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Novel Strategy for Diameter-Selective Separation and Functionalization of Single-Wall Carbon Nanotubes

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ABSTRACT

The problem of separating single-wall carbon nanotubes (CNTs) by diameter and/or chirality is one of the greatest impediments toward the widespread application of these promising materials in nanoelectronics. In this paper, we describe a novel physical–chemical method for diameter-selective CNT separation that is both simple and effective and that allows up-scaling to large volumes at modest cost. Separation is based on size-selective noncovalent matching of an appropriate anchor molecule to the wall of the CNT, enabling suspension of the CNTs in solvents in which they would otherwise not be soluble. We demonstrate size-selective separation in the 1–2 nm diameter range using easily synthesized oligo-acene adducts as a diameter-selective molecular anchor. CNT field effect transistors fabricated from diameter-selected CNTs show markedly improved electrical properties as compared to nonselected CNTs.

Single-wall carbon nanotubes (CNTs) have shown great promise for application in novel nanoelectronic devices, including field-effect transistors,[1−3] memory elements,[4,5] and sensors.[6−8] The electronic properties of CNTs, however, depend strongly on diameter and chirality. Chirality controls whether the CNT is metallic or semiconducting.[9] For semiconducting tubes, the band gap scales approximately with the inverse of the diameter. It was shown recently[10] that diameter plays a key role in the electronic properties of carbon nanotube field effect transistors (CNTFETs) with the on-current of the CNTFET varying by up to 5 orders of magnitude depending on the CNT band gap. For practical applications of CNTFETs, it will be imperative to tightly control the electrical characteristics and therefore the diameter distribution of the source material.

Efforts to separate CNTs by diameter and chirality have met with mixed success. Various strategies have been pursued to separate metallic and semiconducting nanotubes. For instance, enrichment of metallic nanotubes by reaction of carbon nanotubes with amines[11] or diazonium compounds,[12] which react at a faster rate with metallic nanotubes, have been reported, providing a path toward removing metallic tubes from a sample. Other approaches involve complexation with polymers, including single-stranded DNA.[13] Alternatively, ultracentrifugation can be used to separate CNTs by diameter. Recently, Arnold et al. demonstrated diameter selective separation in density gradient ultracentrifugation but only in rather limited quantitities.[14]

Here, we will present a very different approach, utilizing size matching of so-called molecular tweezer or “anchor molecules” to the diameter of the nanotube, and it is based on the arene−arene ($\pi-\pi$) interaction of carbon nanotubes with condensed aromatic compounds to form a host−guest pair, similar to interaction with fullerenes, which has been reported.[15] There are several important ingredients to this approach: (1) The anchor molecule must have a three-dimensional shape that makes it suitable for effective interaction with the tubular shape of the CNT; (2) The interaction must be sufficiently strong to provide an effective coupling, yet not so strong that it cannot be easily undone; (3) The anchor molecule must provide for additional functionalities that enable solubility in a variety of solvents; (4) Ideally, the anchor molecule will also provide opportunities for doping, selective placement, etc.

This list of requirements appears quite daunting, yet we have identified a novel strategy for diameter-selective separation based on simple anchor molecules that embodies most of these requirements. Used in conjunction with methods to separate metallic and semiconducting CNTs, this new method will be very powerful for obtaining either purely metallic or semiconducting nanotubes over a small range of diameters in significant quantities.

Figure 1 shows a simple schematic that captures the key ingredients of this strategy. The anchor molecule is shaped like a folded ribbon such that it fits well to CNTs at an optimum diameter but not well to either larger or smaller diameter tubes. The tail of the anchor molecule provides

