Interactions between Conjugated Polymers and Single-Walled Carbon Nanotubes

David W. Steuerman, Alexander Star, Riccardo Narizzano,[†] Hyeon Choi, Ryan S. Ries, Claudio Nicolini,[†] J. Fraser Stoddart, and James R. Heath*

Contribution from The California NanoSystems Institute and the Department of Chemistry and Biochemistry, University of California, Los Angeles, 603 Charles E. Young Drive East, Los Angeles, California 90095-1569

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The chemical interactions between single walled carbon nanotubes (SWNTs) and two structurally similar polymers, poly{(*m*-phenylenevinylene)-*co*-[(2,5-dioctyloxy-*p*-phenylene)vinylene]}, or PmPV, and poly{(2,6-pyridinylenevinylene)-*co*-[(2,5-dioctyloxy-*p*-phenylene)vinylene]}, or PPyPV, are investigated. The fundamental difference between these two polymers is that PPyPV is a base and is readily protonated via the addition of HCl. Both polymers promote chloroform solubilization of SWNTs. We find that the SWNT/PPyPV interaction lowers the pK_a of PPyPV. Optoelectronic devices, fabricated from single polymer-wrapped SWNT structures, reveal a photogating effect on charge transport which can rectify or amplify current flow through the tubes. For PmPV wrapped tubes, the wavelength dependence of this effect correlates to the absorption spectrum of PmPV. For PPyPV, the wavelength dependence correlates with the absorption spectrum of protonated PPyPV, indicating that SWNTs assist in charge stabilization.

Introduction

The remarkable physical and chemical properties of singlewalled carbon nanotubes (SWNTs) have made these materials attractive candidates for a host of structural and electronic tasks.¹ However, a number of challenges must be met before nanotubes can be exploited for most of these envisioned applications. Those challenges include separating the tubes by conductivity types, scaling synthetic approaches to large scale production, and developing chemical techniques for manipulating nanotubes as rational molecular materials. Progress on all, of these fronts has been proceeding rapidly over the past few years. Gimzewski and co-workers² recently reported synthetic techniques for producing single-crystal ropes of SWNTs in which each tube within the rope is of identical type. Smalley's group³ has described potentially scalable synthetic techniques that utilize carbon monoxide as a feedstock. With respect to chemical techniques, both covalent^{4,5} and noncovalent (polymer-wrapping) techniques for the functionalization of SWNTs have been reported.

Noncovalent functionalization of SWNTs is particularly attractive because it presents the possibility of attaching chemical handles to SWNTs without disrupting the bonding network of the nanotubes themselves. Composite materials based on the polymer wrapping of multiwalled carbon nanotubes using poly-(*p*-phenylenevinylene) (PPV) have been reported⁶ by Friend's group and they subsequently investigated the physical nature of the interaction. Blau and co-workers^{7,8} extended this concept by employing the copolymer poly(*p*-phenylenevinylene-*co*-2,5-dioctyloxy-*m*-phenylenevinylene) (PmPV-*co*-DOctOPV)⁹ for wrapping and purifying SWNTs. Smalley's group¹⁰ utilized a host of water soluble polymers, including poly(vinylpyrrolidone) and polystyrene sulfonate to reversibly water solubilize SWNTs. In this work, the polymers were reported to form a tight, uniform association with the SWNTs that effectively broke up the ropes

* To whom correspondence should be addressed. E-mail: heath@ chem.ucla.edu. Phone: 310-825-2836. Fax: 310-206-4038.

into single strands, and an entropically driven model for that association was proposed. We have also reported on the use of poly{(m-phenylenevinylene)-co-[(2,5-dioctyloxy-p-phenylene)vinylene]}, or PmPV, for wrapping SWNT strands and ropes.¹¹ In that work, we found that PmPV enabled the solubilization of SWNTs and SWNT ropes in chloroform and that the length and diameter distribution of the ropes was dependent on the relative concentrations of PmPV and SWNTs. An excess of PmPV was required to solubilize the SWNTs-a result that is in contrast to the results from Smalley's group on water solubilization. Optical imaging and optoelectronic measurements on single, isolated PmPV-wrapped SWNT ropes revealed that polymer-wrapped SWNTs do not further aggregate into thicker ropes, and that the polymer and nanotube components of a wrapped structure are in intimate electrical contact with each other. This result contrasts with the work from Friend's group, who found that the multiwall NT interaction with PPV is only strong for the excited electronic state of the polymer. One possible difference between PPV and PmPV relates to the helical conformation of PmPV, which may aid in its overcoming steric barriers to wrapping.

