The power of polymer wrapping
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Chapter 2

Understanding the Selection Mechanism of the Polymer Wrapping Technique: Toward Semiconducting Carbon Nanotubes

Non-covalent functionalization of Single-Walled Carbon Nanotubes (SWNTs) using π-conjugated polymers has become one of the most effective techniques to select semiconducting SWNTs. Several conjugated polymers have been used, but their ability to sort metallic and semiconducting species, as well as the dispersions yields, varies as a function of their chemical structure. Here, three polymers are compared, namely, poly[(4,4-di-n-dodecyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl)-alt-(2,1,3-benzothiadiazole-4,7-diyl)] (P12CPDTBT), poly(9,9-di-n-dodecylfluorene-2,7-diyl) (PF12) and poly(3-dodecylthiophene-2,5-diyl) (P3DDT) in their ability to select two types of carbon nanotubes comprising small (~1 nm) and large (~1.5 nm) diameters. P12CPDTBT is a better dispersant than PF12 for small diameter nanotubes, while both polymers are good dispersants of large diameter nanotubes. However, these dispersions contain metallic species. P3DDT, instead presents the best overall performance regarding the selectivity toward semiconducting species, with a dispersion yield for s-SWNTs of 15% for small and 21% for large diameter nanotubes. These results are rationalized in terms of electronic and chemical structure showing that: (i) the binding energy is stronger when more alkyl lateral chains adsorb on the nanotube surface; (ii) the binding energy is stronger when the polymer backbone is more flexible; (iii) the purity of the dispersions seems to depend on a strong polymer-nanotube interaction.

This chapter is based on the article:

2.1 Introduction

Synthesized SWNTs are a mixture of species with different diameters, chiral angles, and electronic types. SWNTs are considered to be the most promising material for a broad range of applications, including the strengthening of materials, field effect transistors (FETs), near-infrared emitters/detectors, chemical sensors, among others. However, the presence of metallic species challenges the implementation of SWNTs in the fabrication of electronic devices.

In order to effectively use SWNTs in electronic applications, besides improvements in the synthetic methods, different post-growth methods to separate metallic and semiconducting tubes have been developed in the last years.

One of them, the polymer wrapping technique, has attracted considerable attention due to its high selectivity toward semiconducting nanotubes, widespread availability of conjugated polymers, and the simplicity and reproducibility of the process. The selection mechanism appears to be related to the \(\pi-\pi\) interaction between the conjugated polymers and the walls of the SWNTs, as well as the interaction with the side chains which help to increase the binding energy and the surface coverage of the tubes.

To date, several conjugated polymers such as polyfluorenes, polycarbazoles, and polythiophenes among others, have been used for the selective dispersion of s-SWNTs. A consensus regarding the principal mechanism responsible for the selectivity, the effectiveness of the separation of semiconducting from metallic species, and the observed differences in dispersion yields has not yet been reached. The mechanism for selectivity is complex, involving the equilibrium of a multicomponent mixture of macromolecules. As such, the successful preparation of a dispersion will depend on several parameters such as the nature of the conjugated polymer, its dispersity and average molecular mass, the choice of solvent, the temperature at which the dispersions are made, the details of the dispersion processing (sonication, aging, centrifugation, etc.) and the type of carbon nanotubes. Concerning the polymer source, the importance of the lateral alkyl tail length to the success of the wrapping process has already been investigated and proven previously. It remains to be clarified how the polymer backbone structure affects the wrapping process, an issue that has already been addressed by some authors, but which remains under debate.

