBMs in the Raman spectra. Since nanotubes are stable under vacuum up to 2000 °C, most carbon containing molecules can be converted to inner tubes in these nanoreactors. I chose samples SC and LT to follow the thermal evolution of the molecules in the nanotube cavities, because these two materials have little or no adsorbed dicoronylene on the nanotube surface.

Raman spectra

The Raman spectra of coronene oligomers are dominated by resonance effects, since they have strong absorption in the visible range. Measurement at a specific laser line displays a subset of encapsulated molecules. As the length of the oligomers increases, their absorption shifts toward the red [158], therefore various excitation lines are needed to follow the polymerization. Raman spectra were measured with laser lines at wavelengths of 482.5, 532, and 785 nm. With green excitation mainly dimers or very short oligomers can be
5. Coronene-nanotube hybrids

Fig. 5.17: Effect of annealing on the Raman spectra of samples SC and LT measured with 532 nm excitation wavelength, showing the growth process of the inner nanotube. The data are normalized to the G mode of the nanotubes and shifted vertically for clarity. Certain areas of the spectra are magnified 10 or 100 times as indicated in the figure.

detected, while the red excitation enhances the contribution of long oligomers to the spectra. Results of the green and blue laser excitation are qualitatively similar, therefore only spectra excited with 532 nm are presented here.

Fig. 5.17 shows Raman spectra for both samples with 532 nm excitation. Sample SC shows no peaks, other than the ones belonging to the nanotubes, while dicoronylene peaks can be detected on sample LT, although with very low intensity. The effect of annealing at 500 and 700 °C is the appearance of a complex pattern around 1400 cm⁻¹ in both cases, similar to those reported in Ref. [43] for coronene oligomers. The group of peaks around 1200 cm⁻¹ are predicted to shift downward as the oligomers get longer. [158] After annealing at 500 °C, on sample SC-500 dicoronylene peaks appear, with very low intensity. On the other hand, dicoronylene peaks on sample LT-500 are more pronounced. The intensity of the lower energy peak of the triplet around 1200 cm⁻¹ increases on sample LT-500 compared to the non-annealed form. Raising the temperature to 700 °C does not cause
5.4. Results and discussion

**Fig. 5.18**: Effect of annealing on Raman spectra of sample SC measured with 785 nm excitation. (The spectra measured on sample LT is characteristically the same, therefore it is not shown here.) Data are normalized to the most intense mode and shifted vertically for clarity. The 700 °C annealed sample (SC-700) is in resonance with this excitation, the scattering intensity of the oligomer is stronger than that of the host nanotubes.

Changes in the high energy range (1100–1600 cm\(^{-1}\)) peaks of sample LT. The spectrum of sample SC-700 looks similar to LT-700. In the low energy range (300–600 cm\(^{-1}\)) the changes are more pronounced. Between 340 cm\(^{-1}\) and 600 cm\(^{-1}\) several peaks appear in the 500 °C annealed samples, at the same Raman shift as on samples HT filled at 450 °C. As the temperature increases the peaks under 430 cm\(^{-1}\) get more intense, while the ones above disappear. Red laser excitation, however, results in strikingly different spectra (Fig. 5.18). At 500 °C still no vibrational modes can be detected beside the ones belonging to the nanotubes in any of the samples. However, at 700 °C very intense peaks appear, even obscuring the nanotube modes, similar to 700 °C annealed samples prepared by high temperature vapor-phase filling. [166] By further increasing the temperature, at 900 °C broad bands appear in the high (1250–1400 cm\(^{-1}\)) and the low (350–500 cm\(^{-1}\)) energy range. After this annealing step, the spectra with different excitation wavelengths look more alike. (Direct comparison of the spectra can be found in the App. C in Fig. C.4.) For annealing temperatures between 900 and 1250 °C the broad bands disappear, while the inner-nanotube radial breathing modes appear in the range between 250 cm\(^{-1}\) and 350 cm\(^{-1}\).
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![Diagram of disordering and coalescence](image)

**Fig. 5.19:** Schematic illustration of the changes in alignment of coronene from ordered stacks to distorted structure inside the SWCNT based on the structures observed by TEM and the fusion of the molecules into an inner nanotube. [P5]

The RBM of the host tubes shifts up upon encapsulation of coronene molecules. Measured with green excitation, the upshift of the RBM of the smaller tubes (\(\tilde{\nu}_{\text{RBM}} = 169\, \text{cm}^{-1}\)) is present up to 700 °C in both sample SC and LT, above it shifts back to its original position. The upshift of the RBM of the smaller tubes (\(\tilde{\nu}_{\text{RBM}} = 169\, \text{cm}^{-1}\)) on the spectra measured with red is not present after annealing. However, the lower energy RBM peak (\(\tilde{\nu}_{\text{RBM}} = 156\, \text{cm}^{-1}\)) is downshifted in the 700 °C and 900 °C annealed samples.