Thus, the chemical picture that is unfolding for noncovalent functionalization of SWNTs is a complex one, and appears to go well beyond a simple picture of $\pi - \pi$ interactions between the NT and the aromatic polymer. In this paper, we attempt to further quantify polymer wrapping of SWNTs by interrogating two PPV analogues, PmPV and the related poly{(2,6-pyridinylenevinylene)-co-[(2,5-dioctyloxy-p-phenylene)vinylene]} (PPyPV). These two polymers are similar structurally, and, in the solution-phase, they are also both characterized by nearly identical absorption spectra, with a strong, broad absorption feature near 420 nm (\sim 3 eV). However, there are significant chemical differences between these two polymers. The pyridine unit in PPyPV makes this polymer a base. The lone pair of the pyridine unit is an sp^2 orbital, orthogonal to the polymer π -system, so there is no major (electronic) difference between PmPV and PPyPV when these polymers are charge-neutral. However, as shown by a number of authors,¹² protonation of

[†] Department of Biophysics, Corso Europa 30, 16100 Genova, Italy.

SCHEME 1: (a) 1-Chlorooctane, K₂CO₃, DMF, 90 °C, 71%; (b) HCHO, HCl, Dioxane/H₂O, 60–70 °C, 77%; (c) PPh₃, DMF, reflux, 83%; (d) (i) EtONa, EtOH/THF, 60%; (ii) I₂ (cat), PhMe, reflux, 100%



PPyPV by HCl is accompanied by a broad absorption band near 580 nm (2.4 eV) and a corresponding loss of absorption intensity in the higher energy absorption band. There is, of course, no analogous protonation in the case of PmPV.

In this paper, we explore, in some detail, the nature of the interaction between SWNTs and both PmPV and PPyPV. Both polymers solubilize SWNTs in CHCl₃. In the case of PPyPV, the SWNT wrapping process promotes protonation of the polymer. We characterize this phenomenon by exploring the three-dimensional phase space of polymer concentration, SWNT concentration, and pH. We also report on the wavelength-dependence of the optoelectronic response of devices fabricated from PmPV- and PPyPV-wrapped SWNTs. For the case of PPyPV-wrapped SWNTs, we find that the SWNT/polymer interaction, at the single structure level, is dominated by protonated polymer. PmPV, on the other hand, appears to interact with SWNTs in its charge-neutral form.

Results and Discussion

Syntheses of the Conjugated Polymers. The syntheses (Scheme 1) of the PmPV and PPyPV polymers are both based on precursors which can subsequently participate in bis-Wittig olefinations. The first task is the preparation of the common bisphosphonium salt in three steps. To start with, hydroquinone (1) was reacted in 1-chlorooctane in DMF at 90 °C in the presence of K₂CO₃ to afford 1,4-bis(octyloxy)benzene (2) in 71% yield. Next, chloromethylation of 2, using an established procedure for aromatic compounds, gave a 77% yield of the bis(chloromethyl) derivative 3. Finally, the bisphosphonium salt 4 was obtained in 83% yield after heating 3 with Ph₃P in DMF under reflux for 3 days. The PmPV and PPyPV polymers were formed in yields of 60-65% as a result of reacting the bis-Wittig reagent, generated on treating 4 with base (NaOEt) in ethanolic THF, with isophthaldehyde and 2,6-pyridinedicarboxaldehyde, respectively. In common with Wittig reactions of this type, the olefinic bonds that are produced are a mixture of cis and trans configurations. However, the necessary isomerizations of cis double bonds to trans ones to give all-trans polymers was achieved by heating the crude polymers in PhMe under reflux in the presence of iodine as catalyst. Because resonances, which appear at ca. δ 3.5 and 4.0 in the ¹H NMR spectra of the



Figure 1. Absorption spectrum of PPyPV as it is protonated by HCl in CHCl₃ solution. The concentration of PPyPV is 0.05 mg/mL, and the protonation was carried in steps of 0.5 mL aliquots of a 1.0N HCl added to the polymer solution, and then recording an absorption spectrum. Spectra, collected every two aliquots, are presented, and proceed with increasing HCl from the solid black line (no HCl) to the dashed gray line. The top right inset is the intensity ratio of the 540 nm protonated (red) absorption feature to the 420 nm (blue) feature.

SCHEME 2: Protonation of PPyPV Polymer



crude polymers, can be attributed to the protons on the *O*-methylene groups attached to the hydroquinone rings carrying cis and trans double bonds at their nearest neighbors, respectively, ¹H NMR spectroscopy was employed to follow the course of the isomerization processes. It was quantitative in both cases. ¹H NMR spectroscopy was also used to determine that the end groups of the polymers were aldehydes. The number average molecular weights (M_n) of the two polymers were determined in THF using a calibrated size exclusion chromatography (SEC) column connected to a UV detector. The number average degree of polymerization was estimated to be around 25 for PmPV and 29 for PPyPV from the M_n values in the knowledge that the molecular weights of the repeating units are 460 for PmPV and 461 for PPyPV.