The SWNT sources used in most polymer wrapping reports are restricted to the well-characterized CoMoCAT (CO disproportionation in the presence of a Co-Mo catalyst) and HiPCO (high-pressure CO method) nanotube samples, composed mostly of small diameter species (\(\approx 1\) nm). Samples of larger average diameter nanotubes have been used only more recently. Large diameter nanotubes are expected to perform better in electronic applications since their walls are less affected by curvature and defects. In particular,
the radial breathing mode (RBM) phonon energy is inversely proportional to the tube diameter, and RBM phonon scattering has been found to degrade the charge transport properties of SWNTs.\textsuperscript{[27]} Finally, the effective masses of charge carriers are inversely proportional to the diameter of the tube, consequently also to the mobility.\textsuperscript{[28]} It is therefore of high interest to develop efficient methods to selectively disperse large diameter s-SWNT for electronic applications.

In this chapter, we investigate the role of different types of polymer backbones in the selection mechanism of s-SWNTs using sources presenting different average diameters, from small (0.8nm-1.2nm) HiPCO to large diameter (1.2nm-1.5nm) arc plasma jet (SO) nanotubes. For this purpose, we compare the selectivity performance of a new polymer, poly[(4,4-di-n-dodecyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl)-alt-(2,1,3-benzothiadiazole-4,7-diyl)] (P12CPDTBT), with that of two well studied dispersing polymers with different backbones, namely poly(9,9-di-n-dodecylfluorene-2,7-diyl) (PF12) and poly(3-dodecylthiophene-2,5-diyl) (P3DDT).\textsuperscript{[14,15,17,29]} The first of these polymers, but with hexyl side chains, is well-known for its use in organic solar cells\textsuperscript{[30,31]} and has the smallest bandgap of all polymers in the present study.

The interaction mechanism between the three types of conjugated polymers and the two different SWNT samples was inferred from the dispersion yields, the selection of s-SWNT and the level of individualization of s-SWNTs in solution.\textsuperscript{[32]} Electronic structure calculations were also carried out to give a further interpretation of the experimental results. The calculated binding energies of the polymers on a nanotube having a diameter close to 1 nm follows the order PF12 < P12CPDTBT < P3DDT, in agreement with the experimentally obtained dispersion yields of samples prepared with HiPCO nanotubes. This is a result of the high curvature of the small diameter nanotubes and the increased flexibility of the polymer backbone in the series from PF12 to P3DDT. For a nanotube with a diameter close to 1.5 nm, the binding energies of PF12 and P12CPDTBT are of the same order of magnitude, and the dispersions yields of the solutions prepared with the SO nanotubes and these polymers are similar. However, the SO:PF12 and SO:P12CPDTBT dispersions contain metallic species, as revealed by the FET characteristics of the devices prepared with them. P3DDT again presents the highest binding energy among all polymers. The geometry of the polymers wrapped around the nanotubes shows that the thiophene rings of P3DDT are closer to the nanotube surface than the other polymers, prompting the system to a considerable mixing (hybridization) of electronic states that can induce a charge transfer, especially in the case of metallic nanotubes.
2.2 Selection of s-SWNTs using conjugated polymers with different backbones

HiPCO and SO SWNTs were dispersed in toluene using P12CPDTBT, whose structure is sketched in Figure 2.1a. The SWNT:polymer ratio used to prepare the samples was optimized to obtain the maximum dispersion yield for a given amount of SWNTs. The ratio was 1:2 weight %, with 3 mg of SWNTs, 6 mg of polymer, and 15 ml of solvent. The procedure used for solution preparation was similar to the one reported by Bisri et al., as described in the methods section. After this first dispersion, an extra step developed in our group was performed, aimed at decreasing the amount of free polymer in the solution. This additional step consists of an extra centrifugation carried out at higher speed and for a longer time, which allows not only to eliminate excess free polymer but also to tune the nanotube concentration in the final suspension. We shall refer to the dispersions prepared with this last step as purified solutions. In this purification step, the concentrations of the dispersions were set in a way that the highest nanotube peak has an absorbance of 0.5.

