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Extraordinary Sensitivity of the Electronic Structure and Properties of Single-Walled Carbon Nanotubes to Molecular Charge-Transfer

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Interaction of single-walled carbon nanotubes with electron-donor and -acceptor molecules causes significant changes in the electronic and Raman spectra. Electron-donating molecules such as tetrathiafulvalene and aniline cause changes opposite to those caused by electron-withdrawing molecules such as nitrobenzene and tetracyanoethylene. Thus, a proportion of the semiconducting SWNTs becomes metallic on electron donation through molecular charge transfer. Electrical resistivity measurements reveal a systematic variation with electron-donating or -withdrawing power of the interacting molecules.

Single-walled carbon nanotubes (SWNTs) exhibit diverse electronic structure and properties arising from the quantization of electron wave vector of the 1D system.^{1–3} SWNTs exhibit significant changes in the electronic structure and chemical reactivity depending on the geometry, doping, chemical environment, and solvent. Electron or hole doping influences the electronic structure of SWNTs and thereby their Raman spectra,⁴ and electrochemical doping also causes similar effects.⁵ Interaction of SWNTs with gold and platinum nanoparticles can give rise to a semiconductor-to-metal transition.⁶ Furthermore, aromatic solvents containing electron donating and electron withdrawing groups have been shown to modify the electronic structure of the nanotubes giving rise to changes in the electrical properties.⁷ Clearly the electron transfer caused by the interaction of SWNTs with other molecules depends on the density of states near the Fermi level.⁸ We have investigated the interactions of various electron-withdrawing (nitrobenzene, tetracyanoquinodimethane (TCNQ), and tetracyanoethylene (TCNE)) and electron-donating (tetrathiafulvalene (TTF) and aniline) molecules with SWNTs to determine the sensitivity of their electronic structure and properties to molecular charge-transfer. We have investigated the effect of these donor and acceptor molecules as measured on both electronic and Raman spectra of the SWNTs. We have also measured the effect of the electron-donor and -acceptor molecules on the electrical resistivity of the SWNTs. It is found that donor and acceptor molecules induce opposite effects in the electronic and Raman spectra as well as in electrical resistivity.

SWNTs prepared by arc discharge using the $Y_2O_3 + Ni$ catalyst were purified by acid and hydrogen treatment following a previously reported procedure.⁹ In order to study the interaction of nitrobenzene and aniline, SWNTs were soaked in the

corresponding liquid placed on a glass slide for 1 h. The solids obtained after drying were examined by electronic absorption and Raman spectroscopies. Electronic spectra were recorded with thin films of SWNTs on a quartz plate. In order to study the interaction with TCNQ, TCNE, and TTF, the compounds were added to a suspension of SWNTs in toluene. The suspensions were drop-coated on glass or quartz plates and dried in vacuum. In order to compare the effects of the different donor and acceptor molecules, we employed interaction with benzene as a reference. Raman spectra were recorded with a LabRAM HR high-resolution Raman spectrometer (Horiba-Jobin Yvon) using a He–Ne laser ($\lambda = 632.8$ nm) on a clean glass slide. Electronic absorption spectra were recorded with a Perkin–Elmer UV/vis/NIR spectrometer.

In Figure 1, we show the S_{22} bands of SWNTs in the electronic absorption spectra. On interaction with nitrobenzene and aniline, the S_{22} band shifts in the opposite directions relative to the benzene reference. Thus, the positions of the S_{22} band maxima are 1010 and 1090 nm respectively on interaction with nitrobenzene and aniline, while the band maximum occurs at 1054 nm on interaction with benzene. Similarly, on interaction with TTF which is a good electron donor, the S_{22} band shifts to 1095 nm while with TCNE and TCNQ band shift to 990 and 1005 nm respectively.