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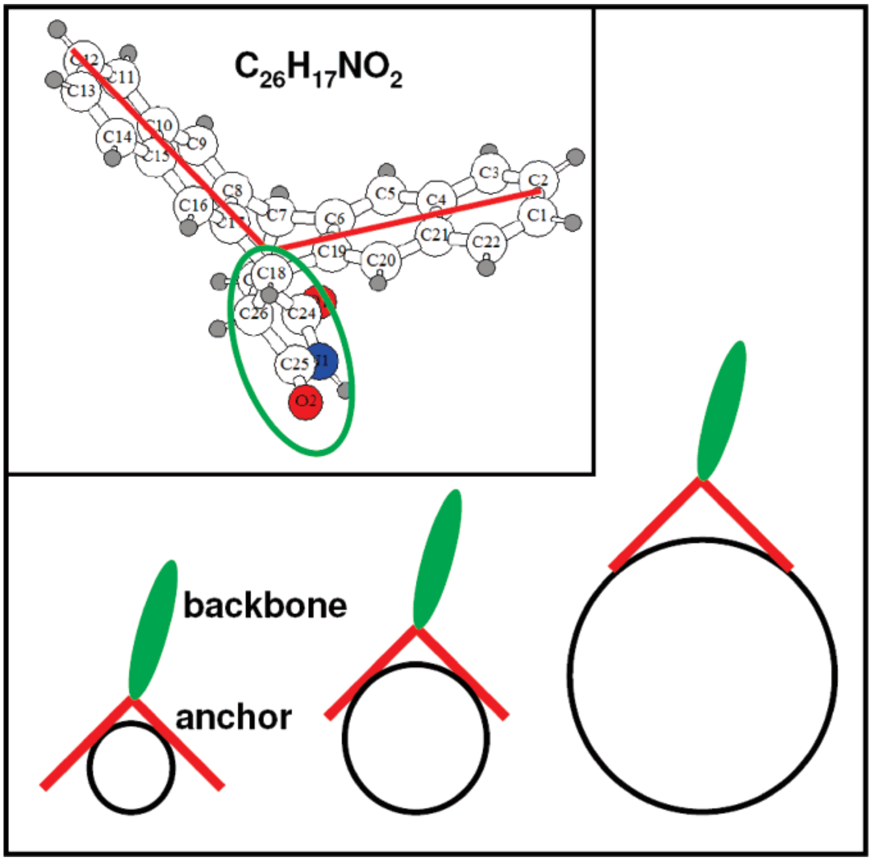


Figure 1. Schematic representation of the interaction of a molecular anchor with different diameter CNTs. The optimal overlap between anchor and nanotube depends on the dimensions of both. For larger diameter tubes, the overlap can disappear completely. The backbone provides a range of functionalities such as solubility, sensitivity to light, doping, molecular recognition, etc. The inset shows the structure of $C_{26}H_{17}NO_2$ as determined by X-ray diffraction.

solubility, as well as the potential for attachment of functional groups that allow selective interaction with other moieties such as surfaces, proteins, and DNA sequences. Of course the critical part of the molecule is the entity that provides the diameter-selective anchor to the CNT. For this we have turned to a class of materials that is well known from the field of organic chemistry, specifically Diels-Alder adducts of acenes, which are easily prepared in a 2:4 reaction of acenes and dienophiles. The tweezer molecule of our choice, $C_{26}H_{17}NO_2$, was prepared simply by heating a mixture of pentacene and maleimide in toluene at 180 °C in a sealed tube, and its structure, as determined by X-ray diffraction, is shown in the inset of Figure 1.[16] It has the shape of a folded ribbon with a folding angle of 126.5°. The two arms of the ribbons consist of two fused conjugated carbon rings, each of which are expected to interact with the CNT by π-stacking. The end-to-end distance of the outer carbon atoms in the anchor is 1.1 nm (C1−C12 in Figure 1). The backbone to the molecule, maleimide, is particularly simple in this case but can be replaced with a large variety of other molecular moieties to provide a plurality of different functions, including photosensitivity, solubility in different solvents, and selective adsorption.

To establish that this molecule interacts with CNTs, we have attempted to make CNT suspensions in solvents in which CNTs normally have very low solubility. For this purpose, the pentacene−maleimide adduct was N-alkylated with 11-bromoundecanol to form a highly soluble N-alkylated product (Scheme 1). Sonication of CNTs in toluene does not result in a stable suspension. But sonication (Bransonic 5200, 47 kHz, 20−30 min) of 2 mg of CNT in 15 mL of toluene containing 60 mg of the alkylated adduct enables a portion of the CNTs to readily go into suspension. To assess the stability of the suspension, it was next subjected to centrifugation, which led to the separation of a fraction of the CNTs. Samples were prepared both from the suspended fraction and from the settled fraction by dropcasting mostly bundled CNTs onto quartz substrates and analyzed by Raman scattering.[17] Figure 2a,b shows Raman spectra obtained over a range of excitation wavelengths for both the precipitate and the solution after centrifugation. In the precipitate spectra (Figure 2a), we see strong peaks in the excitation energy range of 1.6−1.8 eV, characteristic of CNTs with diameters around 1.6 nm, which are strongly suppressed in the solution spectra (Figure 2b).