Figures 2.1b and 2.1c display the absorption spectra of the HiPCO:P12CPDTBT and SO:P12CPDTBT purified solutions, respectively. The peaks centered at 700 nm and 400 nm correspond to absorption by the polymer chains, and since the solutions were purified these peaks are mostly due to polymers wrapping the SWNTs. The sharp peaks in the infrared region are the absorption transitions E\textsubscript{11} from the different SWNT species. The peaks were assigned according to an empirical formula, as reported by Gomulya et al. Note that in the case of SO tubes the E\textsubscript{22} transitions are also visible in the spectral range between 900 and 1200 nm, while for the HiPCO sample these higher energy transitions overlap with the stronger polymer absorption and are not visible. Therefore, the band associated with polymer absorption in the HiPCO samples is apparently stronger than in the SO samples because of the superposition with the E\textsubscript{22} HiPCO nanotubes transitions.

In the absorption spectra, it is not possible to identify clearly if metallic tubes are present after the separation procedure with P12CPDTBT. Therefore, we fabricated field effect transistors using these dispersions to examine their electronic characteristics. This approach has been used previously to obtain information about the content of metallic SWNTs. As mentioned earlier, dispersions were prepared in a way that the highest absorption peaks for both samples have an intensity of 0.5. Given the integrated area of the absorption shown in Figures 2.1b and 2.1c, we expect that these dispersions should have similar nanotube concentrations.
Figure 2.1. a) Chemical structure of P12CPDTBT. b) The absorption spectrum of the small diameter carbon nanotubes solution, HiPCO:P12CPDTBT, after removal of excess polymer. c) The absorption spectrum of the large diameter carbon nanotubes solution, SO:P12CPDTBT, after removal of excess polymer. The chiralities of the SWNTs present in the sample are determined using an empirical formula.\textsuperscript{[15]}

Figure 2.2a shows the output and transfer curves of a representative device fabricated with the HiPCO:P12CPDTBT solution. An on-off ratio of $2 \times 10^7$, with hole and electron mobilities of 2.1 cm$^2$/V.s and 3.1 cm$^2$/V.s, respectively, are shown. Figure 2.2b displays the FET characteristics of a device fabricated with the SO:P12CPDTBT solution, in which an on-off ratio of $3 \times 10^2$ and mobilities of 2.4 cm$^2$/V.s for holes and 4.0 cm$^2$/V.s for electrons are measured. The main difference between the samples fabricated with the HiPCO and the
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SO tubes is the higher on-off ratio of the HiPCO-based FETs due to the lower off current. A higher off current is generally considered an indication of the presence of metallic species, especially in the case of SWNT network transistors with channel length above the average length of the SWNTs. This is an example where a few metallic tubes can degrade the off current without conferring metallic characteristics to the device. We, therefore, conclude that SO:P12CPDTBT dispersions contain traces of metallic tubes.

We have demonstrated that yet another conjugated polymer can select s-SWNTs, with an efficiency that depends on the average nanotube diameter, but the underlying mechanism responsible for this difference is not obvious. To understand this differences, we compared dispersions of HiPCO and SO SWNT obtained with P3DDT and PF12. We started with 6 mg polymer, 3 mg SWNT, and 15 ml toluene. This initial concentration maximizes the dispersion yield but not the purity of the samples.

