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# Noncovalent Engineering of Carbon Nanotube Surfaces by Rigid, Functional Conjugated Polymers

Jian Chen,*,† Haiying Liu,‡ Wayne A. Weimer,† Mathew D. Halls,† David H. Waldeck,‡ and
Gilbert C. Walker‡

*Advanced Technologies Group, Zyvex Corporation, 1321 North Plano Road, Richardson, Texas 75081, and*
*Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260*

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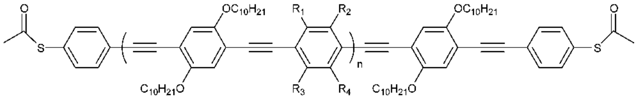
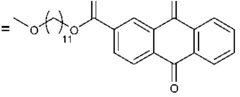
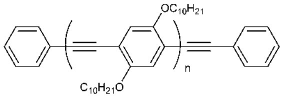
Molecular engineering (cutting, solubilization, chemical functionalization, purification, manipulation, and assembly) of single-walled carbon nanotubes (SWNTs) will play a vital role in exploring and developing their applications.[1] Noncovalent functionalization of carbon nanotubes is of particular interest, because it enables one to tailor their properties while still preserving nearly all of the nanotube's intrinsic properties. SWNTs have been solubilized in organic solvents and water by polymer wrapping[2] and noncovalently functionalized by adhesion of small molecules for protein immobilization.[3] This work reports a new *nonwrapping* approach to noncovalent engineering of carbon nanotube surfaces that leads to a >20-fold enhancement of solubility of small diameter SWNTs and enables superior control of the relative placement of functionalities on the nanotube surface.

Short, rigid conjugated polymers, poly(aryleneethynylene)s (PPE) (**1** and **2**),[4] are used to solubilize SWNTs. In contrast to previous work,[2] the rigid backbone of PPE[4c] cannot wrap around the SWNTs. The major interaction between polymer backbone and nanotube surface is most likely $\pi$-stacking (Figure 1).[3] This approach allows control over the distance between functional groups on the carbon nanotube surface, through variation of the polymer backbone and side chains. This approach represents the first example of carbon nanotube solubilization via $\pi$-stacking without polymer wrapping and enables the introduction of various neutral and ionic functional groups[4] onto the carbon nanotube surface.



(**1a**) $R_1$=$R_4$=H, $R_2$=$R_3$=$OC_{10}H_{21}$
(**1b**) $R_1$=$R_2$=$R_3$=$R_4$=F
(**1c**) $R_1$=$R_4$=H, $R_2$=$R_3$=





**(2)**

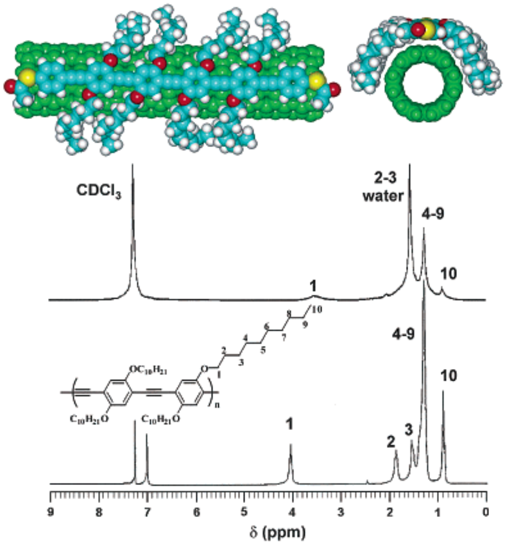


***Figure 1.*** A molecular model of $\mathbf{1a}_{n=1.5}$-$\mathrm{SWNT}_{(6,6)}$ complex (top) and $^1$H NMR spectra (300 MHz, $CDCl_3$) of **1a** (bottom) and **1a**-$\mathrm{SWNTs}_{\mathrm{HiPco}}$ complex (middle).

