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# Conjugated Polymer-Assisted Dispersion of Single-Wall Carbon Nanotubes: The Power of Polymer Wrapping

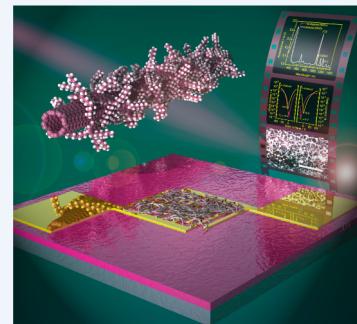
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**CONSPECTUS:** The future application of single-walled carbon nanotubes (SWNTs) in electronic (nano)devices is closely coupled to the availability of pure, semiconducting SWNTs and preferably, their defined positioning on suited substrates. Commercial carbon nanotube raw mixtures contain metallic as well as semiconducting tubes of different diameter and chirality. Although many techniques such as density gradient ultracentrifugation, dielectrophoresis, and dispersion by surfactants or polar biopolymers have been developed, so-called conjugated polymer wrapping is one of the most promising and powerful purification and discrimination strategies. The procedure involves debundling and dispersion of SWNTs by wrapping semiflexible conjugated polymers, such as poly(9,9-dialkylfluorene)s (PFx) or regioregular poly(3-alkylthiophene)s (P3AT), around the SWNTs, and is accompanied by SWNT discrimination by diameter and chirality. Thereby, the  $\pi$ -conjugated backbone of the conjugated polymers interacts with the two-dimensional, graphene-like  $\pi$ -electron surface of the nanotubes and the solubilizing alkyl side chains of optimal length support debundling and dispersion in organic solvents. Careful structural design of the conjugated polymers allows for a selective and preferential dispersion of both small and large diameter SWNTs or SWNTs of specific chirality. As an example, with polyfluorenes as dispersing agents, it was shown that alkyl chain length of eight carbons are favored for the dispersion of SWNTs with diameters of 0.8–1.2 nm and longer alkyls with 12–15 carbons can efficiently interact with nanotubes of increased diameter up to 1.5 nm. Polar side chains at the PF backbone produce dispersions with increased SWNT concentration but, unfortunately, cause reduction in selectivity.

The selectivity of the dispersion process can be monitored by a combination of absorption, photoluminescence, and photoluminescence excitation spectroscopy, allowing identification of nanotubes with specific coordinates [(n,m) indices]. The polymer wrapping strategy enables the generation of SWNT dispersions containing exclusively semiconducting nanotubes. Toward the applications in electronic devices, until now most applied approach is a direct processing of such SWNT dispersions into the active layer of network-type thin film field effect transistors. However, to achieve promising transistor performance (high mobility and on–off ratio) careful removal of the wrapping polymer chains seems crucial, for example, by washing or ultracentrifugation. More defined positioning of the SWNTs can be accomplished in directed self-assembly procedures. One possible strategy uses diblock copolymers containing a conjugated polymer block as dispersing moiety and a second block for directed self-assembly, for example, a DNA block for specific interaction with complementary DNA strands. Another strategy utilizes reactive side chains for controlled anchoring onto patterned surfaces (e.g., by interaction of thiol-terminated alkyl side chains with gold surfaces). A further promising application of purified SWNT dispersions is the field of organic (all-carbon) or hybrid solar cell devices.



## INTRODUCTION

Carbon nanotubes (CNTs) are nanometer-sized carbon allotropes with a tubular one-dimensional structure of high aspect ratio. CNTs have shown tremendous application potential due to a unique set of chemical, mechanical, optical, and electronic properties enabling their use in electronic devices, nanotechnology, materials science, and even biology.<sup>1,2</sup> The first successful synthesis of CNTs was demonstrated by Sumio Iijima in 1991 during his attempts to prepare fullerene from graphite using an arc-discharge method.<sup>3</sup> Before that, other researchers had already visualized high aspect ratio carbon nano-objects under a transmission electron micro-

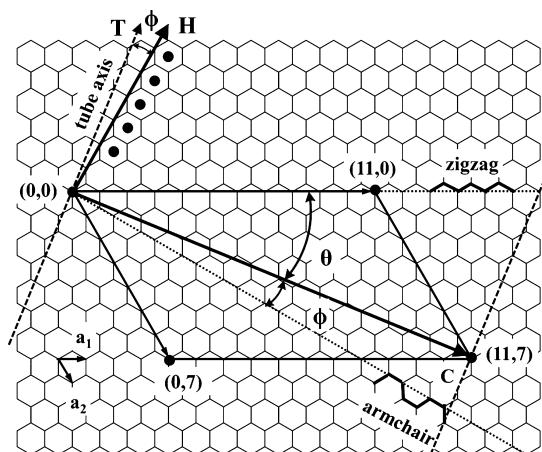
scope.<sup>4</sup> CNTs can be described as rolled graphene sheets, and depending on the way they are rolled, a variety of nanotubes having different numbers of graphene layers composing the nanotubes wall, and different nanotube diameters are generated. CNTs are categorized mainly into two types: single-walled nanotubes (SWNTs), and multiwalled nanotubes (MWNTs). In this Account, we limit our discussion only to SWNTs. These have been up to now the most studied members of the family,

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both for their interesting physical properties and for applications in electronics and optoelectronics.

The rolling of graphene sheets in order to form nanotubes can be described using a vector  $\vec{C}$ , which is defined by the two indices  $(n,m)$  and the lattice vectors  $\vec{a}_1$  and  $\vec{a}_2$  (Figure 1).<sup>5</sup>

$$\vec{C} = n\vec{a}_1 + m\vec{a}_2 = (n, m)$$



**Figure 1.** Building of carbon nanotubes from graphene sheets. Reproduced with permission from ref 5. Copyright 1998 Nature Publishing Group.