Considering that the G-band of SWNTs in the Raman spectrum is highly sensitive to the electronic effects, we have examined the changes in the G-band position on interaction with the electron-withdrawing and -donating molecules. In Figure 2, we show the G-bands recorded with different chemical surroundings. The G-band maximum is shifted to 1582 and 1590 cm^{-1} respectively in the case of aniline and nitrobenzene, compared to 1585 cm^{-1} with benzene. These shifts are similar to those reported by Shin et al.⁷ Carbon nanotubes doped with boron and nitrogen produce shifts in the opposite directions, just as nitrobenzene and aniline. While boron doping (p-type) increases the G-band frequency, nitrogen doping (n-type)

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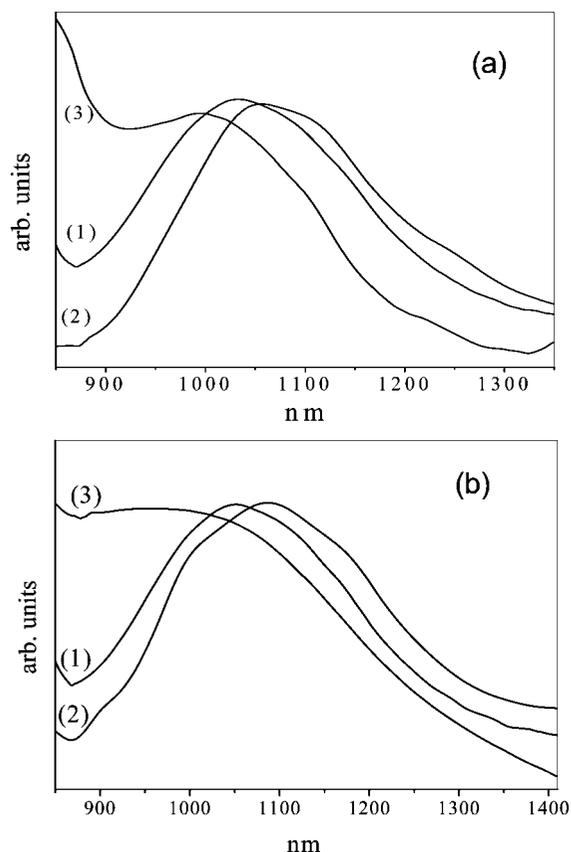


Figure 1. Electronic absorption spectra of SWNTs on interaction with electron donor and acceptor molecules: (a) (1) benzene, (2) aniline, and (3) nitrobenzene; (b) (1) benzene, (2) TTF, and (3) TCNE.

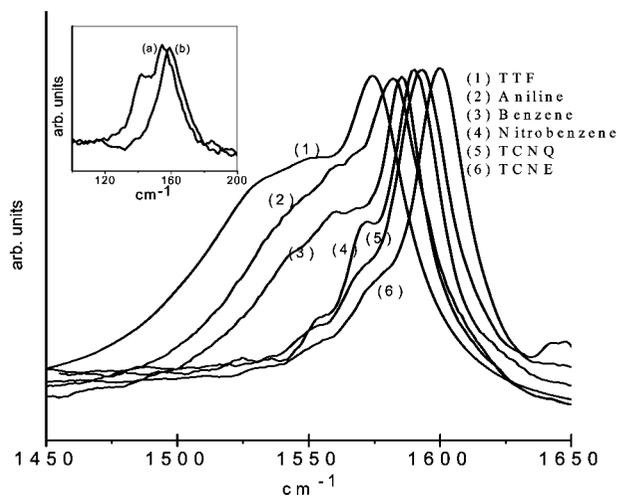


Figure 2. G-bands in the Raman spectra of SWNTs on interaction with electron donor and acceptor molecules. The inset shows RBM bands in the Raman spectra of SWNTs on interaction with (a) TTF and (b) TCNE.

decreases the G-band frequency. We, therefore, surmise that aniline causes n-type doping while nitrobenzene corresponds to p-type doping. Further, the G-band is shifted to 1574 cm^{-1} on interaction with TTF, while with TCNQ and TCNE the G-band maxima occur at 1593 and 1599 cm^{-1} respectively. These shifts are also consistent with the electron-donating or -withdrawing character of these molecules.

