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Toward Quantifying the Electrostatic Transduction Mechanism in Carbon Nanotube Molecular Sensors

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Supporting Information

ABSTRACT: Despite the great promise of carbon nanotube field-effect transistors (CNT FETs) for applications in chemical and biochemical detection, a quantitative understanding of sensor responses is lacking. To explore the role of electrostatics in sensor transduction, experiments were conducted with a set of highly similar compounds designed to adsorb onto the CNT FET via a pyrene linker group and take on a set of known charge states under ambient conditions. Acidic and basic species were observed to induce threshold voltage shifts of opposite sign, consistent with gating of the CNT FET by local charges due to protonation or deprotonation of the pyrene compounds by interfacial water. The magnitude of the gate voltage shift was controlled by the distance between the charged group and the CNT. Additionally, functionalization with an uncharged pyrene compound showed a threshold shift ascribed to its molecular dipole moment. This work illustrates a method for producing CNT FETs with controlled values of the turnoff gate voltage, and more generally, these results will inform the development of quantitative models for the response of CNT FET chemical and biochemical sensors.

Single-walled carbon nanotubes (CNTs) have shown great promise for use as chemical sensors. Various surface modifications have been used to create nanoenabled, all-electronic vapor sensors,[1,2] electrochemical cells for small-molecule detection,[3,4] and fast electronics-based protein detection.[5−7] However, the detection mechanisms for these devices remain incompletely understood. Pyrene-containing compounds have been shown to adsorb specifically onto CNTs through π−π stacking, and this adsorption process has been measured in situ by electrochemical methods.[8] This makes the use of pyrene compounds ideal for exploring transduction mechanisms, since they provide a method to position known chemical groups precisely with respect to the nanotube sidewall.

Here, single-walled CNT field-effect transistors (CNT FETs) were functionalized with the pyrene compounds shown in Figure 1. The turnoff threshold voltage (i.e., the back-gate voltage required to suppress conduction in the FET) was measured for the functionalized devices and found to shift as the acid−base properties of the pyrene molecules were varied.

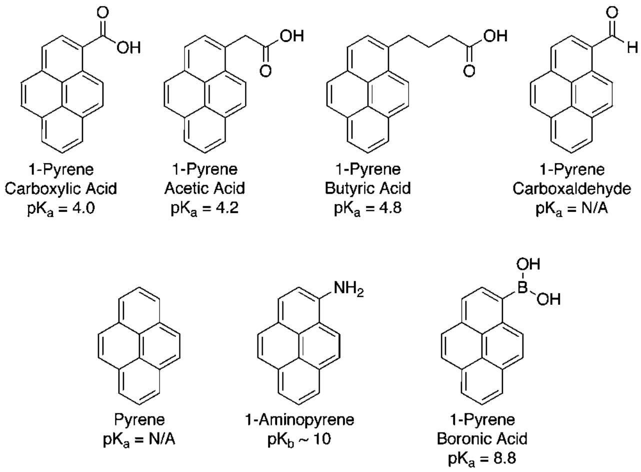

Figure 1. Pyrene compounds utilized in this work. Quoted values of pK_a and pK_b are from refs 10−14. Where actual pK_a values were not avaliable, values were estimated by comparison to those of related compounds: naphthylacetic acid for 1-pyreneacetic acid, naphthylamine for 1-aminopyrene, and phenylboronic acid for 1-pyreneboronic acid.

This shift was attributed to chemical (electrostatic) gating[9] of the CNT FET by protonated/deprotonated groups on the pyrene molecules. The size of the threshold voltage shift was controlled by the distance between the charged group and the CNT sidewall, leading to insights about the nature of the electrostatic interaction. Interestingly, a neutral compound induced a threshold gate voltage shift that was attributed to its intrinsic dipole moment. The magnitude of the observed threshold voltage shifts were in qualitative agreement with estimates of the charge densities associated with the adsorbed pyrene molecules. The work illustrates a practical functionalization scheme and shows how one could tailor the threshold voltage of CNT FETs by judicious choice of a compound. These results also help in building a quantitative understanding of electrostatic detection mechanisms in CNT FET molecular sensors.