Figure 2.2. $I_D - V_D$ output characteristics, $V_G = 0$ V to -50 V, $\Delta V_G = -10$ V for $V_D \leq 0$ V; $V_G = 0$ V to 50 V, $\Delta V_G = 10$ V for $V_D \geq 0$ V (top) and $I_D - V_G$ transfer characteristics (bottom) of FETs fabricated with (a) HiPCO:P12CPDTBT solution and (b) SO:P12CPDTBT solution.
Our aim is to unravel the basic mechanisms involved in the selection process comparing the results of s-SWNT separated by different polymers with different chemical structures. The polymers (Figure 2.3a) were chosen for specific structural features which might affect their interactions with SWNTs. First, all three polymers have lateral dodecyl groups attached to the main chain but differ in geometry. The P3DDT has the lateral groups regioregularly attached to sp² carbons such that the saturated carbon chain is nearly in the same plane of the aromatic ring, while PF12 and P12CPDTBT have them attached to a sp³ carbon, such that the plane containing two dodecyl chains is perpendicular to the aromatic ring to which they are bound. The second difference concerns the presence of heteroatoms: PF12 is an all-carbon polymer while P3DDT has one heteroatom per aromatic ring and P12CPDTBT has several heteroatoms per monomer. The presence of heteroatoms in the conjugated backbone affects the electronic structure, as can be inferred from the position of the energy levels of each polymer reported by other authors: the HOMO (-4.9 eV) and the LUMO (-3.5 eV) of P12CPDTBT are close to HOMO (-5.1 eV) and LUMO (-3.2 eV) of P3DDT, while PF12 has a wider bandgap with the HOMO at -5.8 eV and the LUMO at -2.2 eV.

Figure 2.3. a) Chemical structures of the polymers used to disperse s-SWNTs. b) Absorption spectra of the polymer-wrapped HiPCO solutions. Color code: red curve for P3DDT, the black curve for P12CPDTBT, and orange curve for PF12.
The carbon nanotube sources differ in average diameter, being the small diameter (0.8-1.2 nm) HiPCO and the large diameter (1.2-1.5 nm) SO tubes, with corresponding bandgaps and wall curvatures that decrease as the diameter increases. Figure 2.3b shows the absorption spectra of the solutions obtained with HiPCO tubes and P12CPDTBT, P3DDT, or PF12, after the first step of the dispersion process, i.e., with excess polymer present in the solution. Because the same relative concentrations of polymer and SWNTs were used to prepare the samples, the intensity of the SWNT peaks in the absorption spectra is directly related to the number of individualized tubes and small bundles present in the supernatant, therefore to the dispersion yield. The dispersion yield for HiPCO:P3DDT is 15%, while the one for SO:P3DDT is 21%. These values are calculated comparing the initial weight of the material and comparing it with the amount of material collected after the purification process.

![Figure 2.4](image)

Figure 2.4. a) Steady-state photoluminescence spectra of HiPCO:P3DDT (red), HiPCO:P12CPDTBT (black), and HiPCO:PF12 (Orange). For clarity, the curves are shifted vertically with respect to each other. b) The decay time of the PL measured at 1200 nm for the SWNTs (8,6), the blue lines are bi-exponential fits of the experimental data.

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As shown in Figure 2.3b, P3DDT is the best dispersant for HiPCO nanotubes as the absorption peak at 1300nm from P3DDT dispersion is about twice as high as the same peak from P12CPDTB7T dispersion and more than three times the peak of the PF12:SWNT dispersion.

Figure 2.4a shows the steady-state photoluminescence measurements of the semiconducting HiPCO tubes wrapped by P12CPDTB7T, P3DDT, and PF12. In the case of HiPCO:P12CPDTB7T, the broad peak at 900 nm indicates the presence of a residue of the polymer photoluminescence. For the three samples, the low energy peaks correspond to the main tube chiralities. Figure 2.4b shows the photoluminescence lifetime measured for the (8,6) tubes at 1200 nm. The three samples are well fitted with bi-exponential functions. Tubes wrapped by P12CPDTB7T shows time decays of \( \tau_1 = 6 \) ps and \( \tau_2 = 40 \) ps, PF12 shows time decays of \( \tau_1 = 6 \) ps and \( \tau_2 = 38 \) ps. Those time decays are longer than the time decays shown by the tubes wrapped with P3DDT, which are \( \tau_1 = 3 \) ps and \( \tau_2 = 16 \) ps. This behavior could be attributed to charge/energy transfer due to the formation of twins of SWNTs in the HiPCO:P3DDT solution. Another possibility is that the electronic interaction of P3DDT with nanotubes is stronger than the interaction with the other two polymers, thus accentuating nonradiative relaxation pathways.