**Reactions inside the nanotubes**

Nanoribbons were observed by TEM in high temperature filled samples. [137,158,161,166] Fujihara et al. suggested that coronene molecules dimerize during sublimation, and these dicoronylene molecules then get encapsulated into the nanotubes. [158] The energetics of such a process is unknown, however, it is likely that the strength of the adhesion of dicoronylene via \(\pi-\pi\) interactions to the nanotube surface is at least comparable, if not superior, to the energy profile of the rather bulky dicoronylene molecule entering the nanotube cavity. Intuitively, it is more plausible that the coronene molecules enter the tubes individually and, depending on their kinetic energy (determined by temperature), undergo further rearrangement and chemical reactions.

Our TEM observations indicate that the reaction can start from a stacked arrangement of coronene, even though the mutual orientations of molecules within the stack are unfavorable for direct dimerization and polymerization. The heat treatment process may disturb the stacks and thus align the molecules and facilitate reactions leading to nanoribbons (Fig. 5.5b–d and Fig. 5.19). Therefore, the initial dimerization inside the nanotubes requires high activation energy. The dimers were not observed to form stacked arrangements inside the nanotubes, but aligned parallel to the nanotube axis. This alignment facilitates further oligomerization by \(2 + 2\)-cycloaddition reactions. Therefore, it is
5.4. Results and discussion

Fig. 5.20: Potential reaction products that can be formed from coronene inside SWCNTs. 1) linear coronene oligomer, 2) zigzag coronene oligomer, 3) 7-AGNR, 4) 4-ZGNR.

expected that dimers and oligomers can form at similar temperatures. This is in agreement with the changes observed in the Raman spectra. After the 500 °C annealing only a very small amount of dicrotonylene is present in the low temperature filled sample SC in contrast to the LT. The longer, resonant oligomer appears in both samples at 700 °C. The presence of organized stacks prohibits the dimerization, while dimers can form at lower temperatures outside of the nanotubes. This suggests, that molecule that is in resonance with the 785 nm excitation forms via templated growth inside the nanotube cavity, it is most likely a longer ribbon.

Various ribbon structures were visualized by TEM inside the nanotubes. Annealing over 700 °C is likely to result in the formation of different types of ribbons. The potential reaction products are summarized in Fig. 5.20. [42, 137, 158, 161] Both 1 or 2 structures can be formed via 2 + 2-cycloaddition. [168] 2@SWCNT structure was identified inside an SWCNT having approximately 2 nm diamer on a TEM image by Talyzin et al. [137] However, due to its larger, approx. 1.33 nm width 2 it is not likely to form inside the P2-SWCNT sample. Structures 3 and 4 can be formed after reorganization of carbon atoms, due to the high temperature. Simulated Raman spectra of structures 1, 3, and 4 are shown in App. C (Figs. C.1 and C.2). [158, 166, 169] Lim et al. suggest that the ribbon observed with red laser excitation is structure 1. [42, 158] The calculated Raman spectra of the long coronene oligomer is only available in the 1100–1600 cm\(^{-1}\) range. The lower energy range however, provides information about the width of the ribbons and the edge structure. Similar to nanotubes, GNRs exhibit breathing-like vibrations (BLM), and the position of the BLM strongly depends on the width of the ribbon in the narrow diameter range. Calculations predict BLM energies between 350 and 450 cm\(^{-1}\) for 6–8 AGNR and 4–5 ZGNR structures. [170] The size of these ribbons would allow them to fit in the P2-SWCNT hosts used here.
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Fig. 5.21: Photoluminescence emission of the hybrids annealed at various temperatures, measured with 468 nm excitation. Data are offset vertically for clarity. Dicoronylene peaks are marked with arrows.