Pyrene, 1-pyrenecarboxylic acid, 1-aminopyrene, and 1-pyreneacetic acid were purchased from Sigma-Aldrich; 1-

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pyrenebutyric acid and 1-pyrenecarboxaldehyde from Alfa Aesar; and 1-pyrene boronic acid from TCI. The solvent used for all solutions was high-purity acetonitrile (Honeywell Burdick & Jackson, 99.9% pesticide residue grade). All chemicals were used as received. To make solutions of various pyrenes, concentrated stock solutions (ca. 1 mM) were prepared by dissolving a small amount (ca. 5 mg) of each pyrene in 20.0 mL of CH_3CN. Several minutes of mixing using an ultrasonic bath were required to effect complete dissolution. The stock solutions were diluted to yield 5 μM pyrene solutions in CH_3CN.

CNT FETs were fabricated as described previously.[15] Briefly, CNTs were grown on Si/SiO_2 substrates by chemical vapor deposition at 900 °C using iron nanoparticles as the catalyst. Source−drain electrodes were patterned by photolithography and metallized with 3 nm Ti/40 nm Pd deposited in a thermal evaporator. After liftoff, devices were annealed in ambient atmosphere at 250 °C for 1 h to remove excess photoresist residue.[15] The underlying doped silicon substrate served as a global back gate in a three-terminal FET geometry.

The CNT FETs were characterized by measuring the source−drain current (I) as a function of gate voltage (V_G) at a bias voltage of 100 mV. Two criteria were used to select devices consisting of single semiconducting nanotubes for subsequent experiments: (1) devices dominated by hole conduction, with an ON/OFF ratio exceeding 100, and (2) device resistance in the range 100 kΩ to 2 MΩ. CNT FETs were functionalized by incubation in a solution of one of the pyrene compounds (5 μM in CH_3CN) for 2 h, rinsed for 5 min each in CH_3CN, isopropanol, and deionized water, and then blown dry with clean nitrogen. Previous work on pyrene adsorption onto glassy carbon[16] suggested that this process would lead to complete saturation of available pyrene binding sites; lower values of the pyrene solution concentration or functionalization time might in the future be used to fine-tune the density of adsorbed pyrene molecules. Samples were baked on a hot plate at 120 °C for 2 h to remove remaining solvents. Between 15 and 20 devices were functionalized by this process for each pyrene compound shown in Figure 1.

The effectiveness of the functionalization procedure was confirmed via atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). AFM images (Figure 2a,b) showed that the height of the CNTs increased by ca. 0.8 nm after functionalization, consistent with what would be expected from the interlayer spacing of a graphitic system[17] such as a CNT and an absorbed pyrene compound. The XPS spectrum of a device functionalized with 1-aminopyrene (Figure 2c) showed a peak at 287.0 eV indicative of the C−N bond of 1-aminopyrene bound on the CNT as well as peaks at 284.8 and 289.0 eV characteristic of C−C and C−O bonding, respectively. Consistent with expectations, samples of untreated CNTs, acetonitrile-treated CNTs, and bare SiO_2 treated with 1-aminopyrene did not show the C−N peak (Figure 2c).

Electrical measurements were performed after functionalization, and changes in the $I-V_G$ curve were noted, especially changes in the transistor threshold voltage (ΔV_T) (Figure 3). Functionalization with pyrene compounds had little effect on the CNT FET ON state resistance and hole carrier mobility, consistent with the intuition that noncovalent functionalization should not introduce significant carrier scattering. As discussed below, the results can be explained quantitatively by a picture in which the value of ΔV_T is determined by electrostatic chemical gating of the CNT FET by the adsorbed pyrene molecules.

