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Influence of Polymer Electronics on Selective Dispersion of Single-Walled Carbon Nanotubes

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Abstract: The separation and isolation of semiconducting and metallic single-walled carbon nanotubes (SWNTs) on a large scale remains a barrier to many commercial applications. Selective extraction of semiconducting SWNTs by wrapping and dispersion with conjugated polymers has been demonstrated to be effective, but the structural parameters of conjugated polymers that dictate selectivity are poorly understood. Here, we report nanotube dispersions with a poly(fluorene-*co*-pyridine) copolymer and its cationic

Introduction

Single-walled carbon nanotubes (SWNTs) have attracted tremendous attention from the scientific community since their discovery.^[1-3] Their unique properties, which include high tensile strength,^[4] a high aspect ratio,^[5] thermal and electrical conductivity,^[6-8] and extraordinary optical characteristics,^[9-11] make nanotubes potentially valuable as advanced materials in a variety of applications. Indeed, SWNTs have been incorporated into field-effect transistors,^[12] photovoltaics,^[13] flexible electronics,^[14] sensors,^[15] touch screens,^[16] high-strength fibers,^[17-19] biotechnological constructs,^[20] and various other devices.^[21] Despite recent progress toward commercialization, applications involving the electrical and optical properties of nanotubes have not kept pace with expectations. This is in part due to the nontrivial isolation of electronically pure nanotubes on an industrial scale.^[22] All known SWNT synthesis methods, including highpressure carbon monoxide disproportionation (HiPCO),^[23] carbon vapor deposition (CVD),^[24] arc discharge,^[25] laser ablation,^[26] and plasma torch growth,^[27] produce mixtures of metallic SWNTs (m-SWNTs) and semiconducting SWNTs (sc-SWNTS). Since components of electronic devices require either pure m-SWNTs (electrodes, interconnects, etc.) or pure sc-SWNTs (transistors, sensors, etc.), purification of as-produced SWNTs is imperative. Several methods for separating and purifying SWNTs

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methylated derivative, and show that electron-deficient conjugated π -systems bias the dispersion selectivity toward metallic SWNTs. Differentiation of semiconducting and metallic SWNT populations was carried out by a combination of UV/Vis-NIR absorption spectroscopy, Raman spectroscopy, fluorescence spectroscopy, and electrical conductivity measurements. These results provide new insight into the rational design of conjugated polymers for the selective dispersion of metallic SWNTs.

have recently been reported, including density-gradient ultracentrifugation (DGU),^[28] agarose gel filtration,^[29] electrophoresis,^[30] and selective dispersion using conjugated polymers.^[31] Of these, the latter is promising as it is a low-cost and scalable process. Indeed, it has been demonstrated that sc-SWNTs can be selectively dispersed using a variety of conjugated polymers.^[31–35] However, despite this progress, the selective dispersion of *m*-SWNTs remains elusive.

Dispersion selectivity is influenced by a combination of polymer attributes, including the backbone structure and conformation, the degree of polymerization, and the nature of the side chains.^[36-38] It has been suggested that selectivity arises from a difference in polarity between sc- and *m*-SWNTs, with both p-type and n-type conjugated polymers appearing to be selective for sc-SWNTs.^[39] This was based on calculations of polarizability, which show that *m*-SWNTs are more than three orders of magnitude more polarizable than sc-SWNTs.^[40] This polarizability difference between *m*- and sc-SWNTs has been further supported by a recent study that found *m*-SWNTs to be more readily oxidized than sc-SWNTs,[41] indicating that the metallic tubes can donate electrons more easily, and are more "electron rich", than their semiconducting counterparts. In light of these results, we set out to show that the electronic nature of the conjugated polymer backbone actually does have a significant effect on dispersion selectivity through inductive effects.^[38] We expect that relatively electron-poor conjugated polymers should disperse *m*-SWNTs to a greater extent when compared to structurally similar electron-rich conjugated polymers. Here, we demonstrate this concept through the comparison of a poly(fluorene-co-pyridine) conjugated polymer before and after post-polymerization functionalization. By partially methylating the pyridine units, cationic charges are introduced onto the conjugated backbone, which convert the poly-