Conversely, the solution spectra (Figure 2b) show significant spectral intensity for excitation energies of 1.4−1.5 eV (diameters around 1.15 nm), which are strongly suppressed in the precipitate spectra. Clearly, the precipitate is enriched in larger diameter tubes, while the solution retains an abundance of smaller diameters, indicating the interaction

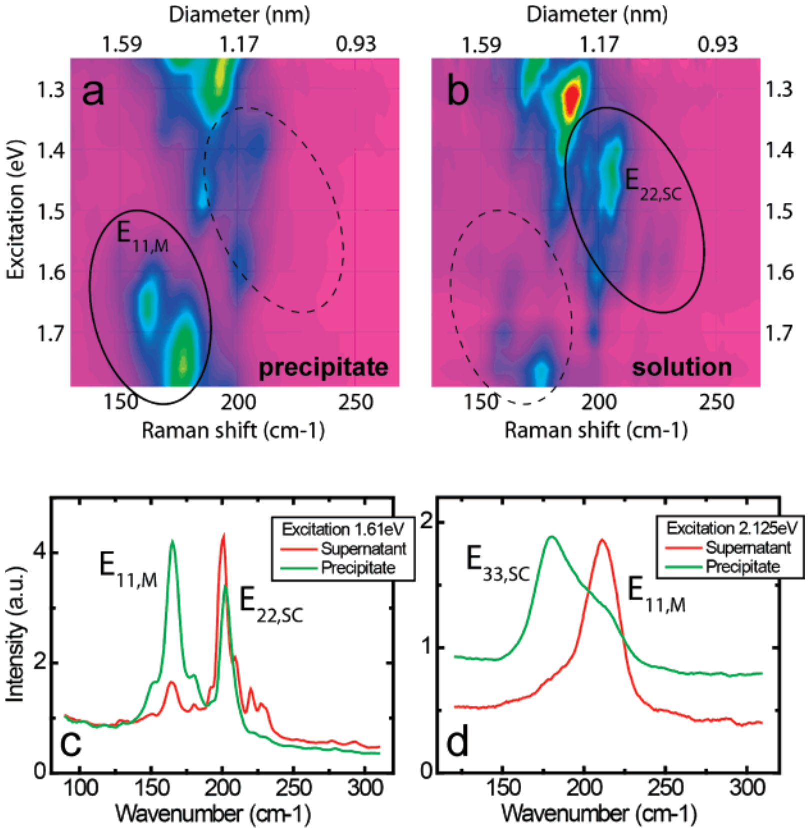
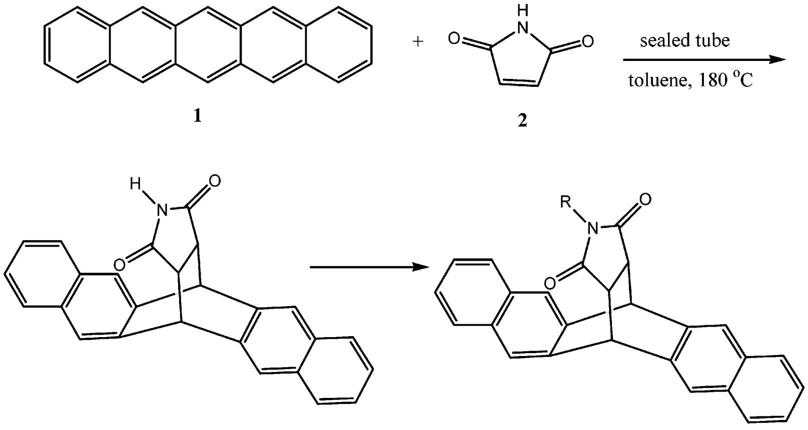


Figure 2. Raman spectra of CNT samples obtained by complexation with a pentacene Diels-Alders adduct and centrifugation. The precipitate (a) is enriched in large diameter nanotubes (diameter >1.2 nm), while the supernatant solution (b) is enriched in smaller diameters. Line spectra at selected excitation wavelengths (c,d) show selective enrichment by as much as a factor 10 after a single selection cycle.