SWNTs are solubilized in $CHCl_3$ by mixing with **1** or **2** along with vigorous shaking and/or bath-sonication.[5] The minimum mass ratio ($R_{\mathrm{initial}}$) of **1a**:$\mathrm{SWNTs}_{\mathrm{HiPco}}$ that is needed to solubilize the $\mathrm{SWNTs}_{\mathrm{HiPco}}$ is about 0.4, and the solubility is about 2.2 mg/mL. This represents the highest reported solubility of $\mathrm{SWNTs}_{\mathrm{HiPco}}$ (the only commercial SWNT material that could currently be produced on large scale with high purity) in organic solvents by *noncovalent functionalizations*. The solubility of $\mathrm{SWNTs}_{\mathrm{laser}}$ and $\mathrm{SWNTs}_{\mathrm{arc}}$ is about 0.5 mg/mL.[6a] The solubility may be improved by changing the polymer's side chain structure and composition.

The polymer wrapping approach works poorly for dissolution of small diameter SWNTs (the solubility of $\mathrm{SWNTs}_{\mathrm{HiPco}}$ is about 0.1 mg/mL, using poly(metaphenylenevinylene) (PmPV)), possibly because an unfavorable polymer conformation is required for PmPV to wrap around small diameter $\mathrm{SWNTs}_{\mathrm{HiPco}}$ (diameter 0.7−0.8 nm).[6c] In contrast, the more rigid **1a** can solubilize small diameter $\mathrm{SWNTs}_{\mathrm{HiPco}}$ at ~2 mg/mL in $CHCl_3$. This difference suggests that a different, nonwrapping, type of interaction exists between PPE and SWNTs.

To test the effect of polymer rigidity on the solubility of $\mathrm{SWNTs}_{\mathrm{HiPco}}$, the backbone lengths of **1a** and **2** were varied (Table 1). PPE polymers with backbone lengths less than 15 nm (the reported persistence length of PPE[4c]) make the $\mathrm{SWNTs}_{\mathrm{HiPco}}$ highly soluble, providing further evidence for an interaction that does not involve polymer wrapping.

The solubility studies support the formation of stable and irreversibly bound complexes between the polymer and the SWNTs in $CHCl_3$, rather than a simple mixture. For **1a**, the measured mass ratio ($R_{\mathrm{final}}$ of **1a**:$\mathrm{SWNTs}_{\mathrm{HiPco}}$) in the final product was 0.38−0.40 and is independent of $R_{\mathrm{initial}}$.[6b] A potential molecular structure for a **1a**-$\mathrm{SWNT}_{(6,6)}$ complex was obtained by modeling (Figure 1).[6d] From this idealized model, the calculated $R$ of **1a**:$\mathrm{SWNT}_{\mathrm{HiPco}}$ is about 0.5−0.6, which is slightly higher than the experimental value

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* To whom correspondence should be addressed. E-mail: jchen@zyvex.com.
† Zyvex Corp.
‡ University of Pittsburgh.

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***Table 1.*** Solubility of SWNTs$_{\text{HiPco}}$ in CHCl$_3$ in the Presence of PPE

| PPE ($n_{\text{average}}$) | avg length (nm) | SNWT$_{\text{HiPco}}$ solubility (mg/mL) |
|---|---|---|
| **1a** (19.5) | 27.9 | ∼2 |
| **1a** (13) | 19.6 | ∼2.2 |
| **2** (16) | 12.0 | ∼2 |
| **2** (10) | 7.9 | ∼1.5 |

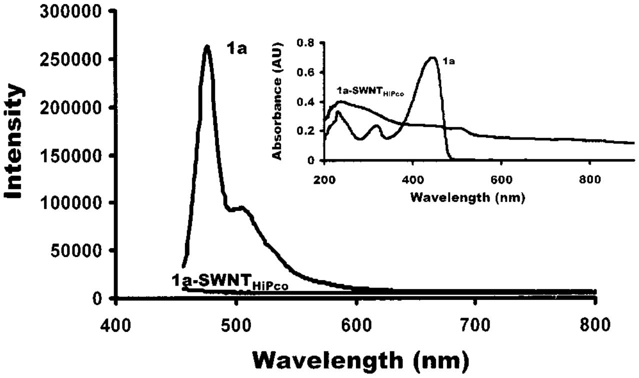

***Figure 2.*** Room-temperature solution-phase (CHCl$_3$) fluorescence spectra (excitation wavelength: 400 nm) and UV−visible spectra (inset) of **1a** and **1a**-SWNTs$_{\text{HiPco}}$ complex.