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mer from being electron-rich to electron-poor. This enables the comparison of two polymers that are identical in length and polydispersity, and differ primarily in their electronic characteristics. We show that the electron-poor conjugated polymer results in dispersions that are enriched in *m*-SWNTs, while the electron-rich counterpart solely selects for sc-SWNTs, thus providing evidence that the electronic structure of a conjugated polymer plays an important role in determining its selectivity for different SWNT types.

Results and Discussion

Considering that the degree of polymerization (DP) of a conjugated polymer can significantly influence its SWNT dispersion selectivity,^[42] it is imperative to minimize length variability when comparing different polymers. For this reason, post-polymerization functionalization is an ideal strategy for the comparison of polymers with different structural and electronic properties. We, therefore, chose to prepare a poly(9,9'-didodecylfluorene-co-pyridine) (P1) copolymer, as the pyridine units within this structure can undergo post-polymerization chemistry. Pyridine-containing polymers have been previously used to disperse SWNTs,^[43,44] with some efficiency demonstrated for dispersing sc-SWNTs, but to the best of our knowledge, the effect of post-polymerization chemistry on SWNT selectivity has not been investigated. Methylation of the pyridine units within this polymer using methyl iodide is a facile process that introduces multiple cationic charges without significantly perturbing the steric bulk of repeat units or the DP. Thus, a drastic effect on polymer electronics can be achieved, and the interaction selectivity of the polymer before and after methylation can be directly compared.

Polymer **P1** was synthesized by the Suzuki polycondensation of 2,2'-(9,9-didodecylfluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1), prepared according to literature procedures (see the Supporting Information),^[45] with commercially available 2,5-dibromopyridine (Scheme 1). GPC analysis showed that **P1** had a number-average molecular weight (M_n) of 13.5 kDa, corresponding to a DP of ~23 and a polydispersity index (PDI) of 1.84. To prepare the methylated polymer **P2**, **P1** was dissolved in CHCl₃ and heated to reflux with an excess of methyl iodide (Scheme 1). The methylation was monitored by ¹H NMR, which indicated the appearance of new sets of peaks centered at 4.72 and 4.84 ppm, corresponding to the pyridine-CH₃ (Py-CH₃) group (Supporting Information, Figure S1). The



Scheme 1. Synthesis of fluorene-pyridine copolymers P1 and P2.

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appearance of two new sets of peaks suggests incomplete methylation, as the electronic environment of these protons will differ depending on whether or not adjacent repeat units are methylated, and also the relative orientation of the methyl groups. Broadening of the peaks in the aromatic region was also observed, corroborating the incomplete methylation of P1. We determined the degree of methylation by comparing the relative integration of the Py-CH₃ group to the aromatic region in the ¹H NMR spectrum, and observed a maximum methylation of ~50% of the pyridine units after 12 h (Supporting Information, Figure S2). Heating at reflux for a total of 36 h did not result in any further methylation (Supporting Information, Figure S2). We hypothesize that pyridine methylation is limited by the decreased nucleophilicity of the nitrogen atom after adjacent pyridines are methylated, resulting in the observed maximum. Despite the nonquantitative methylation, it was still possible to carry out SWNT dispersion studies using the nonmethylated P1 and its partially methylated analogue, P2.