PPyPV/SWNT Interactions in Solution. Of particular interest to this work is the basic character of PPyPV, and how it is influenced through SWNT interactions. PPyPV is readily protonated by adding aqueous HCl to the polymer in CHCl₃ solution (Scheme 2) and, because of the unique absorption signature of protonated PPyPV, this titration is readily followed optically as illustrated in Figure 1. This trend is reversed by deprotonating the polymer back to its charge neutral state through the addition of NH₃. Also shown in Figure 1 is a plot of the relative intensity of the low-energy absorption feature, normalized against the absorption strength of the 420 nm feature, as a function of titrating the polymer. This type of plot is particularly useful because it is a simple representation of the protonation process, and reflects saturation behavior. We will utilize such plots throughout the remainder of this discussion.

Protonation of PPyPV by HCl (Scheme 2) extends its conjugation, and the protonated form of the polymer is further stabilized through interaction with other PPyPV units, as a result of increased interchain interactions, presumably encouraged by strong $[N^+-H^{\dots}N]$ hydrogen bonds, and more efficient charge delocalization. Thus, as the concentration of polymer in solution increases, the polymer begins to aggregate and so increases the



Figure 2. Appearance of protonated PPyPV as a function of polymer concentration in $CHCl_3$ solution. The *y*-axis is the ratio of the red (protonated) to the blue (charge neutral) absorption features in the spectrum of PPyPV.



Figure 3. Influence of SWNTs on the protonation of PPyPV is presented here, for various concentrations of PPyPV, and for various ratios of PPyPV:SWNTs. The bottom trace is pure PPyPV. Note that, in all cases, the presence of SWNTs promotes the protonation of PPyPV.

basicity of the polymer. The result is that, in CHCl₃ solution, when the polymer is present in sufficiently high concentration, the HCl that is normally present in CHCl₃ is sufficient to lead (Figure 2) to significant protonation.

When PPyPV is utilized as a solubilizing agent for SWNTs in CHCl₃, the resultant optical absorption spectrum is reflective of a solution containing a significant concentration of the protonated form of PPyPV, even at very low PPyPV concentrations. In Figure 3, we present data abstracted from the absorption spectra of PPyPV/SWNT solutions, as a function of PPyPV concentration, and for increasing amounts of co-dispersed SWNTs. At the lowest concentrations (0.01 mg PPyPV/ml), and with no SWNTs added, only nonprotonated PPyPV exists in solution. As SWNTs are added to the solution at constant [PPyPV], the quantity of protonated polymer increases. For a 10:1 wt ratio of polymer to nanotubes, and at a PPyPV concentration of 0.01 mg/ml, the increase in the protonated form of the polymer is approximately a factor of 10, as compared to the case with no SWNTs present. We have investigated the distribution of SWNTs and SWNT ropes of these solutions by spin-evaporating a drop of solution onto silicon wafers and interrogating the cast films using atomic force microscopy (AFM). At these low concentrations, the SWNTs exist as short (200 nm to 1 micron) single strands or thin (1-2 nm diameter)ropes. Thus, it appears that SWNTs effectively promote the protonation of PPyPV. There are two obvious mechanistic possibilities for this observation. The first is that polymer/SWNT interactions lead to charge stabilization, and thus lower the pK_a of the polymer. The second possibility is that the nanotubes simply serve as condensation nuclei, thereby increasing the propensity for the polymer to aggregate. Aggregation would indirectly impact the ease of protonation by increasing the polymer/polymer interactions that lead to charge stabilization. As the [PPyPV] concentration is increased (at constant polymer: nanotube ratios), the relative amount of the protonated polymer initially decreases. We believe that this trend is related to the aggregation of the SWNTs to form ropes, and this picture is



Figure 4. HCl protonation of PPyPV as a function of increasing SWNT concentration. The 10:0 curve (open circles) is for just PPyPV, whereas the two other curves represent increasing relative amounts of SWNTs. Note that, although all three curves start out at fairly low values of $R_{r/b}$, as SWNT concentration is increased, the amount of HCl required to fully protonate the polymer is greatly reduced, implying that SWNTs lower the pK_a of the polymer.

supported by AFM measurements. The formation of nanotube ropes has the net affect that there is less nanotube surface area available for the polymer to interact with. As the [PPyPV] concentration is further increased (again at constant polymer: nanotube ratios), the relative amount of protonated polymer increases again.

