NANO LETTERS

2003
Vol. 3, No. 10
1421−1423

Interaction of Aromatic Compounds with Carbon Nanotubes: Correlation to the Hammett Parameter of the Substituent and Measured Carbon Nanotube FET Response

Alexander Star,* Tzong-Ru Han, Jean-Christophe P. Gabriel, Keith Bradley, and George Grüner†

Nanomix Inc., Emeryville, California 94608

Received August 20, 2003

ABSTRACT

We have used field-effect transistor (FET) devices with semiconducting single-walled carbon nanotubes (SWNTs) as the conducting channels to study interactions of aromatic compounds with SWNTs. Electronic detection occurs through charge-transfer effects, monitored as the change of the gate voltage (V_g) dependence of the source-drain current I_{sd}. For monosubstituted benzene compounds, we find that the shift of the $I_{sd} - V_g$ characteristic is proportional to the Hammett sigma values (σ_p) of their substituents.

Single-walled carbon nanotubes (SWNTs) have attracted much recent attention for a variety of potential applications.[1] SWNTs have been incorporated into electronic devices, and such devices can be modified by chemical functionalization of the carbon nanotubes. Aromatic compounds are known to interact strongly with graphitic sidewalls of SWNTs through effective $\pi-\pi$ stacking.[2] These interactions manifest in solubilization of SWNTs in aromatic solvents[3] as well as solubilization in solutions of certain aromatic surfactants[4] and polymers.[5] Moreover, polynuclear aromatic compounds, such as anthracene,[6] pyrene,[7] and phthalocyanine[8] derivatives, have been used for immobilization of chemical and biological molecules onto SWNTs. Whereas different spectroscopic methods have been used to characterize the interaction of aromatic compounds with SWNTs in solution or on the surface, various microscopies can characterize only immobilized species, but not aromatic compounds themselves. In this communication we demonstrate that electronic measurements of SWNTs can be used as a direct method to investigate the interactions of the aromatic compounds with carbon nanotubes.[9]

We have used field-effect transistors fabricated using semiconducting SWNTs (NTFETs).[10] Such devices have been recently explored as chemical[11] and biological[12] sensors. The response of the device characteristics to chemical analytes in the gas phase occurs through charge transfer between the nanotube conducting channel and the analytes, as evidenced by experiments involving electron donating (NH_3) and electron withdrawing (NO_2) molecules.[11b]

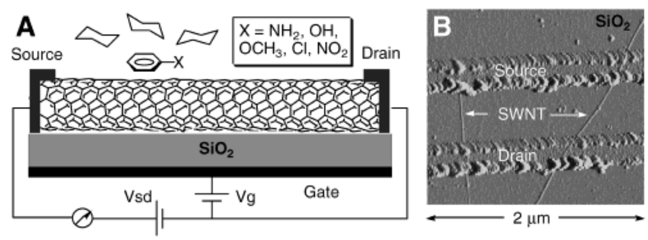

Figure 1. (A) Schematic view of a field-effect transistor device with a SWNT transducer contacted by two Ti/Au electrodes (source and drain) and a silicon back gate. SWNT conducting channel is exposed to cyclohexane solution of benzene derivatives. (b) Atomic force microscope (tapping mode) topograph of the actual nanotube device.

We have examined the effect of monosubstituted benzenes, such as aniline, phenol, anisole, toluene, chlorobenzene, and nitrobenzene on NTFET device characteristics. These aromatic compounds, presumably, all have similar geometry in their noncovalent binding to carbon nanotubes, but their substituents provide different inductive and resonance effects, and consequently their relative electron donating ($NH_2 > OH > OCH_3 > Cl > NO_2$) properties are well known.[13]

Figure 1A depicts the schematic layout of the NTFET device architecture. SWNTs on silicon substrates contacted with metal (Ti/Au) contacts, together with a doped Si back

* Corresponding author. E-mail: astar@nano.com.
† On leave from Department of Physics, University of California, Los Angeles.

10.1021/nl0346833 CCC: $25.00
Published on Web 09/20/2003

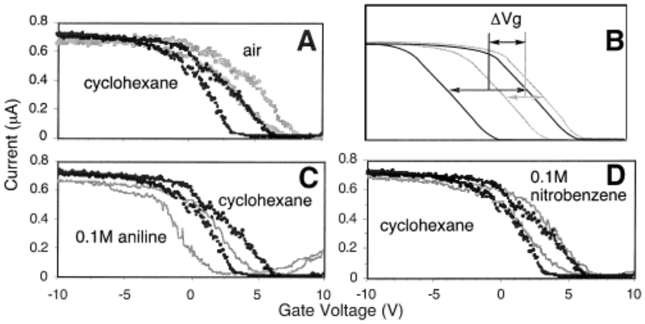

Figure 2. (A) The source-drain current−gate voltage dependence ($I_{sd}-V_g$) of a NTFET device in cyclohexane as compared to air. (B) Schematic $I_{sd}-V_g$ curves illustrating device characteristic at different conditions. The gate voltage shift (ΔV_g) is defined as indicated in the figure. (C, D) $I_{sd}-V_g$ curves for the device recorded in 0.1 M cyclohexane solutions of aniline and nitrobenzene as compared to pure cyclohexane. Device measurements in the presence of all aromatic compounds discussed in this study at 0.1 M concentrations in cyclohexane are presented as Supporting Information.