Prior to nanotube complexation, we investigated the influence of methylation on the electronic properties of **P2** through DFT calculations using the 6-31G(d) basis set.^[46] Calculations were performed on trimers with methyl groups substituted for the dodecyl chains in order to decrease the calculation complexity and time. Electron density maps, color-coded to illustrate electron-rich and electron-poor segments (red and blue, respectively), are shown in Figure 1. Our calculations suggest that methylation drastically alters the electronic landscape of the polymer backbone. Figure 1A shows that the conjugated system for the trimer of **P1** is relatively electron-rich, whereas Figure 1B shows that the conjugated system for the trimer of **P2** is electron-poor. Additionally, we performed DFT calcula-



Figure 1. Electron-density maps of trimers for A) **P1** and B) fully methylated **P2**. Red denotes electron-rich regions, green denotes less electron-rich regions, and blue denotes electron-poor regions.

tions on the trimers of **P2** with varying degrees and positions of methylation to more accurately model incomplete functionalization (Figure S3, Supporting Information). These calculations show that wherever methylation occurs, the adjacent conjugated backbone units become electron-poor. Thus, **P1** and **P2** should be significantly different in terms of their electronics, despite being extremely similar in structure.

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Supramolecular polymer-SWNT complexes of P1 and P2 were prepared with raw HiPCO SWNTs by following previously reported procedures.[47] A few different polymer/SWNT weight ratios were investigated and it was found that a ratio of 1.5:1 polymer/SWNT produced the best dispersions for both P1 and P2 (see the Supporting Information, Figure S4). Additionally, THF, toluene, and a 1:1 mixture of these solvents were chosen for dispersion selectivity studies. The optimized dispersion protocol involved dissolving 15 mg of polymer in 20 mL of solvent before adding 10 mg of SWNTs. The mixture was sonicated for 2 h in a bath sonicator chilled with ice before being centrifuged at 8,346 g for 30 min. The supernatant was carefully removed, filtered through a Teflon filtration membrane with 0.2 µm diameter pores, and the resulting polymer-SWNT residue ("bucky paper") was washed with CHCl₃ until the filtrate did not exhibit any observable fluorescence when excited at 365 nm with a hand-held UV lamp. The bucky paper was redispersed in 5 mL of solvent, sonicated for 1 h in a bath sonicator chilled with ice, and centrifuged again. The resulting polymer-SWNT dispersions were stable on the bench top for at least several months, with no observable flocculation.

To investigate the polymer-SWNT dispersions, we initially performed UV/Vis-NIR absorption spectroscopy shown in Figure 2. Nanotube absorption features depend on their re-



Figure 2. UV/Vis-NIR absorption spectra for P1-SWNT (red) and P2-SWNT (blue) in THF.

spective diameters and chiralities, and arise from the interband transitions of the van Hove singularities, resulting in specific nanotube chiralities with specific transition energies. The absorbance features in the observed range can be grouped into three categories: two semi-conducting regions, S_{11} (830–1600 nm) and S_{22} (600–800 nm), and a metallic region, M_{11} (440–645 nm).^[48] The absorption spectrum for **P1**-SWNT in THF shows sharp peaks in the S_{11} and S_{22} regions, suggesting that the electron-rich **P1** efficiently exfoliates sc-SWNTs in THF. This is corroborated by the intense green color of the **P1**-SWNT solution in THF (Supporting Information, Figure S5). The absence of a broad, featureless absorption background in the spectrum indicates effective nanotube exfoliation and the removal of *m*-SWNTs, consistent with previous reports.^[43] The absorption

spectrum for P2-SWNT in THF also shows sharp peaks in the S_{11} and S_{22} regions, which suggests that the electron-poor P2 likewise exfoliates sc-SWNTs in THF. However, the presence of a broad, featureless, and relatively intense absorption background in this spectrum indicates the presence of *m*-SWNTs, which is confirmed by the presence of peaks in the M₁₁ region (and is consistent with the dark-brown/black color of the P2-SWNT solution in THF, Figure S4, Supporting Information). The overlap of polymer absorption with the M₁₁ region precludes a detailed analysis of the specific *m*-SWNT chiralities present in the sample. In toluene and the 1:1 THF/toluene co-solvent mixture, the P2-SWNT dispersions have no discernible absorbance features outside of the polymer absorbance, which suggests that P2 does not form a stable colloidal dispersion with SWNTs in either of these solvents. As a consequence, these solvent options were not pursued in subsequent studies. A control sodium dodecylbenzenesulfonate (SDBS) dispersion was prepared in D₂O and showed no SWNT selectivity (see the Supporting Information, Figure S9).