The larger diameter SO tubes were also dispersed with the P12CPDTB7T, P3DDT, and PF12. Figure 2.5a shows the dispersion yields of the SO:polymer solutions, the relative ratio between the SWNTs and the polymer was kept at 1:2 weight %. The dispersion yield of SO:P3DDT is 21%. That is three times lower than the dispersion yields of P12CPDTB7T and PF12.

The quality of the dispersions regarding metallic nanotubes content has also been evaluated using the FET performance analysis. Figure 2.5b shows the transfer curve of devices fabricated with the different SO:polymer solutions. The SO:P3DDT devices show \( 10^{-9} \) A off-current, while the devices made with SWNTs wrapped with PF12 and P12CPDTB7T show off current of about \( 10^{-7} \) A, which can be an indication of metallic species in these two dispersions. In the case of HiPCO tubes, P12CPDTB7T, P3DDT, and PF12 dispersions show a low off current, indicating that these dispersions are either free of metallic nanotubes or that the concentration of metallic species is low enough that they do not degrade the off current.
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Figure 2.5. a) Absorption spectra of SO:polymer solutions. Color code: red curve for P3DDT, the black curve for P12CPDTBT, and orange curve for PF12. b) \( I_D - V_G \) transfer characteristics of FETs fabricated with SO:P3DDT, SO:P12CPDTBT, and SO:PF12 solutions.

2.3 Simulation of the interactions between SWNT and the conjugated polymers

In order to rationalize the results obtained with P12CPDTBT, P3DDT, and PF12, we carried out electronic structure calculations and obtained the wrapping geometry of model systems. The conformations and binding energies of these polymers adsorbed on typical small and large diameter nanotubes (8,6) and (12,10) have been studied by the Density Functional derived method DFTB3-D3 (see Methods section). By this method, electronic, electrostatic and dispersion interactions are described approximately as a Density
Functional method but at a lower computational cost. Helical wrapping geometries were assumed to maximize the number of polymer units interacting with the nanotube surface at the expense of some torsional energy necessary to distort the otherwise nearly planar polymer backbone. The energy gain due to polymer-nanotube interaction overcomes the torsional energy for the chosen nanotubes.

Figure 2.6. Optimized polymer-nanotube geometries on (upper) nanotube (8,6) and (lower) nanotube (12,10), using the polymers: (a) P3DDT, (b) PF12, and (c) P12CPDTBT. The molecular structures shown below the hybrid systems are the polymer units used in the calculation of binding energies (BE) per polymer unit. Color code: cyan colored spheres represent nanotubes; for the polymers, atoms are represented by C=gray, H=white, S=yellow, N=blue.

Figure 2.6 summarizes the resulting optimized geometries and polymer-nanotube binding energies. The energy values corresponding to the binding energy (BE) per polymer unit, are shown below the nanotube wrapped structures. These units were chosen so that each polymer unit contains the same number of alkyl tails per polymer unit. The polymer P3DDT, gives the best surface coverage and requires a smaller number of polymer chains to cover the nanotube wall. This is due to a favorable polymer geometry in which both alkyl tails from the corresponding unit attach to the nanotube, thereby holding the polymer
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backbone onto the surface. The thiophene rings arrange over the surface with their centers either over the center of a hexagon or a carbon, as a result of the interactions usually attributed to π-stacking. The polymer binding energies to the near armchair nanotubes are the largest among the studied polymers since both lateral alkyl chains interact with the nanotube wall and the torsional energies required to distort the backbone are only 0.1 eV per unit. However, differently from the other two polymers, no alkyl tails are pointing outwards, and other nanotubes or polymer chains can easily approach and bind forming dyads or small bundles.