Once  $\vec{C}$  is defined on the graphene sheet, which is then folded to join the two edges, a tube with the indices  $(n,m)$  is formed. Consequently, a chiral angle  $\{\theta(n,m)\}$  can be defined as the angle between the vectors  $\vec{C}$  and  $\vec{a}_1$ . Based on hexagonal symmetry considerations, this angle can have values between  $0^\circ$  and  $30^\circ$ . The chiral angle allows the classification of SWNTs into two categories, achiral or chiral. Regarding achiral structures, two types can be formed for  $m = 0$  and for  $n = m$ , which are called zigzag and armchair, respectively (Figure 1). All other combinations of  $n$  and  $m$  in between zigzag and

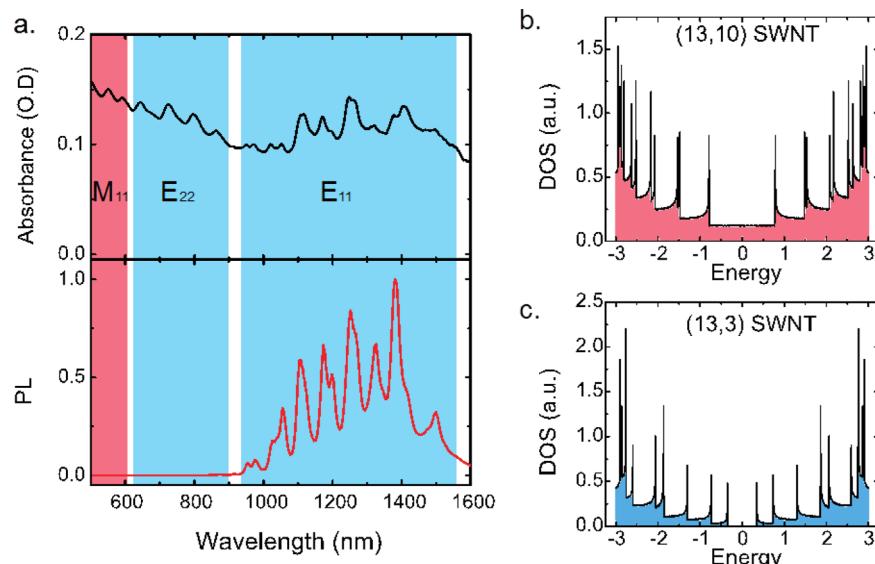
armchair vectors within the graphene honeycomb lattice define all possible tubes, which are chiral.

Determined by the spatial arrangement of the hexagonal  $sp^2$  carbon atoms, SWNTs are classified into metallic SWNTs (m-SWNT) and semiconducting SWNTs (s-SWNT). The nature of the tubes is governed by their indices  $(n,m)$ . When  $|n - m| = 3q$  (where  $q$  is an integer), the nanotubes are metallic or semimetallic, and all remaining nanotubes are semiconducting. Therefore, in an as-synthesized crude mixture, there are approximately one-third metallic and two-third semiconducting SWNTs.<sup>6</sup>

SWNTs can be synthesized in several ways. These include, arc discharge,<sup>7</sup> laser ablation,<sup>8</sup> chemical vapor deposition (CVD),<sup>9</sup> high-pressure carbon monoxide disproportionation (HiPCO),<sup>10</sup> and the CoMoCAT process.<sup>11</sup> All these processes produce mixtures containing single- and multiwalled carbon nanotubes, amorphous carbon, and residual metal catalyst used for nanotube growth. In recent years, there have been many efforts to enhance the selectivity of CNT production. Nevertheless, the best available methods still produce mixtures of metallic and semiconducting SWNTs. Different methods provide variations in the distribution of the  $(n,m)$  indices of the SWNTs within certain diameter ranges. HiPCO SWNTs are obtained by flowing CO gas along with  $Fe(CO)_5$  as catalyst. The procedure generates tubes with rather small diameter, 0.7–1.2 nm. The CoMoCAT method, which is similar to HiPCO, uses cobalt and molybdenum catalysts and produces SWNTs with ~0.8 nm in diameter. Arc-discharge SWNTs are generated by applying very high current to carbon rods, and this process produces larger tubes with diameter of ~1.5 nm.

s-SWNTs hold great promise due to their remarkable optical, electronic and electrical properties. In particular, scattering-free (ballistic) charge carrier transport is one of the most important points of interest.<sup>12</sup> Single s-SWNT-based devices displayed a high charge carrier mobility of up to  $10^5 \text{ cm}^2/(\text{V s})$ .<sup>13,14</sup> For this reasons, SWNTs are still considered as one of the most viable alternative to silicon-based field effect transistors.<sup>15</sup>

The mixed nature of the electronic properties in as-synthesized SWNTs is hampering the application of these



**Figure 2.** (a) Typical absorption and photoluminescence spectra of small diameter ( $<1.5$ ) SWNT mixtures. Density of state plots of m-SWNTs (b) and s-SWNTs (c) The sharp peaks are the van Hove singularities of the SWNTs.

nano-objects in electronic devices. In addition, nanotubes have a tendency to form bundles due to van der Waals interactions. Bundling leads to poor processability and dispersibility. Consequently, postprocessing of crude SWNT mixtures is needed, involving sorting of metallic and semiconducting species, separation by chirality and diameter, and dispersion in a suitable medium (solvent) to prevent rebundling.

In this Account, we discuss current progress in separation and purification of semiconducting SWNTs. The discussion is focused on the use of conjugated polymers in a noncovalent functionalization of SWNTs, by which selection based on chirality and diameter can be performed. After a brief discussion about the fundamental physical properties of carbon nanotubes, aspects of their optical properties are discussed due to their importance for monitoring the selection process. Some recent and successful examples of s-SWNTs selection by polymer wrapping will be extensively discussed. Finally, some of the selection procedures are discussed in relation to device applications.

## ■ ELECTRONIC AND OPTICAL PROPERTIES OF SWNTs

The electronic properties of SWNTs are derived from the electronic configuration of graphene, in which the bonding  $\pi$ -orbitals form valence and the antibonding  $\pi^*$  orbitals form conduction states. The unique one-dimensional structure of SWNTs causes confinement of the  $\pi$ -electrons normal to the rolling axis. The periodic boundary conditions around the nanotube circumference lead to a semiquantization of the energy levels of SWNTs. Therefore, their electronic states are organized in discrete bands with a one-dimensional density of electronic states known as van Hove singularities.<sup>1</sup> Typical density of states plots of m- and s-SWNTs are depicted in Figure 2b,c, respectively.

Coulombic interactions between electrons and holes give rise to excitonic states that show binding energies of several hundreds of millielectronvolts under two photon spectroscopy.<sup>16</sup> Optical resonances predominantly occur in relation to these excitonic states, in place of transitions within the quasi-particle bandgap, both in semiconducting and in metallic tubes.<sup>17</sup> Typically, sharp optical absorption bands are identified between 450 and 550 nm (M11) for small ( $<1.2$  nm) metallic nanotubes and between 650 and 900 nm (S22) and 900–1500 nm (S11) for small ( $<1.2$  nm) semiconducting nanotubes (Figure 2). Therefore, absorption spectroscopy allows identification of the specific CNT species present in the sample, especially when they have been previously unbundled and isolated. Phenomenological models such as the Kataura plot have been developed to correlate absorption peaks and SWNT coordinates.<sup>18</sup>

Photoluminescence excitation (PLE) spectroscopy is largely used to determine the ( $n,m$ ) indices of SWNTs. In this case, emission from the nanotubes is monitored after excitation at different wavelengths. This technique provides information only for SWNTs that are sufficiently efficient emitters with a detectable photoluminescence. Therefore, this technique is not suitable for samples where SWNTs are incompletely debundled.