To further investigate the differences in nanotube populations dispersed by **P1** and **P2**, resonance Raman spectroscopy was performed. This technique allows for the examination of both *m*- and sc-SWNT species within a given sample,^[49] and utilizes laser excitation wavelengths that overlap with the van Hove singularities present in the 1D density of states for a particular SWNT.^[50] As the electronic transitions depend on nanotube chirality and diameter, only a subset of the total nanotube population will be observed for each individual excitation wavelength.^[51]

Thin film samples were prepared from the polymer-SWNT complexes by drop-casting the dispersions onto silicon wafers. A reference SWNT sample was also prepared by sonicating a small amount of the SWNT starting material in CHCl₃ and making a solid film with the same drop-casting method. Raman spectra were collected using three excitation wavelengths: 514, 633, and 785 nm. These excitation wavelengths have previously been shown to be adequate for characterizing the electronic character of HiPCO SWNT samples, as both mand sc-SWNTs can be separately probed.^[52] Figure 3 shows the radial breathing mode (RBM) regions from the three samples at each excitation wavelength (full Raman spectra are provided in the Supporting Information, Figure S6). All Raman spectra were normalized to the G-band at \sim 1590 cm⁻¹ and offset for clarity. Upon excitation at 514 nm, two dominant RBM features are observed in the Raman spectrum: a broad feature arising from sc-SWNTs centered at 180 cm⁻¹, and several sharp peaks from 225 to 290 cm⁻¹ arising from *m*-SWNTs.^[53] The **P1**-SWNT sample shows a single peak in the sc-SWNT region, confirming that *m*-SWNTs are not present in the dispersions prepared using this polymer. Meanwhile, the P2-SWNT sample exhibits peaks corresponding to both sc- and m-SWNTs. This observation is corroborated by analysis of the G-band region at this excitation wavelength, which is shown in the inset of Figure 3 A. The G-band consists of two peaks: a lower frequency G⁻ and a higher frequency G⁺. For sc-SWNTs, both the G⁻ and G⁺ have Lorentzian line shapes, but for *m*-SWNTs the G⁻ exhibits a broader Breit-Wigner-Fano (BWF) line shape.^[54] A broad

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Figure 3. RBM regions of the Raman spectra using A) 514, B) 633, and C) 785 nm excitation wavelengths. The gray boxes denote the locations of signals arising from sc-SWNTs, while the pink boxes represent the locations of signals arising from *m*-SWNTs. The inset in A shows the G-band region, located at ~ 1590 cm⁻¹, upon excitation at 514 nm.

G⁻ is observed for both the raw SWNT and **P2**-SWNT samples, confirming that *m*-SWNTs are present. The **P1**-SWNT sample, however, lacks a BWF line shape in the G-band, which is consistent with the absence of *m*-SWNTs. Both *m*- and sc-SWNTs are in resonance when the 633 nm excitation wavelength is used. For HiPCO SWNTs at this wavelength, *m*-SWNT features are found at ~175–230 cm⁻¹, while sc-SWNTs give rise to peaks at ~230–300 cm^{-1.[48,52]} Both *m*- and sc-SWNT features are ob-

served in the SWNT and **P2**-SWNT samples, while only sc-SWNT features are observed for the **P1**-SWNT sample.