Scheme 1. Schematic of Preparation of the Pentacene-Based Molecular Tweezer



1

2

3

4, R = Br(CH2)11-

of the alkylated adduct with CNTs with diameters smaller than ~1.3 nm.

Two representative Raman spectra are shown in Figures 2c,d. Figure 2c, obtained at an excitation wavelength of 1.61 eV, shows a strong peak at ~160 /cm in the precipitate labeled $E_{11,M}$, which is attenuated by about a factor 10 in the solution. Note that the peak at ~210/cm ($E_{22,SC}$) is virtually unaffected. Similarly, Figure 2d shows a strong peak at ~175/cm in the precipitate ($E_{33,SC}$) that is strongly attenuated in the solution, while the peak at ~220/cm ($E_{11,M}$) is dominant in the solution but almost absent in the precipitate. Thus, we observe very strong diameter-dependent separation of CNTs in a solvent in which all CNT would normally be insoluble. Notice that while the separation is sensitive to diameter, it is not selective to the electronic nature of the nanotube, that is, both metallic and semiconducting nanotubes in the 1.2 nm diameter range are enriched in the solution, while larger nanotubes are depleted. Additional experiments were performed with much smaller molecular anchors based on analogous N-alkylated adduct of anthracene and maleimide. In this case, the end-to-end spacing in anthracene−maleimide adduct is only 0.5 nm, which is too small to effectively interact with CNTs of any diameter, and indeed we observe no improvement in the

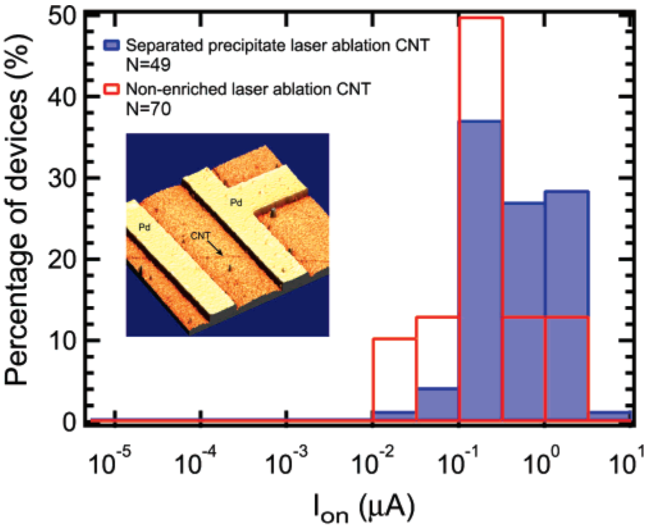


Figure 3. Statistics of the CNTFET on-current (saturation current in on-condition) for nonenriched laser ablated CNTs (yellow) and large diameter-enriched laser-ablated CNTs (blue). A strong reduction is observed in devices with on-currents below 10^{-7} A, while devices with on-currents in the 10^{-6} A range are enhanced. The inset shows an atomic force microscopy image of the device geometry.

solubility of CNTs upon addition of N-alkylated anthracene-based materials to the solvent. However, we anticipate that these anthracene-based adducts may be useful for interaction with and functionalization of smaller fullerenes including C60 and C70. Heptacene-based precursors (seven rings) have a larger end-to-end spacing, enabling interaction with larger diameter CNTs. We have synthesized an example of such molecules, but because this molecule is only sparingly soluble in common organic solvents, it could not be used for separation of larger diameter CNTs. These are only three examples of a much larger family of molecular anchors with a folded molecular plane and extended π-systems, which can be used for separation and/or functionalization of carbon nanotubes.