Figure 2.7. Polymer segments of the same length for (a) P3DDT, (b) PF-12, (c) P12CPDTBT, and (d) PCDTPT. The numbers below the bonds indicate the increase in polymer energy (kJ/mol) to rotate adjacent rings from the ground state value to the average dihedral angle obtained in the helical structures wrapping the nanotubes. The rectangles represent the rigid parts of the backbone that requires more energy to distort than the dihedral angles between the rectangles.

The polyfluorene derivative PF12, in contrast to P3DDT, has the lowest binding energies to the near armchair nanotubes. The main differences are the torsional energies, which are 0.37 eV/unit and 0.29 eV/unit, respectively, in the helices of (8,6) and (12,10) nanotubes, and the adsorption of only one of the alkyl tails per unit over the surface. Similar torsional energies were calculated for P12CPDTBT, which are 0.39 eV/unit and 0.22 eV/unit, respectively. Note that while there is an important difference between these polymers when interacting with (8,6) nanotube, the binding energies on (12,10) nanotube are almost the same (Figure 2.6). In order to make a proper comparison of the flexibility of these polymers, we display in Figure 2.7 the polymer segments having the same length and
indicate the energy required to change the dihedral angle between adjacent rings from the ground state value to the average dihedral angle obtained in the helical structures. We added the polymer poly[(4,4-bis(2-hexadecyl)cyclopenta[2,1-b;3,4-b0]dithiophene)-2,6-diy1-alt-[1,2,5]-thiadiazolo[3,4-c]pyridine] (PCDTPT) to the analysis since, as discussed below, it is a poor dispersant of small diameter nanotubes but it is able to disperse large diameter nanotubes in yields comparable to those observed for P3DDT.

P3DDT has five small rectangles and four bonds through which the rectangles can rotate, making it easy energetically to modify the polymer conformation into a helix. PF12 has the largest rectangles and only two bonds allowing rotation. To adopt a coiled conformation on a small diameter nanotube, the rectangles need to slightly curve, which adds to the torsional energy. P12CPDTBT and PCDTPT have alternating small and large rectangles and have three bonds allowing rotation. The latter polymer, however, has a strong electrostatic interaction between sulfur and nitrogen on neighboring rectangles, making this polymer the most difficult to distort. In the case of small diameter nanotubes, the most stable hybrid structure is made with P3DDT, followed by P12CPDTBT and PF12, which is in correspondence with the dispersion yields shown in Figure 2.3. The PCDTPT polymer is difficult to distort, which result in low dispersion yield of HiPCO nanotubes (Figure 2.8). For large diameter nanotubes, P12CPDTBT and PF12 produce hybrid structures of approximately the same binding energy, in agreement with the experimentally observed similar dispersion yields shown in Figure 2.5. According to the absorbance values seen in Figure 2.3 and Figure 2.5, P3DDT disperses similar concentrations of small and large diameter nanotubes, even though the theoretical analysis predicts more stable structures formed with large diameter nanotubes.

To investigate the influence of a bulkier and stiffer backbone on the dispersion yield of HiPCO and SO tubes, we performed experiments to select s-SWNTs with the polymer PCDTPT with hexadecyl alkyl chains. The chemical structure is shown in Figure 2.7d, and the dispersion yields are given in Figure 2.8b. Although the alkyl chains of PCDTPT are longer than the alkyls chains of the rest of polymers (vide supra) used in this work, PCDTPT showed the same trend, namely a low dispersion yield for HiPCO tubes and a moderate dispersion yield for SO tubes. This is a consequence of its bulky and stiff backbone.

The PCDTPT results support the hypothesis of helical wrapping of the polymers around nanotubes. P12CPDTBT and PCDTPT are very similar in structure but offer different dispersion yields. The most prominent feature that distinguishes these polymers is the backbone flexibility, which is meaningful only when the polymer bends and rolls into a coil.
2.4 Conclusion

We have demonstrated the ability of P12CPDTBT to disperse SWNTs of different diameters. Our comparison of P12CPDTBT with P3DDT and PF12 has shown that for small diameter HiPCO tubes, the flexibility of the backbone impacts the dispersion yields. For larger diameter tubes (SO), the bulkier and less flexible backbones of P12CPDTBT and PF12 gave the best performance. We found that P3DDT interacts more strongly with nanotubes than PF12 and P12CPDTBT. The wrapping of metallic nanotubes from the larger diameter SO source seems to be a common feature of all polymer dispersions.