Theoretical calculations and TEM observations showed that nanoribbons tend to form twisted structures inside the nanotubes. [53, 137, 171, 172] It was predicted based on calculations that nanotubes can be formed from helical nanoribbons, and recently Lim et al. [42] succeeded to grow inner tubes via perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA). The inner tube formation from coronene oligomer is likely to proceed via such twisted ribbons. In the spectra of the 900 °C annealed samples the pronounced D band indicates disordered structure, probably the distortion of the ribbons inside the tubes. Due to the high temperature, reorganization of the carbon structure is also probable. The two broad bands appearing in the Raman spectra agree well with the predicted spectral range of nanoribbon BLMs and the high energy modes. [169, 170] As the temperature is increased further to 1250 °C, the structure of the inner tube reorganizes, the number of defects decreases. The broad peak in between 350 and 500 cm⁻¹ disappears, and instead radial breathing modes corresponding to the inner tubes appear.

Photoluminescence of the stacks and ribbons

The photoluminescence of the hybrids was measured after the different annealing steps with various excitation wavelengths. For sample LT, which contains a small amount of adsorbed dicoronylene beside coronene, traces of dicoronylene can be detected even after annealing to 500 °C (Fig. 5.21). Other studies [26, 158, 166] report annealing at 300 °C in order to remove adsorbed molecules. It seems that after this treatment a substantial amount of the adsorbed species can remain, and therefore the reported PL and Raman spectra cannot be unambiguously assigned to encapsulated species. Sample SC, where no
dicoronylene is formed during encapsulation, do not show any luminescence above the background (App. C, Fig.C.5). As opposed to other studies [161, 166] performed on high temperature-filled samples, GNR transitions were not found in the measured spectral range.

5.5 Conclusion

While systematically varying the synthesis parameters of carbon-coronene hybrids, a series of encapsulated and adsorbed structures were prepared and characterized. The stacked or ribbon arrangement of coronene molecules in SWCNTs were found to depend on the reaction temperature: filling from supercritical CO\textsubscript{2} produces ordered stacks, while vapor-phase filling results in a mixture of arrangements with less stacked molecules as the reaction temperature is increased. High-temperature vapor filling results in the adhesion of coronene dimers to the external surface of the nanotubes, as carbon surfaces tend to facilitate the formation of dicoronylene above the sublimation temperature of coronene. The interaction between dicoronylene and the surface is exceptionally strong. The green fluorescence of aqueous SDS suspensions of coronene-filled nanotubes originates from dicoronylene molecules dissolved in the SDS solution, as proven by the comparison of nanotube-containing suspensions and the nanotube-free filtrate. Annealing of coronene-filled single-walled carbon nanotubes with diameters close to the size of coronene results in the formation of internal nanotubes through complicated polymerization steps, involving dehydrogenated nanoribbon formation as intermediate structures.

Theses:

3. I studied various hybrids prepared from coronene and carbon nanotubes. Based on the comparison of the vibrational and luminescent properties of the different heterostructures, I was able to distinguish between the encapsulated and adsorbed species.

(a) I showed that high temperature vapor filling of coronene results in the formation of dicoronylene on the nanotube surface. The carbon surface has a catalytic role in the dimer formation.

(b) I showed that the formation of the adsorbed by-product can be eliminated by lowering the filling temperature. Encapsulation of coronene using nanoextraction from supercritical CO\textsubscript{2} results in well-defined coronene@SWCNT structure, free from adsorbed oligomers.

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(c) I showed that coronene can be polymerized inside SWCNTs starting from a stacked alignment. The polymerization results in the formation of inner nanotubes via nanoribbons. This method produces GNR@SWCNT structures having a clean outer surface.

(d) I showed that the photoluminescence of coronene in both stack and ribbon form is quenched inside the nanotubes.

Related publications:


6. Conclusion

In my dissertation I performed optical absorption, Raman, and photoluminescence spectroscopy measurements on carbon nanotube-based hybrid materials formed by non-covalent interactions. Both the synthesis and the characterization of such hybrids are a complex problem, with many technical challenges and possible pitfalls. The samples are mixtures of carbon nanotubes with different structural properties and are hard to process due to the strong intertube interactions yielding in the formation of bundles. Molecules can interact both with the interior and the sidewall of the nanotubes, and the elimination of reaction side products is often challenging. I studied both wrapped and encapsulated systems to gain a deeper understanding of their structure. The chosen principal method was infrared and Raman spectroscopy, because the attachment of various molecules is reflected in the vibrational spectra of the hybrid material.