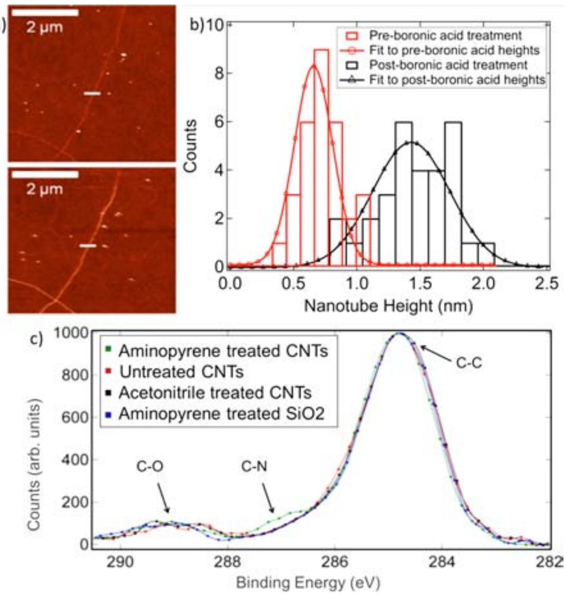

Figure 2. (a) AFM images of a CNT (top) before and (bottom) after treatment with 5 μM 1-pyreneboronic acid. The Z scale is 6 nm. (b) Histograms based on 30 line scans at the same positions before and after treatment with 1-pyreneboronic acid. The evident ca. 0.8 nm increase in height is attributed to the presence of adsorbed pyrene molecules. (c) XPS spectra under several sets of experimental conditions. The peak at 287.0 eV indicates the presence of C−N bonds in the sample of CNTs treated with 1-aminopyrene.

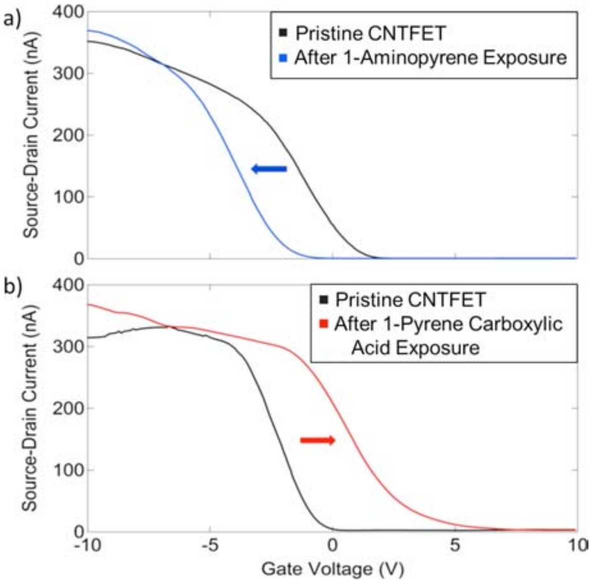

Figure 3. (a) $I-V_G$ plot for a CNT FET functionalized with 1-aminopyrene, showing a shift toward negative V_G. (b) Similar data for a device functionalized with 1-pyrenecarboxylic acid, showing a shift toward positive V_G.

Since a thin surface layer of water exists on CNT FET devices on SiO_2 under ambient atmosphere, its effect on the charge state of the adsorbed pyrene molecules must be considered. Recent work has demonstrated that silanol groups on the surface of SiO_2 cause near-surface water to be considerably more acidic than bulk water (by ca. 2 pH units).[18] Pyrene-functionalized CNT FET devices on SiO_2 are thus best understood as operating in a slightly acidic aqueous medium (ca. pH 5).

The observed values of ΔV_T are summarized in Figure 4; they were reproducible for each of the pyrene compounds tested. Adsorption of pyrene on the CNT FET led to a statistically insignificant shift in V_T (-0.2 ± 0.4 V); a similarly small shift was observed for 1-pyrenecarboxaldehyde (0.4 ± 0.4 V). These findings are consistent with the expectation that both compounds are in a neutral charge state under the experimental conditions and should have little or no effect on the $I(V_G)$ characteristic of the FET. The sign of ΔV_T was positive for each of the three pyrenecarboxylic acids tested and negative for 1-aminopyrene. These observations are consistent with the equilibrium constants listed in Figure 1. As the pK_a values for all of the pyrenecarboxylic acids are less than 5, most of the carboxylic acid functional groups should be deprotonated and negatively charged. The $I(V_G)$ characteristic is thus expected to shift to a more positive gate voltage ($\Delta V_T > 0$). Similarly, for 1-aminopyrene at pH 5, a fraction (ca. 10−15%) of the amine groups should be protonated, leading to a negative value of ΔV_T. The case of 1-pyreneboronic acid is unusual and will be discussed below.