As a consistency check against the picture that SWNTs promote the protonation of PPyPV, we took several SWNT/ polymer solutions, and titrated the polymer to full protonation by adding HCl. Representative data is presented in Figure 4. These experiments revealed two things. First, the amount of HCl required to protonate PPyPV was reduced through the addition of SWNTs. Second, and perhaps most interesting, is that the rate of protonation sharply increased upon the addition of SWNTs. This result indicates quite clearly that the SWNT/ PPyPV interaction is one that significantly lowers the pK_a of PPyPV.

Polymer-Wrapped SWNT Opto-Electronic Devices. In the previous section, we discussed a qualitative molecular picture of polymer/SWNT interactions that was derived from optical and chemical studies of polymer-wrapped SWNT colloids. However, these are complex and heterogeneous solutions, involving nanotubes, free polymer and bound polymer. The polymer itself can exist in the protonated or charge neutral state. The absorption spectroscopy that was used as the major analytical tool in the investigations described in that section is not able to differentiate between the various components. Experiments on single structures can thus be utilized to gain more quantitative insight into these multicomponent materials, and such experiments are the focus of this section. In our previous work, we correlated two-photon fluorescence microscopy of isolated, polymer-wrapped SWNT ropes with AFM measurements of the diameter of those same ropes. We used those measurements to demonstrate that the polymer wraps nanotube ropes, rather than individual SWNTs, which can then aggregate to form ropes. We also demonstrated that the polymer is in intimate electrical contact with the nanotube ropes by using light to modulate the electrical conductivity of small devices consisting of two metal electrodes bridged by a small number (1-3) of PmPV-wrapped ropes. In this section, we further explore these devices by measuring the wavelength dependence of the optically modulated conductivity of both PmPV-wrapped and PPyPV-wrapped SWNT ropes under various conditions of applied bias. We also directly compare the wavelength dependence of the devices with that of the solution-phase absorption spectrum of the polymers.

In Figure 5, we present a SEM micrograph of one of the optoelectronic devices utilized in this work for interrogating polymer-wrapped SWNT ropes. A series of measurements was



Figure 5. Scanning electron micrograph of a device used for measuring the optoelectronic properties of polymer-wrapped SWNT ropes. The electrode gap is 1 micrometer. All the ropes in the image have been artificially colored for clarity. The particular structure here is a PPyPV-wrapped SWNT rope.



Figure 6. Optical gating of PmPV-wrapped SWNT rope devices. All traces correspond to illumination with 3.05 eV light. Trace a is a control device (no polymer, just a nanotube rope). Note the expanded *y*-axis scale, highlighting the absence of any optical effect on this control. Trace b shows photorectification when an applied bias of -25 mV is applied, and trace c shows photoamplification when a positive applied bias (+25 mV) is applied. The current difference between light on and light off was averaged over several traces for each wavelength. That data was then utilized to piece together the wavelength dependence of the response.

performed at various wavelengths for devices containing bare SWNTs and nanotube ropes, and for SWNTs (ropes) wrapped with the two PPV analogues: PmPV and PPyPV. Of the several control devices (SWNTs without polymer) that were tested, none exhibited any sort of optically modulated response (Figure 6a).

In Figure 6b and 6c, we present the on-off difference for negatively and positively biased junctions of PmPV-wrapped tubes, respectively. For either bias, the magnitude of the change in current is similar, and corresponds to about 15-20% of the entire current. The major difference between the two experiments is that current through the polymer/SWNT device is photoamplified for a positive applied bias, but it is photorectified for a negative applied bias. We found this feature to be an intrinsic property of PmPV wrapped NTs, and was not reversed by changing the connections to the two electrodes.

In Figure 7 we present some plots of the photoamplification effect on PPyPV wrapped SWNT rope devices, at a few wavelengths. No effect was observed when negative biases were applied across the device, but the effect at positive applied bias was substantially greater in magnitude than was observed for the PmPV-wrapped tubes.



Figure 7. Optical gating of a PPyPV-wrapped SWNT rope device at various wavelengths. No electrooptical response was recorded when a negative bias (-10 mV) was applied to the device, and one such representative trace is shown for 375 nm excitation. Note that, when a positive bias (+10 mV) is applied across the device, the magnitude of the photoamplification is much greater than for the case of the PmPV-wrapped tubes. The shape of the 635 nm excitation trace was characteristic for wavelengths greater than about 530 nm. For the wavelength-dependent plots, several traces were averaged for each wavelength probed.