The Raman G-band of SWNTs exhibits a significant feature around 1540 cm^{-1} due to the metallic species.^{5,7} The Raman G-band can accordingly be deconvoluted to obtain approximate

estimates of the metallic species relative to the semiconducting species. The metallic feature in the G-band appears prominently on interaction of the SWNTs with aniline and TTF, but nearly disappears on interaction with nitrobenzene, TCNQ and TCNE. Clearly, the donor molecules increase the proportion of the metallic species by transforming the semiconducting species to the metallic species through electron donation. Electron withdrawing molecules, on the other hand, decrease the apparent proportion of the metallic species by withdrawing carriers from the metallic species. This conclusion is consistent with the observation of Shin et al.⁷ Thus, the percentage of metallic like species varies as $\text{TTF} > \text{aniline} > \text{benzene} > \text{nitrobenzene} > \text{TCNQ} > \text{TCNE}$. The percentage of the metallic species is estimated to be less than 10% on interaction with electron-withdrawing molecules, while it is in the range of 35–59% on interaction with electron-donating molecules.

We have followed changes in the G-band with the concentration of TTF and TCNE (Figure 3). In Figure 4a we have shown the variation of the position of the G-band maximum with the concentration of TTF and TCNE. We clearly see that shifts are in the opposite directions with TTF and TCNE. In Figure 4b, we have plotted the variation of full-width at half-maximum (fwhm) against the concentration of TTF and TCNE. The fwhm shows opposite trends with concentration in the case of TTF and TCNE. The variation shown in Figure 4 is also obtained with widths obtained by deconvoluting the G-band into metallic and semiconducting features. The spectra also show an increase in the intensity of the 1540 cm^{-1} feature due to the metallic species with an increase in TTF concentration and decrease in the intensity with an increase in TCNE concentration. These results demonstrate how carrier concentration is affected by the concentration of the electron donor and acceptor molecules.

We find that molecular charge-transfer also affects the Raman bands due to the radial breathing modes (RBM) of SWNTs. Although it is difficult to estimate the proportions of the metallic and semiconducting species by making use of the RBM bands, the occurrence of marked changes in the band shapes due to molecular charge transfer is noteworthy (see inset of Figure 2). We have found the electronic absorption spectra of the donor and acceptor molecules are also affected on interaction with SWNTs. Thus, the $\Pi-\Pi^*$ band of aniline is slightly red-shifted on interaction with SWNTs.

In order to carry out electrical resistivity measurements, vertical SWNT devices were fabricated in a porous anodic alumina (PAA) template,^{10–13} the process involves the deposition of a thin Ti layer on the surface of the wafer to serve as an electrical back-contact. Three subsequent metal layers, 100 nm Al, 1 nm Fe, and 500 nm Al, are then deposited onto the wafer. The Al layers are used to create a nanoporous template, while the thin middle layer (Fe) ultimately serves as the catalyst. The metal films and substrate are then submerged in an acid and anodized using a standard two-step technique. The anodization process forms self-assembled nanopores in the Al layer as it oxidizes and turns to PAA. After anodization, a microwave plasma chemical vapor deposition (MPCVD) system is used to create hydrogen plasma at a microwave power of 300 W and substrate temperature of $900\text{ }^\circ\text{C}$. The substrate is exposed to this plasma for 10 min to reductively open the bottom of the oxide layer. Methane gas is then introduced into the MPCVD chamber to provide a carbon source for growth of the nanotubes from the Fe catalyst on the pore wall. During this process, SWNTs grow with a typical density of one per pore. Subsequently, Pd is electrodeposited into the pore bottoms. Continued Pd electrodeposition past the establishment of bottom contacts