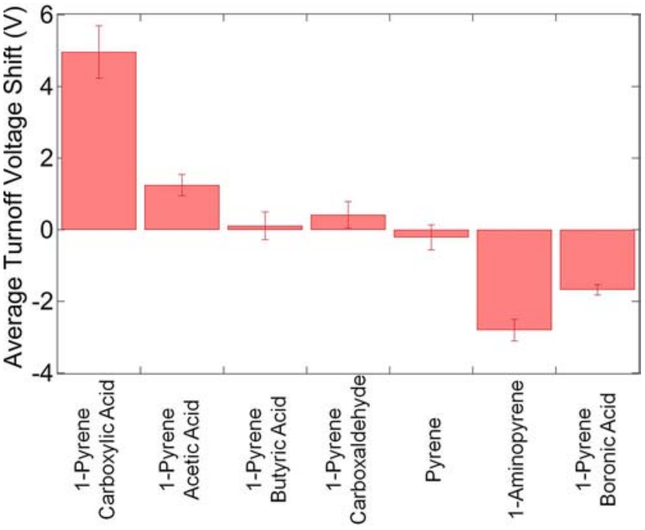

Figure 4. Average threshold voltage shift, ΔV_T, caused by exposure to pyrene compounds. Each value is the average of results from 15−20 devices; error bars are standard errors of the mean.

Interpretation of the data is informed by a calculation of N, the density of singly charged species adsorbed on the CNT sidewall (presumed to be pyrene molecules) required to produce an observed value of ΔV_T: $N = |C\Delta V_T/e|$, where C is the CNT capacitance per unit length and e is the proton charge. The capacitance per unit length of a CNT FET in the backgate geometry is $C = 2\pi\varepsilon\varepsilon_0/\ln(2h/r)$, where r is the CNT radius and h and ε are the thickness and dielectric constant of the insulator between the CNT and the back gate, respectively.[19] For the device geometry used here, this equates to $N \approx 200$ charged molecules μm^{-1} V^{-1}.

The observed threshold voltage shift for 1-pyrenecarboxylic acid, $\Delta V_T = +5.0 \pm 0.7$ V, would require $N \approx 1000$ negative charges/μm. By geometrical stacking arguments, full monolayer coverage of pyrenes comprises ca. 9000 molecules/μm. A lower bound of 3000 molecules/μm is suggested by recent measurements of the coverage for pyrenes coupled to transition-metal complexes that are significantly larger than the functional groups of the molecules used here.[8] For this discussion, a density of 6000/μm is assumed. In a water layer at pH 5, roughly 90% of the carboxylic acid functional groups (i.e., ca. 5000 μm^{-1}) are deprotonated. Since the calculation suggests that 1000 deprotonated groups/μm are needed to produce the observed threshold voltage shift, we conclude that the gating effect of the charged groups is reduced by a factor of ca. 5 due to screening. For 1-aminopyrene ($\Delta V_T = -2.8 \pm 0.3$ V), a similar density of adsorbed molecules would be expected, but only 15% of the molecules should be charged (i.e., 4.5 times fewer than for pyrenecarboxylic acid). This argument leads to a predicted threshold voltage shift of −1.1 V, a factor of ca. 2.5 less than what was observed. This could be explained by a difference in the screening effect in the two cases or an environment with pH lower than 5, which would result in a smaller fraction of deprotonated carboxylic acid groups and a larger fraction of protonated amino groups. With these caveats, this framework provides a satisfactory semiquantitative explanation of the observations.