While mainly sc-SWNTs are in resonance with the 785 nm excitation wavelength for HiPCO SWNTs, a few larger diameter metallic species, most notably the (16,7) and (12,9) chiralities, have been observed in the low-frequency region.[53,55] In our case, neither polymer-SWNT sample exhibits any signals below 200 cm⁻¹, which indicates the absence of large diameter *m*-SWNTs in both samples. The most intense peak in the raw SWNT spectrum occurs at 265 cm⁻¹ and corresponds to (10,2) SWNTs, which are in resonance with this excitation wavelength when bundled.^[56] This peak is often referred to as the "bundling peak" and can be used to identify bundling in a nanotube sample, but only if (10,2) SWNTs are present. Figure 3C shows that a significant decrease in the bundling peak occurs when SWNTs are dispersed with either P1 or P2, giving further evidence that SWNTs are efficiently exfoliated using both of these polymers. This removes the possibility that the increased suspension of *m*-SWNTs using P2 is due to bundles in the dispersion, as opposed to a genuine effect originating from the differences in electronic properties between these conjugated polymers.

To confirm the absence of nanotube bundles, we investigated these samples using atomic force microscopy (AFM). Polymer-SWNT samples were prepared by spin-coating dilute dispersions onto freshly cleaved mica. These samples were analyzed using tapping-mode AFM, and representative images are shown in Figure S7, Supporting Information. Long, filamentous structures were observed in both samples, with heights ranging from 1-5 nm. The smallest diameter features correspond to individual polymer-coated nanotubes, while the larger features could originate from small bundles formed upon spin-coating the polymer-SWNT complexes. The height profiles observed suggest that significant SWNT exfoliation occurs for both polymer samples upon sonication, and that there is no palpable difference in the degree of nanotube exfoliation between P1 and P2. On the basis of these results, it is clear that P1 disperses only sc-SWNTs while P2 disperses a higher proportion of m-SWNTs, alongside some sc-SWNTs.

Photoluminescence (PL) maps were recorded for the polymer-SWNT samples (Figure 4). The locations of various SWNT fluorescence maxima were assigned according to previously published data.^[10] A SDBS-SWNT dispersion was prepared as a control experiment and a multitude of high intensity PL signals were observed, with the most intense peak corresponding to the (8,6) chirality (see the Supporting Information, Figure S10). High intensity PL signals were also observed for the P1-SWNT dispersion, with the most intense peak corresponding to the (7,6) chirality (Figure 4A). The P2-SWNT sample similarly contains the (7,6) chirality as the most intense peak, but the relative fluorescence is dramatically lower (Figure 4B). Despite matching the sample concentrations by obtaining comparable absorption intensities for the (7,6) chirality at 1120 nm (see Figure S8, Supporting Information), the fluorescence intensity for the P2-SWNT sample is an order of magnitude lower than the P1-SWNT sample. The observed fluorescence quenching can be attributed to two possibilities: the presence of

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Figure 4. PL maps A and B correspond to P1-SWNT and P2-SWNT at a similar concentration and plotted on the same scale. C) The same P2-SWNT dispersion as (B) with an adjusted intensity scale.

nanotube bundles or the presence of m-SWNTs. We have already dispelled the possibility of bundles in our polymer-SWNT dispersions (vide supra), so we attribute the observed fluorescence quenching to the increased amount of m-SWNTs dispersed by **P2**, in contrast to the enriched sc-SWNT dispersion with **P1**.

To confirm the difference in *m*-SWNT quantities between our dispersions, we performed electrical conductivity measurements using the Van der Pauw method.^[57] We first prepared square-shaped thin films with dimensions of 0.5×0.5 cm for our polymer-SWNT samples by filtering 100 µL of polymer-SWNT dispersion through a Teflon filtration membrane with 0.2 µm pore diameters clamped between two solvent-resistant aluminum masks under vacuum. The thin films were dried

under vacuum for 15 min and then resistivity was measured by direct contact with four platinum probes placed in the corners of the square-shaped thin film. Voltages from 0 to 250 mV were applied to one pair of contiguous electrodes and the current was measured on the opposite pair of electrodes (e. g. if the thin film corners were labeled from 1–4 clockwise, the first measurement would apply V_{12} and measure I_{43}). The thin film resistance (*R*) was calculated from the slope of the resulting *I-V* curve. The measurements were repeated for all four electrode combinations (i.e. V_{12} , V_{23} , V_{34} , and V_{41}) and the total resistance for the thin film (R_7) was calculated as:

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$$R_{T} = \frac{1}{4} \left(\frac{V_{12}}{I_{43}} + \frac{V_{23}}{I_{14}} + \frac{V_{34}}{I_{21}} + \frac{V_{41}}{I_{32}} \right)$$
(measured in triplicate)

The sheet resistance (R_s) was then calculated as:

$$R_{\rm s}=\frac{\pi R_{\rm T}}{\ln 2}$$

Thin film thickness (t) was measured using white light interference microscopy, and bulk conductivity (σ) was calculated as $R_{\rm s}^{-1}t^{-1}$. The thickness measurements obtained for **P1**-SWNT and P2-SWNT (2.5 and 3.0 µm, respectively, with relative standard errors of 4-14%) allowed us to calculate conductivities of $3.1\pm0.8\times10^{-4}$ and 1.4 ± 0.6 Sm⁻¹, respectively, which gives a difference of four orders of magnitude. This stark contrast suggests that there are more *m*-SWNTs in the nanotube population dispersed by P2, which corroborates our previous spectroscopic analyses. However, it should be noted that the presence of charges and/or salts within the P2-SWNT sample can impact its conductivity. We performed conductivity measurements involving just the polymers P1 and P2 in thin films with mass loadings equivalent to those expected for the polymer-SWNT samples, and observed nonlinear I-V curves, indicating that the polymers are nonconductive and are unlikely to contribute appreciably to the observed conductivity of the polymer-SWNT films. An uncentrifuged SDBS suspension of the raw SWNTs was also cast as a reference thin film by using the same protocol described above. Its conductivity was measured to be 785 ± 114 Sm⁻¹ (full details of these control experiments are provided in the Supporting Information). Although the bulk conductivity of this SDBS-SWNT sample is higher than the P2-SWNT sample, the two materials cannot be directly compared as the SDBS suspension contains a mixture of amorphous carbon, metal catalyst particles, and the raw nanotube mixture that is significantly bundled. Thus, it is not surprising that this sample exhibits higher conductivity, as nanotubes are able to come into closer contact within the SDBS-SWNT sample. Considering the extent of insulating material around the nanotubes in the P2-SWNT sample, the finding that its conductivity is only two orders of magnitude lower than the raw nanotube sample is again indicative of the selectivity for m-SWNTs by the electron-poor cationic copolymer.

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Conclusion

In the pursuit of next-generation polymers for the selective dispersion and purification of SWNTs, understanding the key parameters dictating polymer selectivity is imperative. We have demonstrated that the simple modification of a poly(fluoreneco-pyridine) backbone, such that it is transformed from being electron-rich to being electron-poor, has a significant impact on the electronic nature of SWNTs dispersed. The unmodified copolymer bearing an electron-rich fluorene co-monomer preferentially forms stable colloids with sc-SWNTs, while the methylated copolymer bearing electron-withdrawing cationic charges produces dispersions that are more enriched with m-SWNTs. Although the exact mechanism that directs specificity in conjugated polymer interactions with SWNTs is still under investigation, this work provides a clear indication that polymer electronics plays an important role. Further investigation of rationally designed, electron-deficient conjugated polymers for selective dispersion of *m*-SWNTs is warranted.

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Nanotechnology

D. Fong, W. J. Bodnaryk, N. A. Rice, S. Saem, J. M. Moran-Mirabal, A. Adronov*

Selective Dispersion of Single-Walled Carbon Nanotubes



Conducting materials: Methylation of a poly(fluorene-*co*-pyridine) derivative results in a cationic, electron-poor polymer that exhibits increased selectivity for metallic carbon nanotubes relative to the unmethylated, electron-rich structure (see figure).

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