We also showed that when we fabricated the FETs, the probability of finding metallic tubes in SO:polymer solutions is higher than in HiPCO:polymer solutions. For devices fabricated with large diameter tubes, SO:P3DDT solutions showed lower off current compared to SO:P12CPDTBT and SO:PF12. In the case of HiPCO:polymer solutions, the off currents of the devices prepared with the three polymers indicate a high quality of the solutions in terms of purity.

Figure 2.8. a) Chemical structure of PCDTPT b) Absorption spectra of SO and HiPCO tubes dispersed with PCDTPT.
Concluding, these findings demonstrate that each source of nanotubes requires a particular type of polymer that can be designed for the efficient discrimination of semiconducting SWNTs.

2.5 Experimental section

**Preparation and characterization of semiconducting SWNT dispersion:** HiPco SWNTs (0.8-1.2 nm) were purchased from Unidym Inc. and large diameter (1.2-1.5 nm), high purity SWCNTs processed by arc plasma jet (SO) were purchased from Meijo Nano Carbon Co. Ltd. All SWNTs were used as received. The polymers were solubilized in toluene using a high power ultrasonicator (Misonix 3000) with cup horn bath (output power 69 W) for 10 minutes, followed by overnight stirring at 60 °C. Subsequently, SWNTs were added to form the SWNT:polymer dispersions with a weight ratio of 1:2 (3mg SWNTs, 6mg polymer, 15 ml toluene). These solutions were then sonicated for 2 h at 69 W and 16 °C.

After ultrasonication, the dispersions were centrifuged at 30 000 rpm (109 000g) for 1 h in an ultracentrifuge (Beckman Coulter Optima XE-90; rotor: SW55Ti) to remove all the remaining bundles and heavy-weight impurities. After the centrifugation, the highest density components precipitate at the bottom of the centrifugation tube, while the low-density components, including small bundles and individualized SWNTs wrapped by the polymer, and free polymer chains, stay in the supernatant. One extra step of ultracentrifugation was implemented to decrease the amount of free polymer in solution (enrichment).[33] For this purpose the supernatant obtained after the first ultracentrifugation is centrifuged for 5 h, 55 000 rpm (367 000 g). The individualized s-SWNTs are now precipitated in the pellet, and the free polymer is in the supernatant. Finally, the pellet is re-dispersed by sonication in toluene.

**FET transistor fabrication and electrical measurements:** Field effect transistors were fabricated on silicon substrates (acquired by the Fraunhofer Institute for Photonic Microsystems) with a thermally grown SiO$_2$ dielectric layer (230 nm thickness). Source and drain bottom electrodes (10 nm ITO/30 nm Au) were lithographically patterned forming an interdigitated channel of 20um length and 1mm width. The different SWNTs dispersions tested were deposited by blade coating technique (Zehntner ZAA 2300 Automatic film applicator coater) using 8 μl of s-SWNT dispersion using a blade speed of 3 mm/s. The procedure was repeated 2 times to achieve sufficient SWNT coverage density. After deposition, the samples were annealed at 135 °C for 1 h to evaporate the remaining solvent.

Electrical measurements were performed using a probe station placed in a nitrogen-filled glovebox at room temperature under dark conditions. The probe station was connected to Agilent E5262A Semiconductor Parameter Analyzer. All devices were fabricated and measured in the nitrogen-filled glovebox, without being exposed to air.
The reported charge carrier mobilities were extracted from the \( I_D-V_G \) transfer characteristics in the linear regime (\( V_{DS} = \pm 5 \) V). The gate capacitance was estimated using the parallel plate capacitor model since the nanotube density on the film is above the percolation limit. The quantum capacitance of the nanotube was not taken into account so that the total capacitance value is overestimated; thus underestimating the effective mobility of the devices.

