Diminished Band-Gap Transitions of Single-Walled Carbon Nanotubes in Complexation with Aromatic Molecules

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The electronic and optical properties of single-walled carbon nanotubes (SWNTs) have been investigated by many research groups.[1−5] It is now well-established that the electronic structures of semiconducting SWNTs are characterized by several pairs of van Hove singularities in the electronic density of states.[3,4] Transitions associated with the first (S_{11}) and second (S_{22}) singularity pairs are widely observed in absorption spectra of SWNT samples produced by various methods and thus of different diameters and diameter distributions.[4,5] It has also been reported that the doping of the SWNT surface could have a significant effect on the S_{11} absorption,[4,6−8] and more dramatically that the surface modification via chemical functionalization could effectively eliminate the S_{11} and S_{22} absorption bands.[9] The latter was attributed to significant perturbations in the electronic structure by the surface modification and a disruption to the extended π-network of the nanotube.[9] We report here that a similarly significant effect on the van Hove singularity pairs can be caused by non-covalent complexation of the nanotube with planar aromatic molecules such as pyrenes in solution, resulting in the absence of S_{11} and S_{22} bands in the near-IR absorption spectrum. Since the complexation is reversible, the characteristic absorption bands can be turned on and off with the complexation in a reversible fashion.

The attachment of pyrene and other aromatic species to the carbon nanotube surface via non-covalent interactions ("$\pi-\pi$ stacking") has already been reported in the literature.[10−17] In this work, we synthesized a pyrene derivative with a long alkyl tail, 1-docosyloxymethyl-pyrene (DomP), for the solubilization of SWNTs via non-covalent interactions. Details on the synthesis and characterization of DomP are provided in the Supporting Information.

In the solubilization of SWNTs with DomP, a purified SWNT sample (150 mg)[18] was added to a THF solution of DomP (10 mg/mL, 30 mL). The mixture was sonicated (Fisher Scientific FS 20, 70 W, 42 kHz) for 24 h, followed by centrifuging at 3000g for 20 min. The solid residue was used as the starting material to undergo another round of sonication−centrifuging under the same experimental conditions. The solution in THF thus obtained was centrifuged at a higher speed (Eppendorf Centrifuge 5417R, 25000g) for 3 h. The apparently homogeneous supernatant contained an equivalent of about 22 mg of SWNTs, namely that the non-covalent SWNT−DomP interactions kept about 15% of the starting SWNT sample in solution without precipitation even in such a strong centrifuging field (25000g).

The supernatant containing the solubilized SWNTs and the entire DomP sample was used to prepare specimen for Raman spectroscopy (785 nm excitation) as well as scanning (STEM, Hitachi HD-2000) and high-resolution transmission electron microscopy (HR-TEM, Hitachi HF-2000) characterizations. The Raman results are typical of SWNTs (after removal of DomP), and the electron
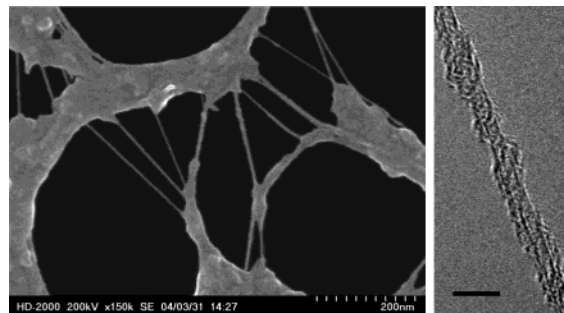

Figure 1. Typical STEM image (acquired in the SE mode) and HR-TEM image (scale bar = 5 nm) of the DomP-solubilized SWNT sample.
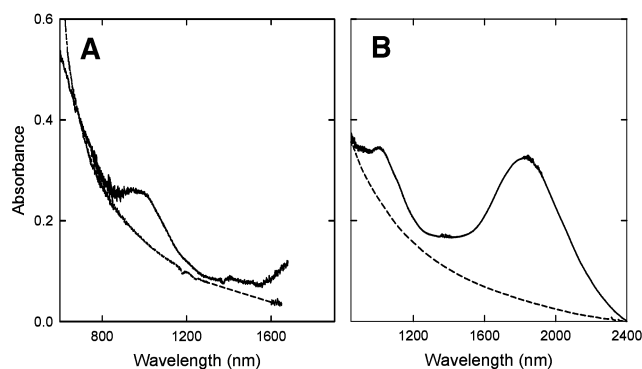

Figure 2. (A) Absorption spectra of the DomP-solubilized SWNT sample in THF (- - -) and in D_2O/SDS suspension after the removal of DomP via dialysis (—), with the nanotube-equivalent concentration in the former being at least 5 times higher than that in the latter. (B) Similarly, absorption spectra of the sample in the solid state before (- - -) and after (—) the removal of DomP.

microscopy images exhibit composite-like morphology with clear evidence for the substantial presence of exfoliated SWNTs (Figure 1).