In the case of polymer-wrapped carbon nanotubes I examined how the strength and type of the interaction between the constituents can be estimated. I showed that the observed attenuation of certain infrared-active modes of the investigated polymer-carbon nanotube hybrids can be explained by the SAIRA effect. I showed that the strength of the SAIRA effect correlates with the conductivity results: hybrids where the carbon nanotubes are more tightly wrapped by the polymer show larger increase in electrical conductivity upon hybrid formation.

I followed the synthesis of $C_{60}@SWCNT$ hybrids and their transformation into double-walled carbon nanotubes. Since these systems have been widely researched, results obtained on these samples was used to optimize our characterization protocol for other type of encapsulated carbon nanotube hybrids. Additionally, I investigated the possible electronic interaction between the inner and outer nanotubes in DWCNTs.

I applied the gathered knowledge on wrapped and encapsulated carbon nanotubes to the complex problem of coronene@CNT synthesis and characterization. This system illustrates both the nanocontainer and nanoreactor application of the CNTs. Even though carbon nanotubes could be ideal candidates to be used as a protective shell for the storage of luminescent materials, I showed that in the case of coronene@SWCNT, in contrast to earlier results, the luminescence is quenched upon the encapsulation. Previous synthesis methods of coronene-carbon nanotube hybrids resulted in both encapsulated and adsorbed molecules, which made the spectroscopic characterization results obtained on these systems unreliable. I optimized the preparation procedure, to achieve coronene@SWCNT
having a clean outer surface, which allowed me to follow the polymerization of the coronene inside the nanoreactor through graphene nanoribbons to DWCNTs by vibrational spectroscopy.
1. I have investigated the hybrid structures formed by polymerization of aniline, carbazole, and dopamine in the presence of carbon nanotubes. The conductivity of the polyaniline-nanotube and polycarbazole-nanotube hybrid electrodes was observed to improve significantly compared to the pristine carbon nanotube electrodes.

(a) I observed the attenuation of the in-plane infrared-active vibrations of polyaniline and polycarbazole upon hybrid formation with carbon nanotubes. I showed that the attenuation can be explained by the surface attenuated infrared absorption (SAIRA) effect, caused by the interaction between the polarizable π-electron network of the nanotubes and the vibrations of the molecules. Based on the observed changes I suggested that polyaniline and polycarbazole develop stronger interaction with the nanotubes than the melanin, resulting in a tight coating. [P2]

(b) I showed that the strength of the SAIRA effect correlates with the conductivity results: hybrids where the nanotubes are more tightly wrapped by the polymer show larger increase in electrical conductivity upon hybrid formation. [P1]

2. I followed the process of C_{60}@SWCNT preparation and its transformation to DWCNT. I used Raman spectroscopy to confirm the successful encapsulation of C_{60} molecules and the inner tube formation. Based on the simultaneous decrease of the intensity of the nanotube transitions in the optical conductivity spectra, I concluded that there is no significant charge transfer between the outer and inner nanotube in DWCNTs. The observed changes can be explained by the localization of the charges. [P3]

3. I studied various hybrid systems prepared from coronene and carbon nanotubes. Based on the comparison of the vibrational and luminescent properties of the different heterostructures, I was able to distinguish between the encapsulated and adsorbed species.

(a) I showed that high temperature vapor filling of coronene results in the formation of dicoronylene on the nanotube surface. The carbon surface has a catalytic role in the dimer formation. [P4,P5]
(b) I showed that the formation of the adsorbed by-product can be eliminated by lowering the filling temperature. Encapsulation of coronene using nanoextraction from supercritical CO$_2$ results in well-defined coronene@SWCNT structure, free from adsorbed oligomers. [P4,P5]

(c) I showed that coronene can be polymerized inside SWCNTs starting from a stacked alignment. The polymerization results in the formation of inner nanotubes via nanoribbons. This method produces GNR@SWCNT structures having a clean outer surface. [P5]

(d) I showed that the photoluminescence of coronene in both stack and ribbon form is quenched inside the nanotubes. [P5]