$R_{\text{final}}$ (0.38−0.40). The difference between the values may arise from the existence of nanotube ropes and impurities such as metal catalyst in SWNTs$_{\text{HiPco}}$.

The $^1$H NMR spectrum of **1a**-SWNTs$_{\text{HiPco}}$ (Figure 1) supports a strong $\pi-\pi$ interaction between **1a** and the nanotube. The CH$_2$ group (C$_1$) shows a significant upfield shift ($\delta$ 3.51) and broadening, as compared to that of free **1a** ($\delta$ 4.05). In addition, the phenylene protons, clearly evident in free **1a**, are too broad to be detected in the complex. These observations are consistent with theoretical evidence for the existence of large diamagnetic ring currents in carbon nanotubes.[7] No substantial shifts are observed for the other CH$_2$ groups,[6e] indicating that, although the polymer backbone interacts strongly with the nanotube surface, the side chain (C$_3$−C$_{10}$) of **1a** is relatively free in solution. In contrast to the PmPV-wrapped SWNTs solution that shows a significant amount of free PmPV,[2b] no free **1a** can be detected in **1a**-SWNTs$_{\text{HiPco}}$ solution, demonstrating a better interaction between **1a** and SWNTs$_{\text{HiPco}}$.

The optical spectroscopy supports a significant $\pi-\pi$ interaction between the polymer and the nanotube (Figure 2). The strong fluorescence of **1a** is efficiently quenched in **1a**-SWNTs$_{\text{HiPco}}$. The quenching likely arises from efficient energy transfer between **1a** and SWNTs, rather than the disruption of $\pi$-conjugation caused by a conformational change. Energy transfer quenching between molecules and for molecules on graphitic carbon and metal surfaces is well known.[8] The lowest energy absorption band for **1a** in the **1a**-SWNTs$_{\text{HiPco}}$ thin film does not shift significantly from that in the free **1a** thin film, indicating that the $\pi$-conjugation of **1a** is largely unchanged.[6f] If the polymer wrapped the nanotube, one would expect a blue shift of **1a**'s lowest energy absorption band because of interruption of the $\pi$-conjugation. The thin film visible and near-IR spectroscopy[6f] of **1a**-SWNTs$_{\text{HiPco}}$ are very similar to those of pristine SWNTs$_{\text{HiPco}}$, indicating that the electronic structures of SWNTs$_{\text{HiPco}}$ are basically intact after polymer complexation. The charge-transfer interaction in **1a**-SWNTs$_{\text{HiPco}}$ is believed to be insignificant on the basis of both absorption[6f] and Raman spectra.[6g]

The transmission electron microscopy (TEM) shows that the majority of SWNTs in **1a**-SWNTs$_{\text{laser}}$ and **1a**-SWNTs$_{\text{arc}}$ are small ropes (2−6 nm),[6f] whereas the majority of SWNTs in **1a**-SWNTs$_{\text{HiPco}}$ are irregular and regular nanoribbon assemblies of small ropes.[6f] The observation of a twisted SWNT nanoribbon on a TEM grid surface is indicative of the robustness of such two-dimensional (2-D) assemblies and further supports a $\pi$-stacking interaction with the polymer backbone oriented along the nanotube long axis. The "Bucky paper" formed from the PPE-SWNTs$_{\text{HiPco}}$ complex shows qualitatively improved mechanical properties over previous bucky paper.[1a] It seems that PPE may increase the adhesion between nanotubes, via better $\pi-\pi$ interactions, so that the resulting bucky paper dissolves more slowly in CHCl$_3$. It should be possible to prevent such 2-D assembly and obtain small ropes and/or individual SWNTs$_{\text{HiPco}}$ by using PPE with bulky and/or ionic functional groups[1d] in the end of the side chain. For applications that require high nanotube concentration (for example, polymer composites), using PPE-SWNTs ($R = 0.4$) solution that is prepared in situ without filtration is recommended. The detailed nature of the $\pi-\pi$ interaction between PPE and different SWNTs requires further studies.