Furthermore, vibration-active modes of SWNTs give rise to four distinguishable scattering features in Raman spectroscopy. These are (i) radial breathing modes (RBM) in the range 100–350  $\text{cm}^{-1}$  corresponding to in-phase movement of carbon atoms in radial direction, (ii) the disorder-induced D-mode

(1250–1450  $\text{cm}^{-1}$ ), (iii) tangential G-modes, that is,  $G^-$ -mode ( $\sim 1570 \text{ cm}^{-1}$ ) due to vibration of carbon atoms along the circumferential direction and  $G^+$ -mode ( $\sim 1590 \text{ cm}^{-1}$ ) due to the carbon atom vibrations along the nanotube axis, and (iv) the  $G'$ -mode (2500–2900  $\text{cm}^{-1}$ ) corresponding to a disorder-based overtone of D-modes. The occurrence of these Raman bands strongly depends on diameter and ( $n,m$ ) indices of the tubes.

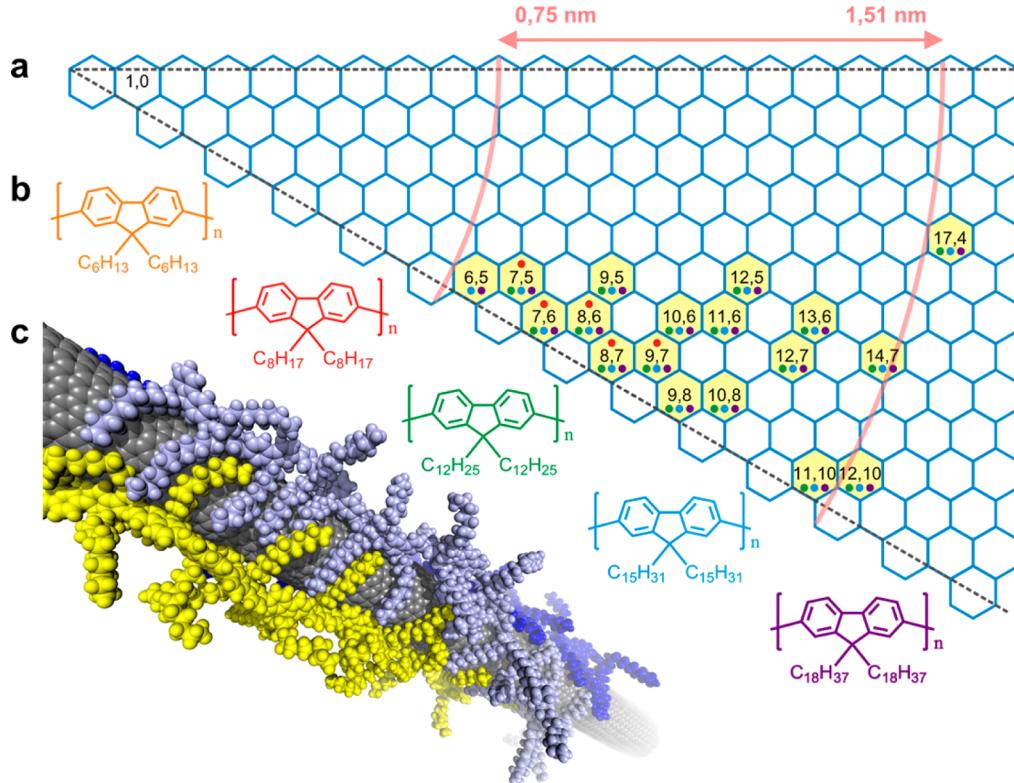
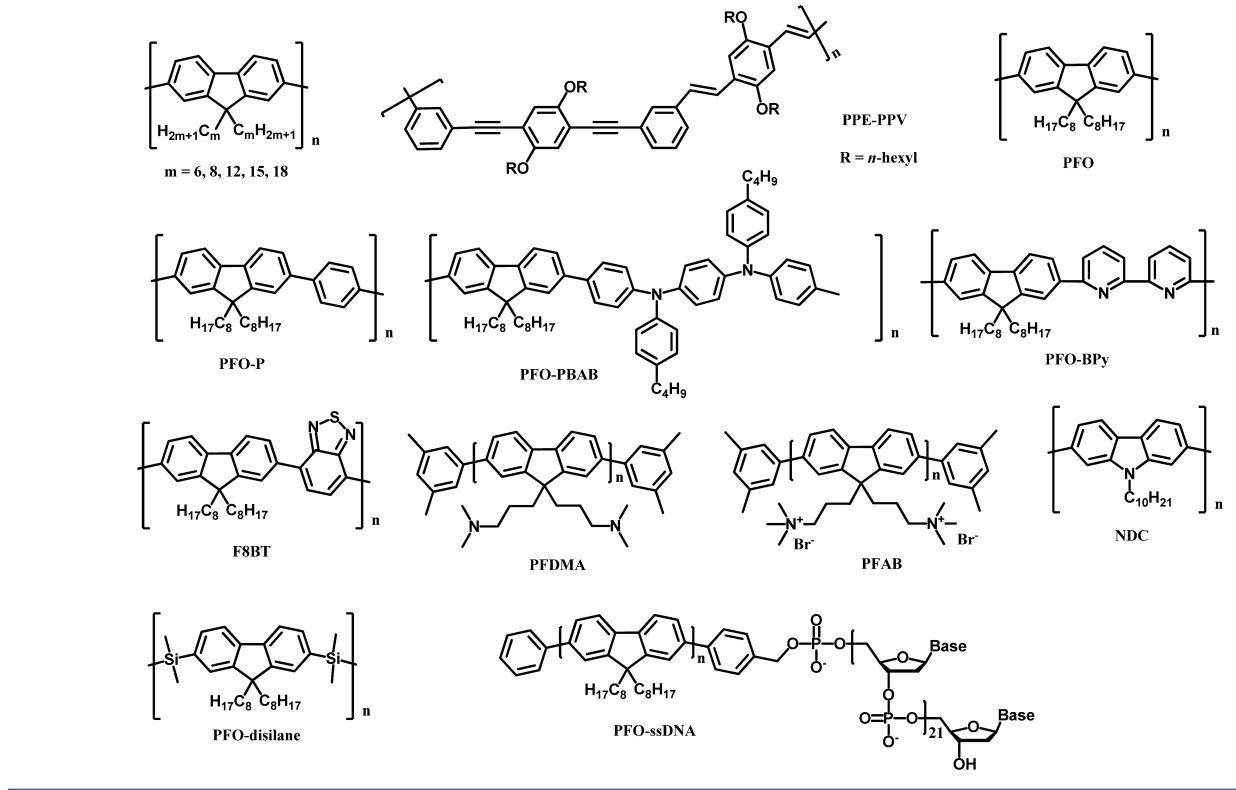
## ■ STATE-OF-THE ART OF SWNT DISCRIMINATION AND SEPARATION