gate, form the basic elements of the NTFET. Multiple nanotubes connected the source and drain electrodes. Figure 1B shows an atomic force microscope image of a device with a number of nanotubes crossing the source and drain electrodes. We have monitored the change of the source−drain current (I_{sd}) as a function of the gate voltage (V_g) both with increasing and decreasing gate voltages. In devices that have a multitude of nanotubes, both metallic and semiconducting nanotubes contribute to the source−drain current. Here we report experiments on devices with only semiconducting nanotubes; such devices have near-zero I_{sd} for positive V_g values. A typical device characteristic in air is shown in Figure 2A. The devices display p-type behavior, known to be related to atmospheric oxygen on the device,[11a,14] and they also exhibit a small hysteresis which is related to a hydration layer.[15]

We have found that the NTFET device characteristics change significantly when one drop of 1 nM solution of the aromatic compound is air-dried on the device. However, drop casting on a device with a cross-section of only a few microns is not a reliable method for comparing the effects of various aromatic compounds. Therefore, we exposed NTFET devices to solutions of these compounds at the same concentrations and measured the device characteristics while in the solutions. As expected, the conductivity of the solvent plays an important role in device operation.[16] In liquids with low conductivity, such as cyclohexane, the device conductance is dominated by the nanotube channel. Consequently, the measured NTFET characteristic changes little compared to what is observed in air (Figure 2B). A small shift (approximately 2 V) to a more negative gate voltage is observed, and the device hysteresis (see below) is largely unaffected.

The devices were exposed to the solutions at concentrations of 0.1 M and 1M and in the following order: chlorobenzene, anisole, phenol, nitrobenzene, and, finally, aniline. After each measurement, the devices were rinsed with cyclohexane and chloroform and blown dry with N_2.

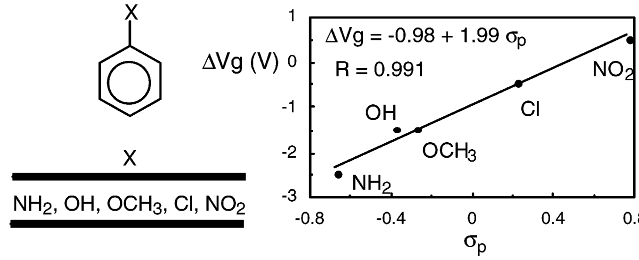

Figure 3. Linear regression analysis of the gate voltage shift (ΔV_g) of NTFET device in 0.1 M cyclohexane solutions of the selected aromatic compounds.

The measured characteristic in air was the same after each measurement and similar to what was found before the application of the solution.

Figure 2 shows the changes in device characteristic with exposure to cyclohexane solutions of representative aromatic hydrocarbons. Exposure to hydrocarbons leads to changes in the device characteristic. Depending on the compound, the $I_{sd}-V_g$ curve shifts toward more negative or more positive gate voltages. The hysteresis increases with concentration of aromatic hydrocarbons in the cyclohexane. To describe the change of the $I_{sd}-V_g$ characteristic, we define gate voltage shift (ΔV_g) as shown in Figure 2B. The hysteresis is defined as the difference of $I_{sd} = 1/2 I_{sd}$ (max), half the maximum value of I_{sd} (observed at −10 V gate voltage) for increasing and decreasing gate voltage at a gate sweep rate of 4 Hz between 10 V and +10 V. The midpoint of the hysteresis is the average voltage shift between the two curves at half the maximum value of I_{sd}. The gate voltage shift (ΔV_g) between the device characteristics for different devices is defined as the change in the midpoints of the hysteresis.

In analogy to what has been suggested for gas sensitivity in air,[11] it is conceivable, that the gate voltage shift is the result of charge transfer between the NTFET device and the aromatic molecules adsorbed onto the carbon nanotube conducting channel. The charge transfer between the monosubstituted benzenes and the nanotube can be estimated from their empirical Hammett σ constants, which are used widely for studying the rates and equilibria of organic reactions.[13] This parameter is defined as zero for benzene (X = H) and is related to the electron donating or electron withdrawing character of substituents (X) on the benzene ring. To establish the correlation between the change in device characteristic upon exposure to the aromatic compounds with various substituents and their Hammett constants, the gate voltage shifts (ΔV_g) were measured on the same device in cyclohexane (0.1 M).[16] As shown in Figure 3, gate voltage shifts correlate with the σ_p values. A clear, approximately linear relation with a positive slope (ρ value) of +1.99 is found between the gate voltage shift and the Hammett values. From Figure 3, zero shift (and correspondingly no charge-transfer between aromatic compound and nanotube) is observed for a benzene derivative with electron withdrawing groups (σ_p = 0.49). This is consistent with the presence of adsorbed electron withdrawing species O_2 on the device in ambient conditions.[10a,13]

Our experiments demonstrate that field effect transistor devices with semiconducting carbon nanotubes as conducting channels can be used as effective tools for the study of interactions of aromatic compounds with SWNTs. Moreover, quantitative information on charge transfer between the compounds and the SWNTs can be extracted. Thus, our observations may pave the way for sensitive electronic detection of chemical reactions in liquids.

Acknowledgment. We thank the technical staff at Nanomix for their assistance with device fabrication and measurements.

Supporting Information Available: Experimental details for NTFET device fabrication, measurement setup, solvent tests, aromatic compounds in cyclohexane, linear free energy relationship analysis, and table with correlation between hysteresis and gate voltage shift. This material is available free of charge via the Internet at http://pubs.acs.org.

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NL0346833