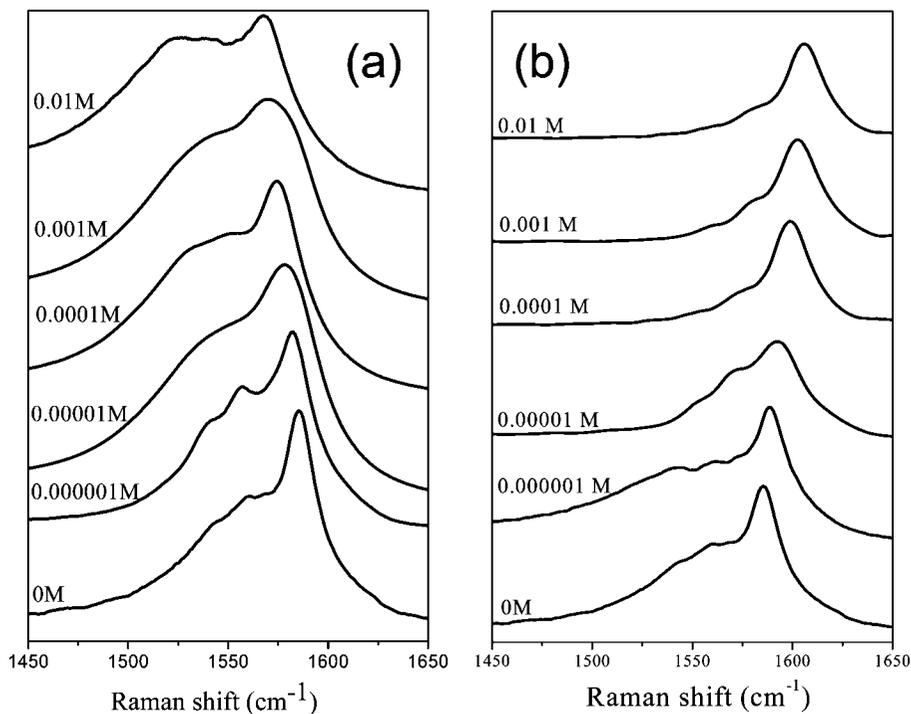


Figure 3. Shifts of the G-band of SWNTs on interaction with varying concentrations of (a) TTF and (b) TCNE.

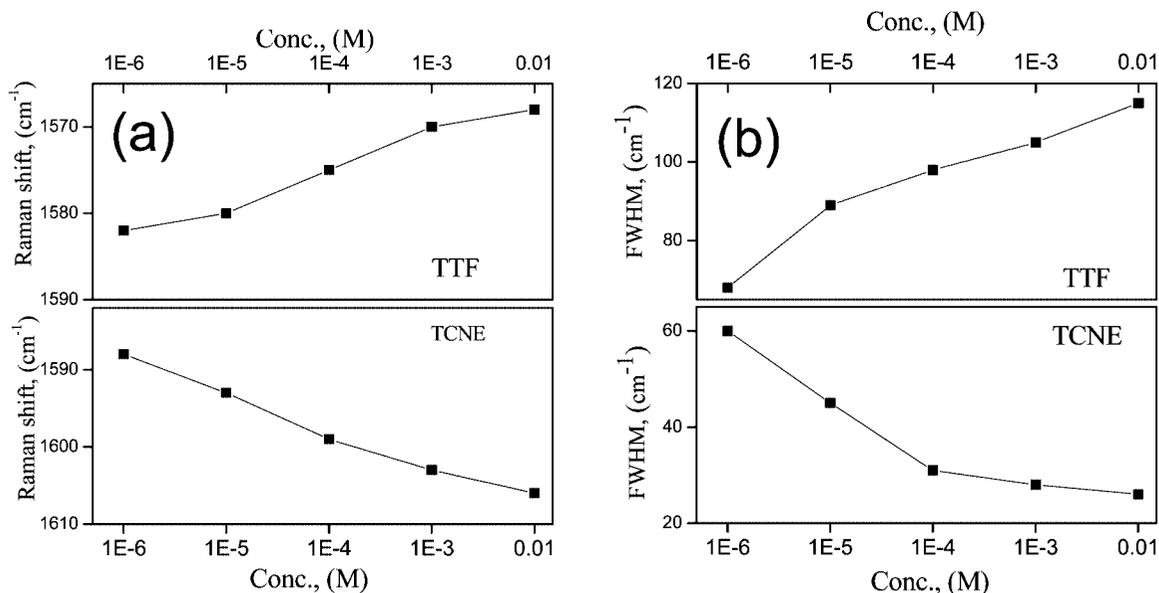


Figure 4. Variation of (a) the position and (b) the fwhm of G-band with the concentration of TTF and TCNE.