Many methods to disperse and discriminate SWNTs are based on functionalization of their walls, which can be broadly classified into two categories: covalent and noncovalent functionalizations.<sup>19</sup>

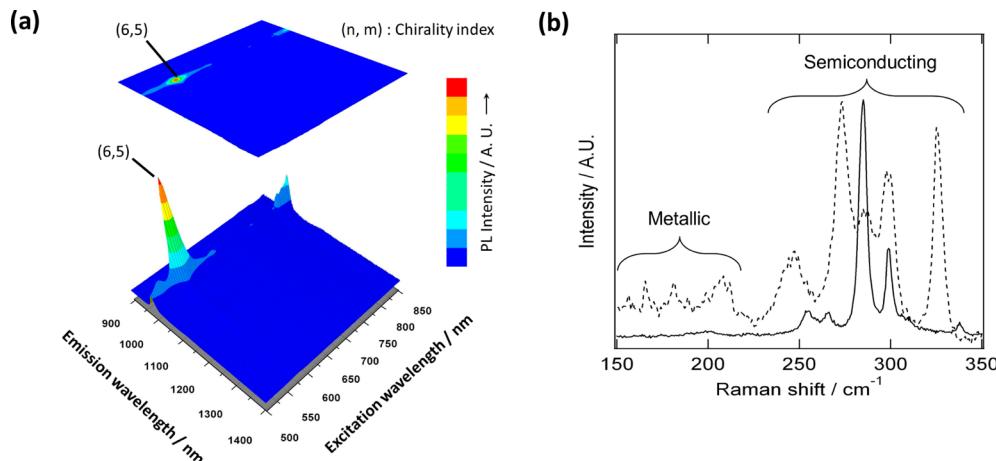
Noncovalent strategies are considered superior because covalent bond formation on the nanotube wall causes modification of their electronic properties.<sup>20</sup> Several noncovalent techniques are reported that use surfactants (such as sodium dodecyl sulfate, SDS)<sup>21</sup> or single-stranded DNA (ssDNA)<sup>22</sup> to obtain high concentration SWNT dispersions ( $>1 \text{ mg/mL}$ ) in water. In the case of surfactants, the hydrophobic tails organize along the walls of CNTs, while the polar head groups form a hydrophilic shell thus making the nanotubes dispersible in water.<sup>21</sup> This technique works well for the individualization of SWNTs and represented a great step forward in the investigation and understanding of their properties; however the method does not allow discrimination of different types of SWNTs.

Density-gradient ultracentrifugation using bile acid salt (e.g., sodium cholate) wrapped SWNTs represents an improved method as it allows sorting of metallic and semiconducting tubes as well as sorting by diameter.<sup>23</sup> SWNTs are encapsulated by bile acid salt molecules via interaction of their hydrophobic part with the SWNT surface leading to a homogeneous dispersion. After ultracentrifugation in a density gradient medium, layers containing specific nanotubes of different diameters and chirality can be isolated. Repeated centrifugations produce fractions with a narrow distribution of nanotube diameters. Ultracentrifugation with sodium cholate gives access to semiconducting SWNT mixtures where >97% of the s-SWNTs possess diameters in a narrow range of  $\pm 0.1 \text{ \AA}$ .

DNA interacts with SWNTs through  $\pi-\pi$  stacking between nucleobases and the  $\pi$ -surface of the nanotubes, resulting in helical wrapping of the nanotube surface.<sup>22</sup> The hydrophilic, charged functional groups of DNA are exposed toward the medium (water) and support dispersion. DNA wrapping can be highly selective; Zheng et al. described preferential interaction of ssDNA with SWNTs of specific chirality.<sup>24</sup> Due to the presence of negative charges, the hybrids become negatively charged. Therefore, when the aqueous dispersion is injected into an anion exchange column, the DNA–SWNT hybrids are bound to the positively charged stationary phase. Then, due to differences in binding ability of metallic or different semiconducting SWNTs, their separation by anion exchange chromatography is possible. Zheng et al. described the separation of 12 different semiconducting SWNT species from a synthetic mixture with the help of several highly specific DNA sequences in such a chromatographic purification method.<sup>25</sup> In a recent report, separation of m- and s-SWNTs was accomplished by pH-controlled interaction with ssDNA.<sup>26</sup> As a further advantage of this protocol, a complete removal of DNA after separation of s-SWNTs was possible since the

**Scheme 1.** Synthetic Conjugated Polymers Used for Dispersion and Selective Sorting of Semiconducting SWNTs

**Figure 3.** (a) Chirality map of polyfluorene-wrapped SWNTs. Selected SWNTs are highlighted in yellow; the color of the dots inside the hexagons represent the polyfluorene derivatives that are able to select the nanotubes (with the color code used for the chemical structures). (b) Chemical structures of the polyfluorene derivatives tested: PF6, PF8 (commonly known as PFO), PF12, PF15, and PF18; the numbers indicate the alkyl chain length. (c) Structure of SWNT–polymer hybrids as obtained by molecular dynamics simulation; the image depicts three PF12 chains wrapped around a (12,10) nanotube. Reproduced with permission from ref 33. Copyright 2013 Wiley-VCH.



**Figure 4.** (a) PL/PLE maps of CoMoCAT SWNTs dispersed with PFO–BPy in *p*-xylene. (b) Raman spectra in the region of the radial breathing modes (RBM) of PFO–BPy-dispersed SWNTs (solid line) and pristine SWNTs (dotted line). Excitation: 633 nm. Reproduced with permission from ref 37. Copyright 2011 The Chemical Society of Japan.

nanotubes precipitate upon alteration of the pH value due to a transition of ssDNA into a higher order secondary structure.

