Summary

"Nano-" is a prefix in the metric system denoting a factor of 10^{-9}. Today the terms "nano-material" and "nano-technology" have become parts of our everyday vocabulary, as we can see examples in almost every field of science, engineering, as well as commercial marketing and movies.
For decades, the field of solid-state electronics and optoelectronics has been dominated by silicon. However, we have to face the fact that this material and the current technology are approaching their limits in scalability. Either new nano-technologies or new materials have to be explored in order to continue industry's scaling trend of Moore's Law. Tremendous interest in terms of new materials goes to carbon, the most promising candidate to take over the position of silicon in the foreseeable future.
Carbon is one of the most abundant elements found on the planet and appears in versatile forms from soot to diamond and from graphene to carbon nanotubes. In particular, the last two materials possess unique chemical, physical and electronic properties. The carbon nanotube can be considered one of the core members in the carbon family and has remained at the forefront of nanotechnology research for two decades.
In this thesis, we present a series of studies on two kinds of SWNT-based one-dimensional organic-inorganic hybrids, namely "peapods" and "polymer-wrapped SWNTs". We aim to understand the fundamental physical properties of these hybrid systems and to find applications in electronic and optoelectronic devices.
The name "peapods" in this work refers to the hybrids in which organic small molecules (peas) are encapsulated in single-walled carbon nanotubes (SWNTs) (pods). We introduce the family of visible-light-emitting "peapods" by encapsulating thiophene oligomers in SWNTs in chapter 2 and 3. We characterize the properties of these nano-hybrids with a series of comprehensive experimental techniques and gain deeper understanding of their structural and electronic properties based on density functional theory (DFT) calculations.
In chapter 2, we present the peapods with sexithiophene inside SWNTs (6T@SWNT). We evidence the encapsulation of the organic molecules by using Raman spectroscopy and high-resolution transmission electron microscopy (HRTEM). Interestingly, the molecules inside SWNTs are arranged in two lines along the sidewall.
The photoluminescence excitation spectrum of 6T@SWNT and of 6T in diluted solution show an almost super-imposed main feature at around 450 nm, while the high-energy part of the peapod spectrum is more pronounced

with respect to that of the molecules in solution. This special feature of the excitation spectra indicates a possible energy transfer from higher excited states of the SWNTs to the encapsulated 6T molecules. The photoluminescence of the peapods compared to that of 6T in solution shows broader and less resolved features. The photoluminescence lifetime of the peapods is shorter than that of the 6T molecule in the same solvent.
Such nano-hybrids represent a promising photon source in future optoelectronic devices.
A family of peapods with thiophene oligomers (quaterthiophene (4T), quinquethiophene (5T) and sexithiophene (6T)) encapsulated in carbon nanotubes are presented in chapter 3. The configuration and kinetics of the encapsulated molecules inside the SWNTs are demonstrated by HRTEM, showing two arrays of molecules parallel to the SWNT walls. The distance between the molecular array and the side wall remains constant (around 0.3 nm), even though the diameter of the host carbon nanotubes varies. The molecules bend and rotate inside the tube during the observation, leading to different contrast in the time-dependent micrograph. Visible photoluminescence can be observed from all peapods with quantum yields up to 30% in the case of 6T@SWNT. DFT calculations demonstrate van der Waals interaction as the bonding mechanism between the tube and the encapsulated molecule. This is reflected in the electronic structure as well as in the measured Raman spectra. Only for small tubes, a considerable tube distortion and charge transfer is predicted. Interaction between pea and pod seems to exist, however, in the excited state as evidenced by optical measurements.
The other hybrid objects investigated in this study are “polymer-wrapped SWNTs”. These nano-hybrids consist of well-dispersed SWNTs wrapped with conjugated polymers.
In chapter 4 we report on the photophysics of semiconducting SWNTs sorted by wrapping with different polyfluorene derivatives. The side chain functionalities are used for achieving SWNT dispersions in different solvents. We observe that the quality of SWNT dispersions is influenced by the molecular weight and the structure of side-chains of the polymer. The intrinsic lifetime of the small diameter SWNTs measured in ensemble is found to be in the range of 28-40 ps. Moreover, we provide evidence of energy transfer from tubes with larger band gap to those with smaller band gap occurring in small SWNT bundles.
In chapter 5, we investigate the mechanism of poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO)-carbon nanotube interaction in toluene, which leads to a selective sorting of only 5 kinds of semiconducting SWNTs. The interaction

is dominated by the octyl-octyl zipping mechanism that locks the polymer chains onto the nanotubes, similarly to what has been observed in the β-phase of PFO in toluene. The preference manifested by this polymer to certain nanotubes depends on the tube diameter and chirality: the cylindrical template has to provide an appropriate diameter to the coiling of chains and the carbon-carbon motif of bonds has to be in a proper direction to allow good contact between octyl chains and the nanotube wall. The fluorene-nanotube interaction plays a smaller role in the polymer adsorption on nanotube walls. More importantly, we find that PFO selectivity is strongly dependent on the solvent: it may induce the formation of polymeric supramolecular structures in solution that are transferred to the nanotube walls.

We explore the possibility of using PFO sorted semiconducting SWNTs in field-effect transistors (FETs) and demonstrate ambipolar operation in solution processed SWNT transistors in chapter 6. A simple and highly scalable solution-based method for the preparation of semiconducting SWNT dispersions is demonstrated.

Carrier mobility in the range 10^{-3}-10^{-2} cm^2/V s for both holes and electrons is obtained. Extrinsic effects on the electrical characteristics of SWNT FETs are studied. The hole mobility increases upon exposure to air and the threshold voltage of the p-channel shows a positive shift. On the contrary, the n-channel characteristics degrade upon air exposure and completely disappear after 24 hours. Annealing in air converts ambipolar FETs into p-type-only devices with a larger current hysteresis. This work points out the origin of the variation of electrical behavior of SWNT transistors and further shows the importance of air and water-free environments for device preparation.