Figure 8. Wavelength dependence of the optically gated conductivity in polymer-wrapped SWNT rope devices. Plots a and b are for PmPVwrapped ropes, and exhibit photoamplification and photorectification, respectively. Trace c reveals photoamplification of the current through a PPyPV-wrapped rope at an applied bias of 25 mV. This system only exhibited photoamplification at postive applied bias. No effect was recorded at negative applied bias.

The wavelength dependence of these photoamplification/ rectification effects were performed for both polymer/SWNT systems from 375 to 805 nm in 5 to10 nm increments. The absolute value of the wavelength-dependence of the illumination on the current response through representative devices is presented, along with the polymer absorption spectra, in Figure 8.

For the PmPV device, a nonzero photoresponse was only at wavelengths shorter than 505 nm. These data represents the optically excited polymer interacting with the NT to effectively yield the spectrum of the polymer. The photoelectrical response of the device exhibits a redshift from the solution phase polymer absorption spectrum, a response which is consistent with the fact that the polymer wrapping the tubes is at 4 K and in the solid state. Thermochromic shifts of up to 0.4 eV have been observed previously in similar PPV systems.¹³ This redshift trend

is further enhanced in the solid state where interchain interactions additionally stabilize the polymer, thus resulting in an increased conjugation length.

The UV-vis absorption spectrum of the PmPV polymer yields just a single broad peak, but the data from the device exhibits a highly structured spectrum. The structure is well above the signal-to-noise level (see the error bars in Figure 8) and we found that, for the identical device, given the same value of applied bias (V_c), the structure was reproducible. Similar (but not identical) structure was observed in other PmPV/SWNT devices. The nature of the structure is not clear, but it may be vibronic in origin. This suggestion seems feasible, given the low temperature of the measurement. However, for the same device, the structure in the photocurrent spectrum did change as a function of applied bias. This change can be seen in the differences between Figure 8a ($V_c = 10$ mV) and 8b ($V_c = -5$ mV).

Devices using the PPyPV polymer yielded conceptually similar results to that of PmPV. The spectral response of this device at a bias of 10 mV can be seen in Figure 8c. Once again, a large red shift was present, when compared to solution data. Although they are less obvious, some sharper features in the spectrum were observed between 1.6 and 1.9 eV photon energies. The major difference between the PPyPV and the PmPV nanotube devices was that the PPyPV devices yielded only a photoamplification response at positive applied bias and no photomodulation at negative applied bias.

Some insight into the mechanism of the photoamplification/ rectification process can be gained by considering the efficiency of the process. The fluence of the focused light was measured to be about 5 mJ (in a 1 cm^2 area). First, we make the generous assumption that the absorption cross section of the polymer/ NT device is the actual physical area of the device (7×10^{-7}) cm ? 1×10^{-4} cm). Then, taking 2.8 eV to be the maximum in the photoamplification effect of a PmPV-wrapped SWNT (rope) device, we calculate that, for every photon that hits the device, the increase in current is approximately $10^2 - 10^3$ electrons. Given that our absorption cross section is a gross over-estimate, the actual increase in current is more likely closer to 10⁴ electrons. Clearly, even in the photoamplification mode, the device is not harvesting light. Instead, we believe that the photoeffect is similar to a voltage gating phenomenon. When the polymer absorbs a photon, the electronically excited state of the polymer has a different dipole moment than the ground state. The result is that the chemical potential the nanotube experiences, in the vicinity of the excited state polymer, is modified. That change in chemical potential then exerts a gating field onto the nanotube, thereby either amplifying or rectifying conductivity. This result is a variation on the chemical sensing properties of nanotubes that were originally reported by Dai's group.¹⁴ It also implies that not only is the chemical interaction between the nanotubes and the polymers an intimate one, but also that this type of measurement may provide a technique for carrying out extremely sensitive absorption spectroscopy experiments.

The data presented in Figure 8 argue strongly that there is a correlation between the polymer absorption spectrum and the wavelength dependence of the photomodulated conductivity of these devices. Given this correspondence, it is interesting to note that for the PPyPV-wrapped SWNT ropes, the photomodulated conductivity spectrum is dominated by the lowest energy polymer absorption feature, i.e., the feature that corresponds to the protonated polymer. Given the nature of the experiment, this means that the polymer that is most closely associated with

the tube is protonated. Recall that, from the previous section, we discussed two possibilities for nanotube-mediated PPyPV protonation. One possibility was that polymer/SWNT interactions lead directly to charge stabilization, whereas the second possibility was that the nanotubes simply serve as condensation nuclei, thereby increasing the propensity for the polymer to aggregate. Given the optoelectronic results on single PPyPVwrapped tubes, it appears most likely that the mechanism by which the nanotube directly stabilizes the charged polymer is the right one.