Krupke et al. reported discrimination of metallic and semiconducting SWNTs from a raw mixture using dielectrophoresis.<sup>27</sup> When a SDS–SWNT dispersion was brought into an electric field gradient generated by a microelectrode array, the metallic tubes migrated toward the electrodes due to their larger dipole moment, while the s-SWNTs remained in a stationary position. In addition, also size exclusion chromatography<sup>28</sup> and aqueous two-phase extractions have been used for separating and sorting of s-SWNT.<sup>29,30</sup>

## ■ SWNT WRAPPING BY CONJUGATED POLYMERS

For efficient dispersion and discrimination of SWNTs in organic solvents, several conjugated polymers as well as block copolymers were used. The general principle of this method is a wrapping of the conjugated backbone around the nanotube wall through van der Waals interactions. The side chains of the polymer support isolation and dispersion of the hybrids in common organic solvents. Hereby, the efficacy of the process is a complex interplay of conjugated polymer main chain structure (enabling  $\pi$ – $\pi$  interactions), molecular weight (defining chain length), and substitution pattern (density and structure of side groups). However, reliable design rules were not available until now. The first article reported in 2007 by Nish et al. described the use of poly(9,9-diethylfluorene) (PFO) and poly[(9,9-diethylfluorene)-*alt*-(1,4-benzo-2,10,3-thiadiazole)], F8BT (Scheme 1) for selective dispersion of semiconducting SWNTs.<sup>31</sup> For the resulting s-SWNT dispersions, the authors found a much higher selectivity of discrimination between semiconducting tubes in comparison to procedures using bile acid salts. Absorption and Raman spectroscopy were used to prove the absence of m-SWNTs. The most prominent feature of this selection method is a distinctly increased photoluminescence quantum yield (PLQY) of the s-SWNTs reaching 1.5%, that is, 10-times higher than the PLQY obtained with surfactants (0.1%).

The influence of polymer backbone structure and solvent on the selectivity of SWNT sorting was investigated by Hwang et al.<sup>32</sup> They suggested that a medium to poor solvent for the conjugated polymer, such as toluene or xylene, is favored for enhancing the discrimination power for specific SWNTs. In fact, when a good solvent is used to disperse SWNTs, such as

chloroform or tetrahydrofuran (THF), the SWNT sorting selectivity diminishes. Other polyfluorene-based copolymers such as poly[9,9-dihexylfluorene] (PFH), poly[(9,9-diethylfluorene)-*alt*-(1,4-phenylene)] (PFO-P), and poly[(9,9-diethylfluorene)-*alt*-(*N,N'*-diphenyl)-*N,N'*-di(*p*-butyloxy-phenyl)-1,4-diaminobenzene] (PFO–PBAB) were also shown to be able to discriminate s-SWNTs though less efficiently than PFO.

PFO itself showed effective interactions only with smaller diameter SWNTs (0.8–1.2 nm). Recently, we demonstrated that poly(9,9-dialkylfluorene)s with increasing lengths of alkyl chains can interact with nanotubes of larger diameter up to 1.5 nm (Figure 3).<sup>33</sup> Therefore, the wrapping and selection mechanism of nanotubes is not only dictated by the nature of the polymer backbone but also by the length of the alkyl side chains. The chirality map depicted in Figure 3 illustrates that polyfluorenes with two *n*-hexyl side chains are mostly ineffective for SWNT dispersion, while PFO wraps only a few varieties of low diameter, chiral SWNTs. However, polyfluorenes with longer alkyl chains (*n*-dodecyl, *n*-pentadecyl, and *n*-octadecyl) are able to discriminate chiral SWNTs with larger diameter (>1.2 nm) at a high SWNT concentration.<sup>33</sup> Theoretical studies further suggested that polyfluorenes with longer aliphatic side chains wrap SWNTs more effectively and also restrict rebundling. However, for longer aliphatic side chains, the selectivity toward chiral sorting decreases.

Jakubka et al. showed that selective dispersion of SWNT species by PFO and poly(9,9-diethylfluorene-*alt*-benzothiadiazole) (F8BT) (Scheme 1) depends strongly on the choice of the organic solvent, as well as concentration and molecular weight of the polymer.<sup>34</sup> Low-to-medium molecular weight polymers show better selectivity for specific SWNTs at low concentrations of the dispersion. However, with higher molecular weight polymers, the concentration of the SWNT dispersion increases at the expense of selectivity. This result is explained with an increasing viscosity of the dispersion, thus causing reduced diffusivity of SWNTs.

F8BT has also been employed by Tange et al. for its selective extraction of large diameter (>1.3 nm) SWNTs with a specific chirality index (15,4).<sup>35</sup> In the author's opinion, the chirality selection occurs as a consequence of strong interaction between polymer and specific SWNTs due to an exact matching of energy levels between polymer and third order van Hove transitions of the (15,4) SWNT in addition to the structural

match between polymer backbone and SWNT surface. The diameter of the (15,4)-SWNTs is 1.38 nm, further demonstrating that selective polymer wrapping works also for larger diameter SWNTs.

A 9,9-bis(aminopropyl)-functionalized polyfluorene, poly[9,9-di(*N,N*-dimethylaminopropyl)fluorene] (PFDMA), as well as the corresponding ammonium salt, poly[9,9-di(*N,N*-trimethylammoniumpropyl)fluorene dibromide] (PFAB) (Scheme 1), were also studied for SWNT dispersing ability in different media such as toluene and D<sub>2</sub>O. The results were discussed in comparison to the well-described standard PFO.<sup>36</sup> Although PFAB and PFDMA could disperse higher concentrations of nanotubes in comparison to PFO, the selectivity toward specific s-SWNTs is reduced, probably due to the presence of metallic tubes and SWNT bundles. This is reflected in a shorter exciton lifetime of (6,5) and (7,5) tubes wrapped by PFDMA and PFAB compared with the values for PFO-selected tubes. The shorter lifetimes are attributed to exciton energy transfer from s-SWNTs [(6,5) or (7,5)] to metallic tubes present in the mixture.<sup>36</sup>