To assess the impact of the use of diameter-selected tubes on the performance of simple electronic devices we have fabricated CNTFETs from both large diameter enriched and nonenriched CNT samples. On the basis of previous work, one would expect the larger diameter nanotubes (sediment after ultracentrifugation) to exhibit larger on-currents than the smaller ones, as the smaller bandgaps of larger tubes reduce the injection barrier at the source contact. A statistical comparison is shown in Figure 3 for 49 enriched and 70 nonenriched devices. Devices were fabricated on heavily p-doped Si substrates with a 10 nm thick SiO_2 gate dielectric thin film. Forty nanometer thick Pd source and drain contacts were defined on top of the CNT with a spacing of 300 nm as shown in the inset in Figure 3. While the nonenriched samples show a strong peak at $\sim 10^{-7}$ A, the enriched samples show a remarkable shift to much higher on-currents, as well as strong reduction at small on-currents, indicating improved device performance after nanotube separation and enrichment in larger diameters. All results shown here were obtained after single enrichment cycles, that is, one iteration of solution, centrifugation, and separation. Even with this single cycle, we observe selective enrichment by as much as a factor 10 (see Figure 2c,d). We anticipate that the selectivity can be further improved by repeated enrichment cycles, either with the same Diels-Alders adduct or by using a progressive sequence of adducts that allows selection of nanotubes over a varying range of diameters. Because the binding between the molecular anchors and the CNTs is rather weak, removal of the anchors by annealing is straightforward. Pentacene-related fluorescence is readily apparent in functionalized nanotubes but is easily removed by annealing the substrate at 500 °C for 1 min.

The molecular group that forms the tail attached to the anchor group is worth further attention. In the present study, it was chosen to enhance solubility. But it can incorporate almost any functionality of interest, including doping, optical response, and attachment selectivity (DNA, protein, etc). For instance, a short single-stranded DNA sequence may allow the self-assembly of CNT supramolecular assemblies, such as ribbons, or may enable their binding to preprogrammed surface sites for self-assembly of CNT integrated circuits, sensors, etc.

In conclusion, we have presented a novel general strategy for diameter-selective separation and functionalization of single-wall carbon nanotubes. The method proposed and demonstrated here will enable the rational design of a broad variety of molecular anchors and functional backbones with excellent diameter selectivity. If so desired, the present method may be combined with complementary techniques to separate semiconducting and metallic CNTs.[11−14,18]

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References

(1) Avouris, Ph. *MRS Bull.* **2004**, *29*, 403.
(2) Bachtold, A. et al. *Science* **2001**, *294*, 1317
(3) Javey, A. et al. *Nano Lett.* **2004**, *4*, 447.
(4) Cui, J. B. et al. *Appl. Phys. Lett.* **2002**, *81*, 3260.
(5) Radosavljevic, M. et al. *Nano Lett.* **2002**, *2*, 761.
(6) Zhang, Y. et al. *J. Phys. Chem. B* **2006**, *110*, 4671.
(7) Tang, X. et al. *Nano Lett.* **2006**, *6*, 1632.
(8) Kong, J. et al. *Science* **2000**, *287*, 622.
(9) Zhou, C. et al. *Phys. Rev. Lett.* **2000**, *84*, 5604.
(10) Chen, Z. et al. *Nano Lett.* **2005**, *5*, 1497.
(11) Maeda, Y. et al. *J. Am. Chem. Soc.* **2005**, *127*, 10287.
(12) (a) Strano, M. S. et al. *Science* **2003**, *301*, 1519. (b) Kim, W.-J. et al. *Chem. Mater.* **2007**, *19*, 1571.
(13) Strano, M. S. et al. *Nano Lett.* **2004**, *4*, 543.
(14) Arnolds, M. S. et al. *Nat. Nanotechnol.* **2006**, *1*, 60.
(15) Sugula, A. et al. *J. Am. Chem. Soc.* **2007**, *129*, 3842.
(16) Mitzi, D. B.; Afzali, A. *Cryst. Growth Des.* **2007**, *7*, 691.
(17) Kataura, H. et al. *Synth. Met.* **1999**, *103*, 2555
(18) (a) Peng, X. et al. *Nat. Nanotechnol.* **2007**, *2*, 361. (b) Nishi, A. et al. *Nat. Nanotechnol.* **2007**, *2*, 640.

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