It was also observed that varying the compound containing the carboxyl group (carboxylic acid to acetic acid to butyric acid) led to a systematic reduction in the measured value of ΔV_T ($+5.0 \pm 0.7$ to $+1.2 \pm 0.3$ to $+0.1 \pm 0.4$ V, respectively). This progression is attributed primarily to successively larger displacements of the charged carboxyl group away from the CNT sidewall; a secondary contributing factor is the reduced probability of deprotonation of the carboxyl group because of the differing pK_a values of the compounds. Molecular dynamics (MD) simulations (see the Supporting Information for details) indicated that the distance between the CNT sidewall and the carboxyl group of 1-pyrenecarboxylic acid is 0.34 nm, approximately equal to the interlayer spacing for graphene. This is interpreted as the effective electrostatic radius of the CNT and the pyrene molecule, each extending 0.17 nm into the adjoining space, so the relevant distance for electrostatic influence (i.e., the distance between the centers of the electron charge distributions) is 0.17 nm. The carboxyl group in 1-pyreneacetic acid is 0.12 nm farther from the CNT than in the case of 1-pyrenecarboxylic acid. If Coulomb interactions between the carboxyl group and the CNT are assumed and the reduction in protonation caused by the change of 0.2 units in pK_a is taken into account, this increased distance corresponds to a reduction in the interaction strength by a factor of 3.2, which can be compared with the observed reduction in ΔV_T by a factor of 4.1 ± 1.3. MD simulations indicated that the carboxyl group on 1-pyrenebutyric acid is 0.18 nm farther away than that of pyrenecarboxylic acid. This distance change coupled with the change in pK_a corresponds to a reduction by a factor of 4.3 and a predicted threshold shift of roughly 0.7 V. The measured shift for 1-pyrenebutyric acid is smaller ($+0.1 \pm 0.4$ V), possibly because of more effective screening by water molecules, which can more readily penetrate between the carboxylic acid group and the nanotube surface for this molecule.

In contrast to other acids tested, functionalization with 1-pyreneboronic acid led to a negative value of ΔV_T (-1.7 ± 0.1 V); that is, the *sign* of the threshold voltage shift was characteristic of a base rather than an acid. To explain this, two facts are noted: (1) 1-pyreneboronic acid is a weak acid (pK_a = 8.8), so at pH 5, virtually all of the boronic acid molecules would be expected to be charge-neutral, and (2) the B−O bonds in boronic acids are highly polar, with the boron (oxygen) atoms bearing a partial positive (negative) charge; thus, 1-pyreneboronic acid acts as an adsorbed dipole. Quantum-chemical simulations indicated a molecular dipole moment of ca. 2.6 D nearly coplanar with pyrene group. If a random orientation of the pyrenes adsorbed onto the CNT is assumed, on average the dipole will be oriented with the positively charged boron atom located closer to the CNT sidewall than the negatively charged oxygen by a distance of ca. 0.05 Å. On the basis of these considerations, it would be expected that the threshold voltage shift would be *negative* and approximately one-third that observed for the 1-aminopyrene case ($\Delta V_T = -2.8 \pm 0.3$ V). The observed value of the threshold voltage shift, $\Delta V_T = -1.7 \pm 0.1$ V, is thus attributed to the electrostatic effect of this dipole. The near-zero values of ΔV_T observed for pyrene and 1-pyrenecarboxaldehyde are consistent with this explanation, since neither of those species contains a bond as polarized as the B−O bonds in 1-pyreneboronic acid.

To summarize, we have demonstrated that pyrene compounds, which specifically absorb onto CNT FETs via a $\pi-\pi$ stacking interaction, can modify the transistor $I(V_G)$ characteristic through an electrostatic gating process. Acidic or basic functional groups interact with the interfacial water present on the CNT FET and become charged. These charged species anchored to the CNT gate the device, modifying the nanotube surface potential through electrostatic interactions. The change in surface potential results in a positive (negative) shift of the turnoff threshold voltage for negatively (positively) charged functional groups. Water-mediated local gating is thus a primary mechanism behind the responses of CNT FET molecular sensors. The magnitude of the threshold voltage shift was found to depend sensitively on the distance between the charged group and the CNT sidewall, behavior that can be understood qualitatively using an electrostatic model. The behavior of CNT FETs functionalized with uncharged 1-pyreneboronic acid is attributed to the effect of the molecular dipole moment, suggesting an explanation for reports in the literature where exposure to neutral molecules was found to elicit a distinct response from CNT FET sensors.[20,21]

Future work will involve experiments in buffer solution to modify the local pH at the SiO_2−water interface. This should modulate the degree of protonation for a given species and lead to threshold voltage shifts. The data presented here and obtained through the further investigations will inform the development of MD-based simulations that go beyond existing structural studies[22−24] to calculate the response of CNT FET chemical sensors due to electrostatic interactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CNT FET schematic and details of the MD simulations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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