Experimental Section

General Methods. Chemicals were purchased from Aldrich and used as received. Solvents were dried, distilled, and stored under argon. Melting points (mp) were determined on an Electrothermal melting point apparatus and are uncorrected. Elemental analyses was performed by Quantitative Technologies Inc. Ultraviolet-visible (UV-vis) spectra were obtained using a Varian Cary 100 Bio spectrophotometer. Absorption measurements of polymeric sample solutions were carried out in CHCl₃ with a concentrations of 1.0×10^{-4} and 1×10^{-5} M relative to the polymer repeating units. Proton and carbon nuclear magnetic resonance (¹H NMR and ¹³C NMR) spectra were recorded on a Bruker AM360 at 25 °C, using the deuterated solvent as lock and the residual solvent as internal standard. Electron Impact Ionization Mass Spectrometry (EI-MS) was performed on a AUTO-SPEC instrument. Molecular weights of polymers were determined by using a Dynamax solvent delivery module system, Styragel HR3 column, and a Dynamax PDA-2 diode array detector, at a flow rate of 1.0 mL/min. All molecular weights were measured against polystyrene standards in THF.

1,4-Bis(octyloxy)benzene (2). A solution of hydroquinone (1) (6.5 g, 59 mmol), 1-chlorooctane (20 mL, 118 mmol), and K₂CO₃ (32.6 g, 236 mmol) in DMF (240 mL) was heated for 5 d at 90 °C. The product was isolated by extraction with light petroleum, washed with H₂O, dried (Na₂SO₄), and evaporated to afford **2** as white solid (14 g, 71%). m.p. 56–57 °C (light petroleum); ¹H NMR (360 MHz, CDCl₃): δ = 6.82 (s, 1H), 3.89 (t, *J* = 6.6 Hz, 2H), 1.75 (p, *J* = 6.7 Hz, 2H), 1.44 (p, *J* = 6.7 Hz, 2H), 1.31–1.28 (m, 8H), 0.88 (t, *J* = 6.6 Hz, 3H); ¹³C NMR (90 MHz, CDCl₃): δ = 153.2, 115.4, 68.7, 31.8, 29.4, 29.2, 26.0, 22.6, 14.1.

2,5-Bis(chloromethyl)-1,4-bis(octyloxy)benzene (3). 1,4-Bis(octyloxy)benzene (2) (9.5 g, 28 mmol) was added to a mixture of dioxane (80 mL), 37% aqueous HCHO solution (17 mL) and concentrated HCl (12 mL), saturated with HCl gas. The mixture was kept at 60–70 °C with continuous introduction of HCl for 9 h. After cooling, ice/water (300 mL) was added, and the precipitate was filtered off. Crystallization from light petroleum yielded 1,4-bis(chloromethyl)-2,5-dioctyloxybenzene (3) as colorless needles (9.4 g, 77%). m.p. 80 °C; ¹H NMR (360 MHz, CDCl₃): $\delta = 6.91$ (s, 1H), 4.63 (s, 2H), 3.98 (t, J = 6.5 Hz, 2H), 1.80 (p, J = 6.5 Hz, 2H), 1.48 (p, J = 6.5 Hz, 2H), 1.35–1.29 (m, 8H), 0.89 (t, J = 6.5 Hz, 3H); ¹³C NMR (90 MHz, CDCl₃): $\delta = 150.6$, 127.0, 114.3, 69.1, 41.3, 31.8, 29.3, 26.0, 22.6, 14.1; EI-MS: 430.2–432.2 [M]⁺; calcd for C₂₄H₄₀Cl₂O₂ (431.5): C 66.81, H 9.34; found: C 66.73, H 9.56.

2,5-Bis(methyl triphenylphosphonium chloride)-1,4-bis-(**octyloxy)benzene (4).** A mixture of 1,4-bis(chloromethyl)-2,5dioctyloxybenzene (**3**) (1.45 g, 3.36 mmol) and Ph₃P (2.69 g, 10 mmol) in anhydrous DMF (20 mL) was heated under reflux for 3 d. The resulting solution was added dropwise into Et₂O (100 mL) to precipitate out the product. The white precipitates (2.66 g, 83%) were collected via filtration and dried under vacuum. m.p. > 200 °C; ¹H NMR (360 MHz, CDCl₃): δ = 7.75–7.73 (m, 3H), 7.66–7.63 (m, 12H), 6.68 (s, 1H), 5.34 (d, J = 12.7 Hz, 2H), 2.99 (t, J = 5.8 Hz, 2H), 1.32–1.19 (m, 5H), 1.13–1.04 (m, 5H), 0.90 (t, J = 6.7 Hz, 3H); ¹³C NMR (90 MHz, CDCl₃): δ = 150.4, 134.7, 134.2, 134.14, 134.09, 130.0, 129.95, 129.88, 118.5, 117.5, 116.3, 115.8, 67.8, 31.7, 29.2, 29.1, 28.6, 25.7, 22.5, 14.0.