**Supporting Information Available:** The thin film vis-NIR spectra of **1a** and **1a**-SWNTs$_{\text{HiPco}}$; TEM and SEM images of **1a**-SWNTs (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) The new polymers (**1a**, $n_{\text{average}} = 19.5$ and $n_{\text{average}} = 13$; **1b**, $n_{\text{average}} = 19$; **1c**, $n_{\text{average}} = 19$) and known polymers (**2**, $n_{\text{average}} = 16$ and $n_{\text{average}} = 10$) were synthesized and characterized according to literature method[4] (Liu, H.-Y.; et al., manuscript in preparation). Three types of SWNTs were used in this study: (1) purified HiPco-SWNTs (SWNTs$_{\text{HiPco}}$, Carbon Nanotechnologies, Inc.); (2) purified laser-grown SWNTs (SWNTs$_{\text{laser}}$); (3) purified electric arc-grown SWNTs (SWNTs$_{\text{arc}}$). Typical preparation procedure for **1a**-SWNTs$_{\text{HiPco}}$ complex: 14.7 mg of SWNTs$_{\text{HiPco}}$ was sonicated in 29.4 mL of CHCl$_3$ for 30 min to give an unstable suspension of visible insoluble solids. Next 14.7 mg of **1a** was added, and most of the visible insoluble solids became soluble simply by vigorous shaking. The resulting solution was further sonicated for 10−30 min to give a black-colored stable solution with no detectable solid precipitation for over 10 days. The product was collected by PTFE membrane filtration (0.2−0.8 $\mu$m pore size), washed with CHCl$_3$, and dried at room temperature under vacuum to give 20.6 mg of free-standing black solid film (bucky paper). The procedures for **2**-SWNTs$_{\text{HiPco}}$, **1c**-SWNTs$_{\text{HiPco}}$, **1b**-SWNTs$_{\text{HiPco}}$, **1a**-SWNTs$_{\text{laser}}$, and **1a**-SWNTs$_{\text{arc}}$ are similar except that slightly longer sonication is required in the case of the later three complexes. The as-prepared SWNTs$_{\text{HiPco}}$ and CVD-grown multiwalled carbon nanotubes (MWNTs) can also be solubilized in CHCl$_3$ by a similar procedure.

(6) (a) The purified SWNTs$_{\text{HiPco}}$'s solubility in CHCl$_3$ is less than 0.03 mg/mL,[1f] and the purified SWNTs$_{\text{laser}}$ and SWNTs$_{\text{arc}}$ are insoluble in CHCl$_3$. (b) The $R$ data in three **1a**:SWNTs$_{\text{HiPco}}$ reactions are as follows: (1) $R_{\text{initial}} = 1.00$, $R_{\text{final}} = 0.40$; (2) $R_{\text{initial}} = 0.40$, $R_{\text{final}} = 0.38$; (3) $R_{\text{initial}} = 0.40$, $R_{\text{final}} = 0.39$. (c) Dalton, A., personal communication. (d) The **1a**$_{n=1.5}$-SWNT$_{(6,6)}$ complex's structure was fully optimized using the UFF empirical potential developed by Rappe et al. (*J. Am. Chem. Soc.* **1992**, *114*, 100024). (e) Because of the presence of trace water,[2b] we cannot determine the chemical shift of the C$_2$ group. (f) See Supporting Information. (g) Weimer, W. A.; et al., unpublished results.

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