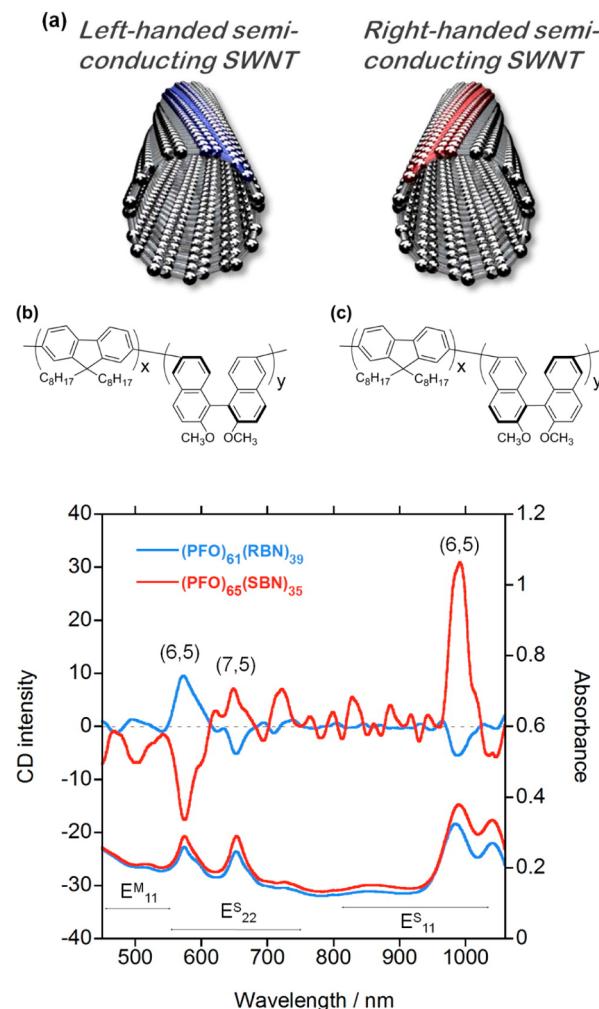
Ozawa et al. reported a selective, “one-pot” extraction of (6,5)-CoMoCat SWNTs with an enrichment up to 96–97% in using an alternating copolymer of 9,9-dioctylfluorene and bipyridine units (PFO-BPy, Scheme 1) in *m*- or *p*-xylene.<sup>37</sup> The purity of the (6,5)-SWNT dispersion in *p*-xylene was confirmed by PLE spectroscopy (Figure 4). Raman spectroscopy showed the absence of any metallic nanotubes. Also in this case, the authors discuss that the choice of solvent has a strong influence on the sorting selectivity. For example, when *o*-xylene or toluene are used, PFO-BPy interacts with both (6,5) and (7,5) nanotubes, while, in THF, several types of chiral tubes such as (6,5)-, (7,5)-, (8,3)-, and (8,4)-SWNTs could interact with the polymer. For polyfluorenes it was already reported that dispersion in THF distinctly reduces the sorting selectivity for s-SWNTs.<sup>32</sup> Both PFO and PFO-BPy cause a “selective extraction” of (7,5) tubes from CoMoCat SWNTs, since as-grown CoMoCat SWNTs are rich in (6,5) and (7,5) tubes. However, the selectivity of PFO-BPy (~97%) was much better than that of PFO (~90%), thus indicating a subtle influence of the polar BPy moiety.

Polyfluorene is a wide band gap polymer, thus the presence of the polymer chains around the SWNT can be a drawback in device application because it can hinder charge transport between neighboring SWNTs. Wang et al. introduced a degradable PFO copolymer, poly[(9,9-dioctylfluorene)-*alt*-1,1,2,2-tetramethyldisilane] (Scheme 1) showing a selectivity for SWNT sorting similar to PFO.<sup>38</sup> The copolymer contains disilane groups, thus making it degradable when treated with hydrofluoric acid (HF). Therefore, selective SWNT dispersion in toluene followed by enrichment of s-SWNTs via filtering (to remove the excess polymer) and redispersion in a DMF–HF mixture removes the wrapped polymer. However, the s-SWNT discrimination power is decreased in comparison to that obtained for PFO.

As already mentioned, ssDNA wrapping has been also explored for discrimination of s-SWNTs.<sup>22,24</sup> Recently, the use of a block copolymer combining conjugated polymer and ssDNA blocks (PFO-*b*-ssDNA, Scheme 1) was reported as new strategy for s-SWNT selection, manipulation, and positioning into an electronic device.<sup>39</sup> In this system, the conjugated polymer block is used to interact with s-SWNT (showing a selectivity similar to PFO), while the interaction of the ssDNA blocks was used for controlled self-assembly. Molecular

dynamics (MD) simulations showed that the polymer–SWNT hybrids are very stable if the PFO block interacts with the SWNT wall. When the DNA block is interacting with the walls, the polymer detaches within 1 ns.

Akazaki et al. demonstrated judicious separation of left- and right-handed semiconducting SWNTs by copolymers composed of fluorene and chiral binaphthol units (PFO)<sub>x</sub>(RBN)<sub>y</sub> and (PFO)<sub>x</sub>(SBN)<sub>y</sub> (Figure 5).<sup>40</sup> The dioctyl-functionalized



**Figure 5.** Graphical representation of (a) semiconducting SWNT enantiomers and chemical structures of (b) (PFO)<sub>x</sub>(RBN)<sub>y</sub> and (c) (PFO)<sub>x</sub>(SBN)<sub>y</sub>. (d) Vis–NIR absorption and CD spectra of SWNTs extracted with (PFO)<sub>61</sub>(RBN)<sub>39</sub> and (PFO)<sub>65</sub>(SBN)<sub>35</sub>. Reproduced with permission from ref 40. Copyright 2012 American Chemical Society.

fluorene units support preferential dispersion of semiconducting SWNTs while the chiral binaphthol units bring in the capability for the discrimination of SWNT enantiomers. A simple sonication method enabled the isolation of left- and right-handed semiconducting SWNT enantiomers as confirmed by circular dichroism (CD) spectroscopy. Vis–NIR absorption and CD spectra of the nanotube dispersions displayed characteristic E<sub>11</sub> and E<sub>22</sub> bands of semiconducting SWNT enantiomers.

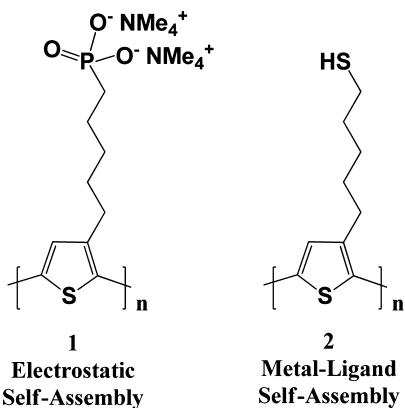
## ■ DEVICE APPLICATIONS

The importance of obtaining highly pure semiconducting nanotubes is strongly related to their possible application in electronic and optoelectronic devices. The existence of a bandgap in s-SWNTs makes them very attractive in comparison to competing carbon materials (e.g., graphene, which is a semimetal) for transistor and solar cell applications.