Poly{(m-phenylenevinylene)-co-[(2,5-dioctyloxy-p-phenylene)vinylene]} (PmPV). A 5% NaOEt in EtOH solution (2.8 g, 6 mmol) was added dropwise to a solution of 4 (1.91 g, 2 mmol) and isophthaldehyde (0.27 g, 2 mmol) in a mixture of anhydrous EtOH (20 mL) and THF (20 mL) at ambient temperature. The reaction mixture was stirred for an additional 24 h. The resulting polymer was precipitated twice from MeOH and then dried to afford crude **PmPV** (0.55 g, 60%) as a yellow resin. ¹H NMR (360 MHz, CDCl₃): $\delta = 7.60 - 7.30$ (m, 6H), 7.20 - 6.50 (m, 4H), 4.09 (t, J = 6.5 Hz, 2H (trans-fragment)), 3.51-3.49 (m, 2H (cis-fragment), 1.90 (p, J = 6.5 Hz, 2H), 1.56 (br, 2H), 1.25 (m, 8H), 0.86 (br, 3H). A sample of the crude PmPV (0.55 g) and I_2 (0.002 g) were refluxed in PhMe (20 mL) for 4 h. The solvent and iodine were evaporated off poly{(m-phenylenevinylene)-co-[(2,5-dioctyloxy-p-phenylene)vinylene]} under reduced pressure and the product was dissolved in CHCl3 and precipitated out with MeOH. The resulting precipitate was dried to afford PmPV as a yellow resin (0.5 g). ¹H NMR (360 MHz, CDCl₃): $\delta = 7.64$ (s, 1H), 7.55–7.46 (m, 4H), 7.37 (t, J = 7.5Hz, 1H), 7.21 (s, 1H), 7.16 (s, 3H), 4.09 (t, J = 6.5 Hz, 2H), 1.90 (p, J = 6.5 Hz, 2H), 1.55 (p, J = 6.5 Hz, 2H), 1.35 (m, 8H), 0.87 (t, J = 6.5 Hz, 3H); ¹³C NMR (90 MHz, CDCl₃): δ = 151.0, 138.3, 128.5, 126.9, 125.7, 124.0, 111.1, 69.8, 31.8, 29.4, 26.3, 22.7, 14.1; calcd for C₃₂H₄₄O₂ (460.7): C 83.43, H 9.63; found: C 82.59, H 9.72.

The molecular weights and polydispersity (PDI) of PmPV (M_w =19 000; PDI = 1.6) were determined in THF by using an SEC instrument equipped with a UV detector. The SEC system was calibrated by using polystyrene standards prior to use. The number-average degree of polymerization was estimated to be $n \approx 25$ from M_n and the molecular weight of the repeating unit, 460. The degree of polymerization of the lower molecular weight polymer was confirmed by NMR end-group analysis.

Poly{(2,6-pyridinyleneyinylene)-co-[(2,5-dioctyloxy-p-phenylene)vinylene]} (PPyPV). A 2.5% solution of NaOEt (0.7 mmol) in EtOH was added dropwise to a solution of 4 (0.21 g, 0.22 mmol) and 2,6 pyridinedicarboxaldehyde (0.03 g, 0.22 mmol) in a mixture of anhydrous EtOH (1 mL) and THF (3 mL) at ambient temperature. The reaction mixture was stirred for an additional 26 h. The resulting polymer was precipitated twice from MeOH and then dried to afford the crude PPyPV (0.05 g, 65%) as a yellow resin. ¹H NMR (200 MHz, CDCl₃): $\delta = 7.90 - 7.50$ (m), 7.30 - 6.90 (m), 6.80 - 6.60 (m), 4.01 (brs, 2H (trans-fragment)), 3.51 (brs, 2H (cis-fragment), 1.83 (brs, 2H), 1.48 (brs, 2H), 1.64 (brs, 8H), 0.78 (brs, 3H). A sample of the crude PPyPV (0.03 g) and I₂ (11 μ L of 0.01% iodine in PhMe solution) were heated under reflux in PhMe (3.5 mL) under argon atmosphere for 6h. The solvent and iodine were evaporated off under reduced pressure and the product was dissolved in CHCl3 and precipitated out with MeOH. The resulting precipitate was dried to afford PPyPV as a yellow resin (0.02 g). ¹H NMR (200 MHz, CDCl₃): $\delta = 7.89$ (s, 1H), 7.81 (s, 1H), 7.59 (brs, 1H), 7.40-7.15 (m, 7H), 4.01 (brs, 2H), 1.84 (brs, 2H), 1.49 (brs, 2H), 1.22 (brs, 8H), 0.80 (brs, 3H); ¹³C NMR (90 MHz, CDCl₃): $\delta = 155.1, 148.7, 132.7, 129.2, 127.8,$ 126.0, 110.4, 69.5, 31.6, 29.2, 29.5, 26.1, 22.5, 13.9; calcd for