to SWNTs results in the formation of Pd nanoclusters that concentrically surround SWNTs on the top PAA surface.¹⁴ Many of the clusters exhibited cubic or a combination of cubic and pyramidal geometries. A thin layer consisting of Ti (~20 nm) and Au (~50 nm) was deposited by physical vapor deposition on top of the PAA membrane to achieve the top contact for the electrical resistivity measurements. Bottom contacts were taken from the Ti-coated Si substrates. The $I-V$ characteristics of this SWNT obtained by conducting AFM measurements exhibit a nearly linear behavior, establishing that the electrical contacts were well established. The $I-V$ characteristics of the SWNT bundle prepared as above and soaked in the liquids of electron-withdrawing and electron-donating molecules were measured using a Keithley 236 multimeter.

Figure 5 presents the $I-V$ characteristics of the SWNTs in air and in the presence of aniline, anisole, chlorobenzene and

nitrobenzene, with the inset showing the calculated resistance at a bias voltage of 0.05 V. The resistance of the SWNTs is 492 Ω in air at a bias voltage of 1 V. At a forward bias, the resistance decreases markedly in the presence of electron withdrawing molecules such as nitrobenzene and chlorobenzene, whereas it increases in the presence of electron donating molecules such as aniline and anisole. Thus, the relative values of resistance (compared to pure SWNTs) were 5.1 and 1.5 in the presence of aniline and anisole, respectively, at 1 V, the corresponding values in the presence of the chlorobenzene and nitrobenzene being 0.61 and 0.44, respectively. At a bias voltage of 0.05 V, the resistance of the SWNTs is 1.0 k Ω in air. In the presence of aniline, anisole, chlorobenzene and nitrobenzene, the relative values of resistance are 6.6, 1.7, 0.5, and 0.3, respectively. SWNTs under ambient conditions usually show p-type behavior.¹⁵ It is possible that, in the presence of electron-

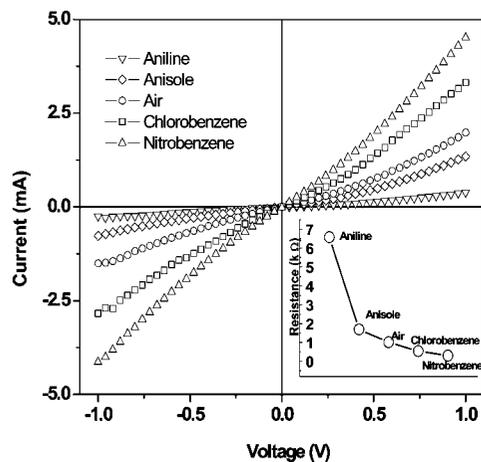


Figure 5. I – V characteristics of the SWNTs in air and in the presence of different aromatic molecules attached with electron-withdrawing and electron-donating groups.

donating molecules, the number of hole carriers is reduced, causing an increase in the resistance. In the presence of electron-withdrawing molecules, more holes are generated in semiconducting SWNTs. Interestingly, that the resistance varies proportionally with the Hammett substituent constants, the order being $\text{NH}_2 > \text{OCH}_3 > \text{Cl} > \text{NO}_2$. This trend reflects the changes in the nature and the concentration of carriers as well as their mobilities brought about by interaction with electron donor and acceptor molecules. The I – V curves become more nonlinear as one goes from aniline to nitrobenzene. The slope of the I – V curve also increases going from nitrobenzene to aniline, due to the presence of a higher proportion of metallic like nanotubes in the presence of aniline.

In conclusion, the present study establishes the high sensitivity of SWNTs to molecular charge-transfer. This feature of SWNTs may be useful in many of the applications such as sensors and nanoelectronics.

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