Directed self-assembly of semiconducting SWNTs is a promising approach toward carbon nanotube transistors, based on single nanotubes or nanotube networks of controlled density. Kwak et al., as previously mentioned, were able to select semiconducting SWNTs by PFO-*b*-ssDNA block copolymer wrapping. Afterward, they successfully self-assembled them into a channel between patterned electrodes previously modified by complementary ssDNA strands. The self-assembled field effect transistors demonstrated ambipolar operation with a high reliability of the self-assembly process.<sup>39</sup>

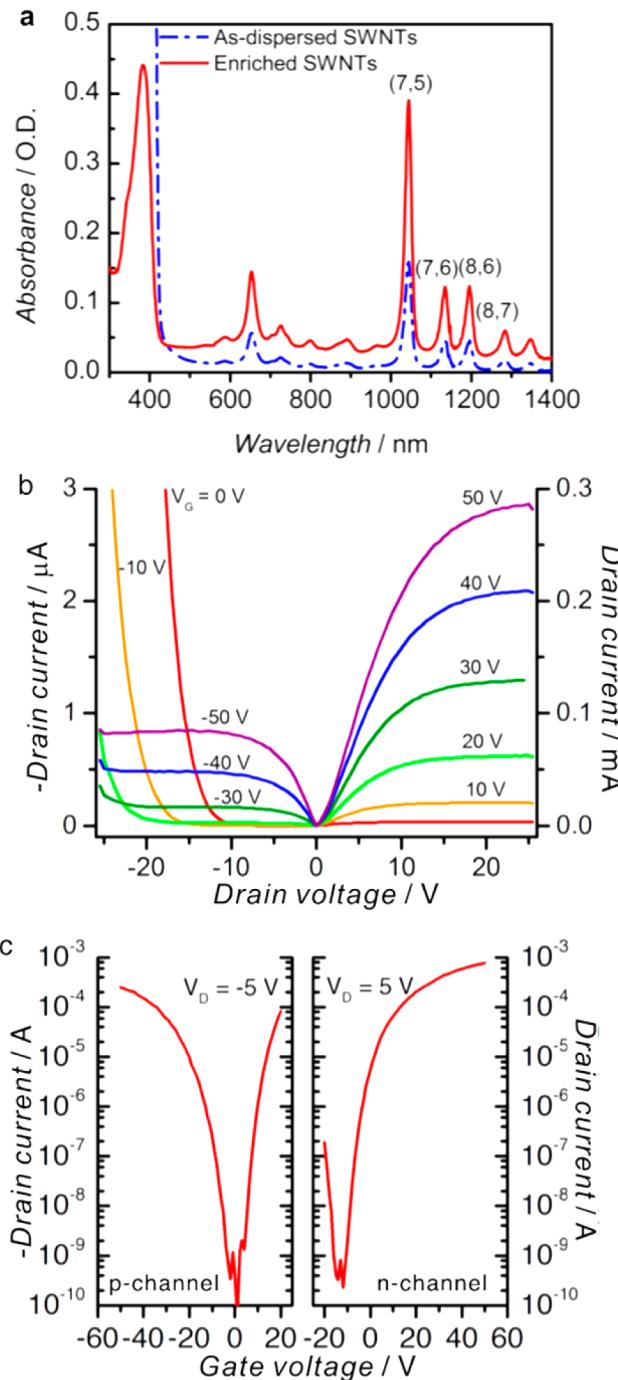
Lobez and Afzali recently described a novel strategy for the directed self-assembly of SWNTs. Regioregular polythiophenes (Scheme 2) with reactive side chains have been used for

**Scheme 2. Side Chain Functionalized Polythiophenes Used for Directed Self-Assembly of SWNTs on Specific Patterned Surfaces**



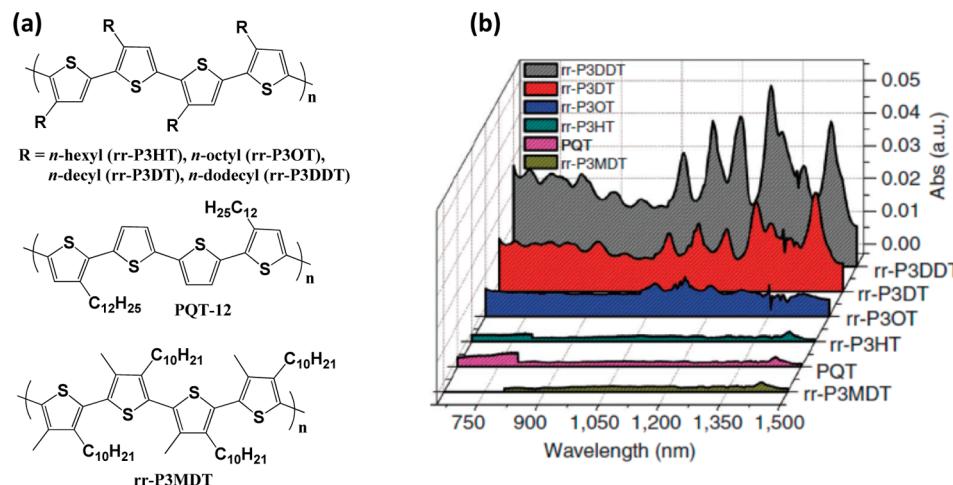
selecting s-SWNTs followed by self-assembly onto suited surfaces.<sup>41</sup> Side chain functionalization with phosphonate groups (**1**) enables directed self-assembly of the hybrids by electrostatic forces, while thiol functions (**2**) support interactions with gold (or silver) surfaces. This process seems very promising for the selective deposition of SWNT/polymer hybrids onto patterned surfaces. Nevertheless, the application of this selective deposition procedure toward high performance transistor devices is yet to be realized.

Till now, the most successful utilization of polymer wrapped SWNTs was shown for network field effect transistors. However, to achieve high performance transistor devices is still a challenge. The excess of polymer, which does not wrap nanotubes but deposits together with SWNTs into the transistor channel, hampers the electrical transport resulting in low charge carrier mobility. Izard et al. used multiple filtration and iterated rinsing to remove the residual polymer.<sup>42</sup> Bisri et al. developed a double-step ultracentrifugation procedure to enrich semiconducting CoMoCAT nanotubes and to remove residual polymer.<sup>43</sup> In this way, they obtained polymer–nanotube dispersions containing less than 7 µg/mL of polymer, which is most probably only the one attached to the SWNT walls (Figure 6a).



**Figure 6.** (a) Optical absorption spectra of as-dispersed s-SWNTs (dashed line) and the enriched s-SWNTs (solid line) in toluene solution (dispersing polymer, PFO). Output (b) and transfer (c) curves for s-SWNT-FETs fabricated from the enriched polymer/s-SWNT dispersion. Reproduced with permission from ref 43. Copyright 2012 Wiley-VCH.