C₃₁H₄₃NO₂ (461.7): C, 80.65; H, 9.39; N, 3.03; found: C, 78.69; H, 9.17; N, 2.83. Calculated for HCl protonated once every three repeat units: C, 78.58; H, 9.22; N, 2.96. The molecular weights and polydispersity (PDI) of **PPyPV** ($M_w = 24\ 246$; PDI = 1.8) were determined in THF by using an SEC instrument as described above. The GPC measurements of the polymer shows that the number-average molecular weight (M_n) is 13 543, corresponding to 29 repeating units.

Preparation of the SWNT/Polymer Complex. SWNTs were produced by the HiPco method³ and used as received from Rice University. SWNTs (0.3 mg) were added to a solution of the polymer in CHCl₃ solution (1 mg in 5 mL). Sonication for 30 min gave a stable transparent solution.

UV-vis and Photoluminescence Measurements. The polymer which was used in these experiments was synthesized shortly before use. The nanotubes were added to the chloroform solutions of the polymer in CHCl₃ right before use. The solutions were placed in a 1 mm path length quartz cell. The solid-state samples were produced shortly before they were tested in order to reduce polymer oxidation. The solid-state samples were created by spin-coating the composite material onto a cleaned glass substrate. The UV-vis experiments were carried out on a Varian Cary 100 Bio spectrophotometer. The photoluminescence spectroscopy was carried out using a Fluorolog-3 (Instrument S. A. & Co.) using a xenon lamp for the excitation source. The fluorescence was collected from the front face of the cuvette to minimize the self-absorption effects from the optically dense sample.

Fabrication and Interrogation of Polymer/SWNT Optoelectronic Devices. Polymer/SWNT devices were prepared by spin-coating a dilute solution of CHCl₃, polymer, and SWNTs onto a Si wafer that was coated with 0.2 micrometers of SiO₂ and was pre-patterned with electrodes. The electrodes (200 nm wide, 1 micrometer gap) were fabricated using standard electronbeam lithography techniques and consisted of a 5 nm bottom layer of Ti, coated with a 50 nm thick layer of Au. It is generally possible to fabricate better electrical contacts to SWNTs and SWNT ropes by depositing the electrode materials directly on top of the nanotubes.¹⁵ However, such a process involves steps such as the spin-coating of resist materials on top of the nanotubes, and thus can potentially disrupt the nanotube/polymer superstructure. The chosen method of depositing the polymerwrapped nanotubes directly on top of the patterned electrodes not only leads to poorer electrical contacts, but it also presumably retains the superstructure of the polymer-wrapped tubes. In any case, the results discussed here, except where explicitly noted, were highly reproducible across several devices.

The electrodes were connected to larger, macroscopic pads for wire-bonding to the pin-outs of a chip carrier. After the device was assembled, the chip carrier was mounted onto the coldfinger of an immersion cryostat that was equipped with quartz window optical ports. The output of a quartz-halogen lamp was filtered through a water cell to remove infrared frequencies, and then was wavelength selected through a singlepass monochromator, before being directed through quartz windows of the cryostat onto the device. The optical response of the device was then explored as a function of wavelength, and all measurements reported here were carried out at 4 K. One terminal of the junction was held at a constant bias ($V_c \approx$ ± 10 mV, for example), whereas the other terminal was grounded through a picoammeter. Current through the device was monitored as a function of whether light was incident on the device. Because the current amplifier was not sufficiently

fast to couple to a lock-in detection scheme at the low signal levels, the incident light was manually modulated.

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(9) Subsequently, in the text, we prefer to use the short abbreviation PmPV for poly{(*m*-phenylenevinylene)-*co*-[(2,5-dioctyloxy-*p*-phenylene)-vinylene]}, the same *meta*-linked PPV isomer used by Blau and co-workers (ref 7) which was abbreviated as (PmPV-*co*-DOctOPV) by Dalton et al (ref 8). Similarly, poly{(2,6-pyridinylenevinylene)-*co*-[(2,5-dioctyloxy-*p*-phenylene)vinylene]} has been abbreviated in the text to PPyPV by us.

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