**Related publications**


List of publications


Appendices
Appendix A

Conducting polymer-nanotube hybrids

Scanning electron microscopy

Fig. A.1: SEM images of CNT on ITO before and after electropolymerization with PANI: (A) CNT on ITO before coating, (B) CNT on ITO coated with PANI by using 0.1 M aniline solution as electrolyte, 10 scans at rate of 50 mV/s. (C) CNT on ITO coated with PANI after two scans at rate of 50 mV/s and 0.5 M aniline solution as electrolyte. [P1]
Appendix A. Conducting polymer-nanotube hybrids

UV-Vis-NIR absorption spectra

![UV-Vis-NIR spectra](image)

**Fig. A.2:** UV-Vis-NIR spectra of the conductive polymer-nanotube hybrids and the respective references. The spectra were measured on samples coated on ITO. The spectrum of the ITO is subtracted from the spectrum of pure polymers and the nanotube reference. The spectrum of the ITO+CNT is subtracted from the spectra of the hybrids. Absorption spectra were recorded on a Shimadzu UV-310PC scanning spectrophotometer. [P1] Polymer-nanotube hybrids shift their absorption bands to longer wavelengths in comparison to the pristine materials.
Appendix B

Peapods and DWCNTs

Fullerene (C\textsubscript{60})

Molecular and electronic structure of C\textsubscript{60} [173]

vibrational modes:

point group: \textit{I}_h

infrared-active modes: 4T\textsubscript{1u}

Raman-active modes: 2A\textsubscript{g} + 8H\textsubscript{g}
Appendix B. Peapods and DWCNTs

Fig. B.2: Raman spectra of $C_{60}$. Black arrows indicate the $H_g$ modes, green arrows the $A_g$ modes.

Fig. B.3: Infrared spectra of $C_{60}$. The arrows indicate the $T_{1u}$ modes. The asterisk indicates extrinsic peaks from CO$_2$. 
Additional spectroscopy data

**Fig. B.4:** Extracted $M_{00}$, $S_{11}$, $S_{22}$ and $M_{11}$ transition energies of the CoMoCat SG nanotubes. [134] The average diameter of the nanotubes is 0.75 nm.

**Fig. B.5:** Optical transmission, measured on self-supporting films. The spectra are scaled to the $\pi - \pi^*$ transition of the nanotubes.
Appendix C

Coronene-nanotube hybrids

Coronene \((\text{C}_{24}\text{H}_{12})\) and the related oligomers

Coronene:

- **Point group:** \(D_{6h}\)
- **Infrared-active modes:** \(3\ A_{2u} + 11\ E_{1u}\)
- **Raman-active modes:** \(6\ A_{1g} + 5\ E_{1g} + 12\ E_{2g}\)

Dicoronylene:

- **Point group:** \(D_{2h}\)
- **Infrared-active modes:** \(18\ B_{1u} + 33\ B_{2u} + 33\ B_{3u}\)
- **Raman-active modes:** \(34\ A_g + 34\ B_{1g} + 19\ B_{2g} + 15\ B_{3g}\)
Simulated Raman spectra of the different ribbons

**Fig. C.1:** Structure and calculated Raman spectra of a) coronene and its oligomers [158] b) zigzag 4-GNRs with various lengths [166].
Fig. C.2: Raman spectra of a) 7-AGNR and b) 4-ZGNR in $zz$-polarization, obtained by summation of Lorentzians of widths 20 cm$^{-1}$ at the frequencies of calculated Γ-point phonons of $A_g$ symmetry. Due to the lack of calculated Raman intensities, the single Lorentzians are of equal height. [169]
Appendix C. Coronene-nanotube hybrids

Additional spectroscopy data

Fig. C.3: Raman spectra of sample HT (measured with 530.9 nm excitation) compared with the corresponding references: coronene and dicoronylene (measured with 1064 nm laser excitation), P2-SWCNT reference (measured with 530.9 nm excitation). Data are normalized to the most intense mode and shifted vertically for clarity.

Fig. C.4: Raman spectra of the 900 °C annealed coronene@P2-SWCNT hybrid (SC-900) with 532 and 785 nm laser excitation. Peaks marked with asterisks belong to the nanotubes.
Fig. C.5: Photoluminescence emission spectra measured with various excitation wavelength on the annealed SC samples. For comparison the HT sample (green line) is presented as well, which shows peaks originating from dicoronylene. The peaks marked with asterisks are overtones of the excitation.
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