Field-effect transistors based on random s-SWNT networks in a bottom contact configuration with a channel length of 20 µm demonstrated ambipolar transport characteristics (Figure 6b), in which both holes and electrons displayed a mobility of about 3 cm<sup>2</sup>/(V s) and on/off ratio of >10<sup>6</sup> (Figure 6c). To the best of our knowledge, this is the highest on/off ratio ever achieved for solution-processed SWNT transistors, demonstrating the high purity of the s-SWNTs achieved by polymer wrapping.



**Figure 7.** (a) Chemical structures of regioregular poly(3-alkylthiophene)s used for s-SWNT sorting and (b) absorption spectra of the resulting polythiophene/SWNT dispersions. Reproduced with permission from ref 44. Copyright 2011 Nature Publishing Group.

Recently, regioregular poly(3-alkylthiophene)s (rr-P3ATs) were extensively employed for nanotube dispersion. Here, especially rr-P3DT (alkyl = *n*-decyl) and rr-P3DDT (alkyl = *n*-dodecyl) showed reasonable dispersion capability for both HiPCO<sup>44</sup> and CoMoCAT nanotubes<sup>45</sup> as proven by optical spectroscopy (Figure 7). The dispersions containing selectively sorted s-SWNTs were deposited onto Si/SiO<sub>2</sub> substrates to fabricate field effect transistors. The devices displayed unipolar charge carrier transport with hole mobility up to 12 cm<sup>2</sup>/(V s) and on/off current ratio of  $\sim 10^6$  for HiPCO nanotubes,<sup>44</sup> while only modest results were achieved for CoMoCAT nanotubes (hole mobility 1.18 cm<sup>2</sup>/(V s); on/off ratio  $2.4 \times 10^4$ ).<sup>45</sup>

All of the above-mentioned results have been obtained with small diameter (HiPCO and CoMoCAT) s-SWNTs. However, larger diameter tubes (1.5 nm) may possess advantages over smaller diameter SWNTs, such as less charge carrier scattering and a reduced number of defects on the SWNT walls, possibly resulting in improved electrical transport. First efforts in this direction have been made by using dithiafulvalene–thiophene copolymers, as well as poly(9,9-diethylfluorene-*alt*-benzothiadiazole) (F8BT) to separate arc-discharge grown SWNTs.<sup>46,35</sup> As mentioned in the previous section, Gomulya et al. separated semiconducting carbon nanotubes up to 1.5 nm in diameter by utilizing polyfluorene derivatives with long alkyl side chains.<sup>33</sup> By application of ionic liquid gating, enabling very high charge accumulation, transistors fabricated from larger diameter arc-discharge nanotubes demonstrated charge carrier mobility values reaching 16.4 cm<sup>2</sup>/(V s) for both holes and electrons with a very steep subthreshold swing. These results could confirm the longstanding hypothesis that larger diameter nanotubes allow improved charge carrier transport due to reduced charge carrier scattering with phonon modes.<sup>47,48</sup> Noteworthy, the solution processability of polymer-wrapped carbon nanotubes enabled the development of flexible and highly stretchable carbon nanotube transistors,<sup>49</sup> as well as printable electronic circuits.

Another recently demonstrated application for polymer wrapped carbon nanotube hybrids is the one in photovoltaic devices. Polymer wrapped SWNTs can be considered as a nanoheterojunction consisting of the wrapping polymer and the nanotube.<sup>50</sup> However, an efficient use of such nanoheterojunctions in real devices is very challenging. Polymer-wrapped nanotubes have been used as electron donors to form a type-II

heterojunction in blends with fullerenes. These devices demonstrated peak external quantum efficiency up to 18% in the infrared region and NIR power conversion efficiencies (PCE) of 1.3%.<sup>51</sup> “All-carbon” solar cells have been fabricated by utilizing P3DDT-wrapped HiPCO SWNTs with metallic nanotube and graphene as electrodes and C<sub>60</sub> as electron acceptor material.<sup>52</sup> However, these kinds of solar cells only demonstrated a PCE of <0.4%. Obviously, there are some vital aspects that require attention when applying s-SWNTs in solar cells. One of them is their diameter-dependent bandgap. Wang et al. described the use of two different types of s-SWNTs, where the smaller bandgap SWNTs (CoMoCat) showed 4-times higher external quantum efficiency (EQE) compared with HiPCO SWNTs.<sup>45</sup> In their system, the authors postulate a charge transfer from the polymer-wrapped SWNTs to C<sub>60</sub>. Dabera et al. used P3HT-wrapped nanotubes as hole extraction layers of solar cells containing [poly[4,8-bis[(2-ethylhexyl)-oxy]benzo[1,2-*b*:4,5-*b*]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-*b*]thiophenediyl]] (PTB7)/PC<sub>70</sub>BM as active blend with a PCE of 7.6%.<sup>53</sup> More work will be necessary to improve solar cells based on polymer-wrapped SWNTs. Hereto, the precise understanding of the interaction mechanism between wrapping polymer and nanotube will be crucial.

## CONCLUSIONS

In summary, polymer-wrapped SWNTs pave new ways toward sophisticated fields of SWNT application. Specific noncovalent interactions between conjugated polymers and SWNTs first allow the isolation of s-SWNTs as required for applications in field effect transistors and solar cells. Although many techniques such as density gradient ultracentrifugation, dielectrophoresis, size exclusion chromatography, aqueous two-phase extraction, and dispersion with surfactants (SDS) or biopolymers (DNA) for noncovalent surface functionalization as well as covalent modification by chemical reactions have been developed, conjugated polymer-wrapping of SWNTs provides a convenient, selective, and scalable alternative. Conjugated polymers in this aspect offer several benefits such as (a) selective separation of s-SWNTs from metallic ones, (b) sorting of nanotubes with specific (*n,m*) indices and diameters, and (c) even the separation of SWNT enantiomers. Complete removal of metallic nanotubes and isolation of s-SWNTs with specific

(*n,m*) indices will also enable a more detailed understanding of structure–function relationships, especially for device applications. Establishing clear relations between chemical structure of conjugated polymers and their ability for effective and selective SWNT sorting is, therefore, a challenge of primary importance that needs further investigations. An additional next step will be the controlled deposition of polymer-wrapped s-SWNTs onto suited substrates for application in nanoelectronic devices, guided by interaction between substituents and functions of conjugated polymers and substrates (e.g., thiol functions with gold or silver electrodes or reacting trialkoxysilyl esters with surface hydroxy functions).

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### Notes

The authors declare no competing financial interest.

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