**Optical characterization of the semiconducting SWNT dispersion:** Optical measurements were performed to check the concentration of the carbon nanotubes selected by the polymers. Absorption spectra were recorded by a UV–Vis–NIR spectrophotometer (Shimadzu UV-3600). Photoluminescence (PL) measurements were performed by exciting the samples at 800 nm (or with the 400 nm second harmonic) with a Kerr mode-locked Ti-Sapphire laser, delivering 150 fs pulses with a repetition frequency of 76 MHz. Time-resolved PL measurements were recorded by a streak camera with a NIR-sensitive photocathode (Hamamatsu Photonics) working in synchroscan mode (time resolution around 2 ps). All spectra were corrected for instrumental response.

**Polymer Synthesis:** The homopolymers P3DDT and PF12 have been synthesized following procedures described in the literature.\(^{39,40}\) P3DDT was received after Soxhlet extraction with methanol, acetone, ethyl acetate and hexane. For the herein reported experiments the hexane fraction with \( M_n = 19.200 \) g/mol and \( M_w = 22.300 \) g/mol was used. PF12 was purified by Soxhlet extraction with methanol, acetone, ethyl acetate and dichloromethane. From the dichloromethane fraction a high molecular weight PF12 with \( M_n = 280.000 \) g/mol and \( M_w = 589.000 \) g/mol was obtained. P12CPDTBT was synthesized by direct arylation polycondensation (DAP), following a published procedure.\(^{41-43}\) The synthesis was carried out in dry N,N-dimethylacetamide with palladium acetate as a catalyst and potassium carbonate as a base. After Soxhlet extraction with methanol, ethyl acetate, n-hexane and dichloromethane. The further used polymer fraction was received from the dichloromethane extraction. P12CPDTBT was synthesised in two batches. The first batch was synthesised with \( M_n = 4000 \) g/mol and \( M_w = 25.200 \) g/mol, and the second batch with \( M_n = 11.500 \) g/mol and \( M_w = 57.200 \) g/mol. Both batches showed relatively broad molecular weight distribution, typical for DAP products. PCDTPT was synthesized according to previous procedures reported by Bazan et al.\(^{44}\)

**Computational details:** The conformation and electronic structures of hybrid polymer-nanotube systems has been studied by the Third order Self-Consistent Charge Density Functional Tight-Binding with empirical dispersion (DFTB3-D3) and 3OB parameter set.\(^{45-48}\) This method has shown a performance comparable to the Density Functional Perdew-Burke-Emzerhof (PBE) \(^{49}\) for ground state geometries, heats of formation and reaction energies, at a low computational cost, and is especially suitable for large systems.
Nanotubes were modeled as finite molecules with open ends and hydrogen saturation of the end bonds. Two s-SWNT were chosen, (8,6) (length 52 Å) and (12,10) (length 53 Å), for their high concentrations in the dispersions prepared in this work, representing small and large diameter species, respectively. The ground state geometries were optimized and frozen in the polymer-nanotube calculations. The polymers were built as oligomers of approximately the same length: 16 thiophenes for P3DDT, 8 fluorenes for PF12, and 6 (7) P12CPDTBT units. The ground state geometries were calculated. In each case, a helical polymer structure was built on the nanotube and allowed to relax with a frozen nanotube geometry. The converged helical geometry was used to compute the energy of the isolated helical oligomer. The torsional energy is the energy difference between the helical and ground state structures. The binding energy is calculated as \( BE = E(\text{oligomer}) + E(\text{nanotube}) - E(\text{hybrid}) \).
2.6 References


The power of polymer wrapping