The THF solution of the DomP-solubilized SWNTs in the presence of DomP was used in absorption measurements. The nanotube equivalent concentration in the solution was 0.7 mg/mL, with the DomP concentration of 8.8 mg/mL. While the nanotube equivalent concentration was relatively high, there were no S_{11} and S_{22} bands in the observed vis/near-IR absorption spectrum (Figure 2A). The same solution was dropped onto a glass slide to evaporate off the solvent THF. The absorption spectrum of the sample (SWNTs with DomP) in the solid state also exhibited no S_{11} and S_{22} bands (Figure 2B). On the other hand, the deposition of an equivalent amount of purified SWNT sample without DomP on the same substrate allows ready observation of the characteristic S_{11} and S_{22} transitions at 1850 and 1030 nm, respectively.

Scheme 1

DomP   DomP-SWNT
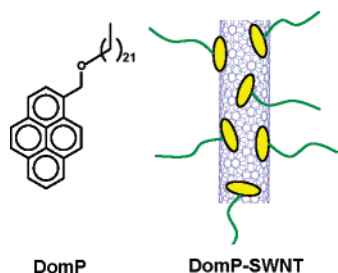
The absence of the S_{11} and S_{22} absorption bands for SWNTs in the solution with DomP may be attributed to effects associated with the complexation of the nanotube with DomP species, which is responsible for the nanotube solubilization. Such complexation is likely based on the non-covalent attachment of the planar pyrene moiety in DomP to the nanotube surface (Scheme 1),[10,11] and thus reversible under different experimental conditions. In order to remove the attached DomP species from the nanotube surface, the solution of SWNTs with DomP was treated in two different ways. One was to transfer the solution into a polyvinylidene fluoride (PVDF) membrane tubing (cutoff molecular weight ∼250 000, Spectrum Laboratories) for dialysis against THF until the disappearance of the characteristic pyrene absorption peaks at 330−350 nm. As a result of the DomP removal in the dialysis, most of the nanotubes precipitated out of the solution. The other way was to reflux the SWNT−DomP sample with cyclohexane for 12 h, followed by repeated cycles of cyclohexane washing−vigorous centrifuging. The solid residue contained primarily the recovered nanotubes according to thermogravimetric analysis. Both treatments were purposely designed to be under relatively mild experimental conditions so as not to invoke any processes for defunctionalizing covalently attached species. The successful removal of DomP from the nanotube in both treatments lends strong support to the conclusion that the complexation is non-covalent in nature. As expected, the recovered SWNTs exhibit the characteristic S_{11} and S_{22} absorption bands (Figure 2). These results suggest that the diminished band-gap transitions of semiconducting SWNTs are due to the non-covalent complexation and that the effect on the transitions is reversible in accordance with the reversibility of the complexation.

It is known in the literature that the doping of SWNT surface could have a significant effect on the S_{11} absorption band, resulting in a reduction or even elimination in absorptivity, but much less effect on the S_{22} absorption band because of the higher energy.[8] So far, elimination of both S_{11} and S_{22} absorption bands can be achieved only via covalent chemical modification of the SWNT sidewalls.[9] Thus, it is often suggested that the solubilization of SWNTs by non-covalent techniques, such as those based on interactions with aromatic species, better preserves the nanotube electronic structures. The results reported here represent the first experimental demonstration that the non-covalent complexation of a semiconducting SWNT with aromatic molecules can also affect the nanotube electronic structures and the associated optical transitions in a dramatic fashion.

While the mechanism for such an effect is not clear, we suspect that the SWNT−DomP complexation via non-covalent interactions probably changes the nanotube's electronic density of states. Conceptually, a complex in which a SWNT is non-covalently covered by a layer of planar aromatic moieties (Scheme 1) may be viewed as a highly defective double-walled carbon nanotube

(DWNT), so that the electronic density of states may be significantly different from that in the naked SWNT. In fact, theoretical calculations have shown that, in a DWNT of small enough diameter, the electronic structure of the inner (semiconducting) tube could be strongly perturbed by the external layer, with energy gaps vanishing as a result of the overlap of the conductance and valence bands.[19] This is an interesting mechanistic issue for further experimental and theoretical investigations.

Recent reports based on calculations and transistor device measurements suggested the presence of charge-transfer effects in a SWNT adsorbed with small aromatic molecules.[13] The results presented here demonstrate that the electronic properties of SWNTs are indeed vulnerable to effects of planar aromatic moieties in a relatively strong and noninvasive fashion. Thus, there might be opportunities to manipulate or even control such properties for specific applications.

Supporting Information Available: Synthesis and absorption spectrum of DomP and other characterization results of DomP−SWNT. This material is available free of charge via the Internet at http://pubs.acs.org.

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