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Pyrenecyclodextrin-Decorated Single-Walled Carbon Nanotube Field-Effect Transistors as Chemical Sensors**

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Single-walled carbon nanotubes (SWNTs) have a unique quasi-1D electronic structure which displays remarkable versatility and promises wide applicability.[1,2] Among their many potential applications, field-effect transistors (FETs), fabricated with SWNTs, have been found[3] to be sensitive to various gases – for example, oxygen, nitrogen dioxide, ammonia, etc. – and so FETs of this type can operate as gas sensors[3a–c] on account of (i) their high sensitivity, (ii) their fast response time, and (iii) their compatibility with dense-array fabrications.

Success in the noncovalent functionalization of carbon nanotubes, however, has provided[4–9] yet a further opportunity to employ these entities as chemical and/or biological sensors. For example, FET devices, using SWNTs, functionalized with DNA,[6] proteins,[7] enzymes,[8] and dextrans[9] are already showing considerable promise for the electronic detection of biological compounds. For these applications, the SWNTs are generally decorated by means of noncovalent bonding interactions with bifunctional molecules that can be anchored, on the one hand, onto the nanotubes, yet are able, on the other hand, to sense a particular biomolecule, thus permitting their detection with FET devices. The methods, however, for the noncovalent functionalization of the nanotube surfaces, which are required to provide the interfaces that are selective towards the binding of a wide range of analytes, are not well established.[10] What is lacking currently is the ability to carry out quantitative investigations on the sensitivities offered by noncovalently functionalized SWNT/FETs. These fundamental and technological problems have to be addressed before chemical sensors and biosensors, using noncovalently modified carbon nanotubes, can be applied to goals such as environmental monitoring, medical diagnostics, and gene chip technologies. Recently, we designed and fabricated pyrene-modified β-cyclodextrin (pyrenecyclodextrin)-decorated SWNT/FET devices which behave as chemical sensors in aqueous solution, detecting organic molecules as a consequence of their molecular recognition by the pyrenecyclodextrin derivative. In this Communication, we describe the results of our investigation.

Possessing, as they do, a hydrophobic inner cavity and a hydrophilic outer surface, cyclodextrins (CDs)[11] have become accepted as one of the best readily available and inexpensive receptors for organic substrates in aqueous solution on account of (i) their low toxicity, (ii) their promiscuous recognition of organic substrates, and (iii) their propensity for solubilizing organic compounds in water. We have, therefore, prepared a pyrenecyclodextrin derivative and used it (Fig. 1) to fabricate pyrenecyclodextrin-decorated SWNTs for FET-sensing devices. Five organic compounds (Fig. 2), viz., 1-adamantanol (1-ADA), 2-adamantanol (2-ADA), 1-adamantanecarboxylic acid (1-ACA), sodium cholate (SC), and sodium deoxycholate (SD), were employed as the substrates for sensing, because these molecules are known[12] to be included inside the cavity of β-CD with a range of different binding affinities and are not expected to have any direct interaction with the SWNTs. Following immobilization of a first layer of pyrenecyclodextrin molecules (the hosts) on the surfaces of the SWNTs, it should then be a simple matter of monitoring the conductance change of the SWNT/FET in order to detect a second layer of bond species (the guests). Our experimental results indicate that the threshold voltage of the pyrenecyclodextrin-SWNT/FET devices shifts towards a negative gate voltage (V_g) in the presence of the organic molecules. Remarkably, the magnitude of the threshold voltage movements in the pyrenecyclodextrin-SWNT/FET devices in the presence of the organic compounds depends markedly on the magnitudes of the complex formation constants (K_S) exhibited by the pyrenecyclodextrin with these organic molecules whose structures are illustrated in Figure 2. Herein, we will explore (i) how the pyrenecyclodextrin-decorated SWNTs interact with and respond to the various organic compounds in solution, and (ii) how the understanding that results is enabling highly

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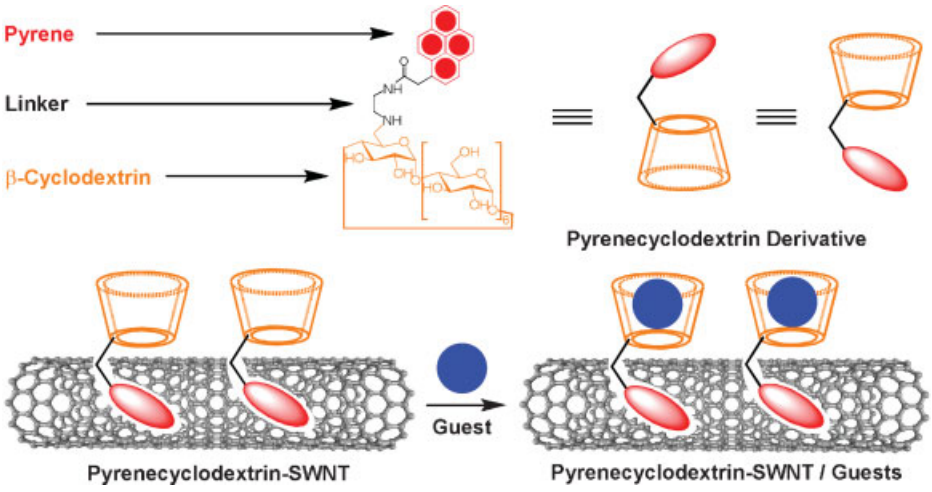

Figure 1. Schematic drawing of the pyrenecyclodextrin-decorated SWNT hybrids and how they interact with guest molecules when they are being sensed in an FET device.

selective SWNT/FET sensors to be developed for the electronic detection of organic compounds.

The pyrenecyclodextrin derivative was synthesized by the condensation of mono(6-aminoethylamino-6-deoxy)-β-CD with 1-pyreneacetic acid in *N*,*N*-dimethyl formamide (DMF) solution. The pyrene units in the pyrenecyclodextrin derivatives associate with the surfaces of the SWNTs by means of π–π stacking interactions,[5a,i] facilitating the formation of the pyrenecyclodextrin-SWNT hybrids. In UV-vis titration experiments, since both the SWNTs and pyrene units exhibit absorptions around 345 nm, the absorption of the SWNTs was subtracted from the apparent absorption spectrum obtained in each titration experiment. Gradual increases in the absorption peak intensity of the pyrenecyclodextrin (5.64×10^{-5} mol L^{-1}) around 345 nm, upon addition of the SWNTs (0–3.50×10^{-3} g L^{-1}) in DMF at 25 °C, can be attributed[13] to the interaction between the pyrene units and the SWNTs, that is, the pyrene units become attached to the surfaces of SWNTs. These hybrids were prepared by (1) adding the pyrenecyclodextrin to a DMF solution of the SWNTs, followed by sonication at room temperature for 5 h, or (2) immersing SWNT-coated silicon wafers into a DMF solution (1.13×10^{-3} mol L^{-1}) of the pyrenecyclodextrin overnight. The weight percentage of the pyrenecyclodextrin in the hybrids was found to be ca. 46 wt% by thermogravimetric analysis (TGA) measurements. An atomic force microscopy (AFM) image (Fig. 3a) reveals that the average length of the SWNTs is ca. 2.0 μm and that their average height is ca. 1.5 nm. The average height of the pyrenecyclodextrin-decorated SWNTs is ca. 4.0 nm (Fig. 3b and c); a measurement that indicates that the average height of the pyrenecyclodextrin layer is about 2.5 nm. The pyrenecyclodextrin molecules are coated uniformly only onto the surfaces of the SWNTs and do not stick to the SiO_2 surfaces. The assembly of the pyrenecyclodextrin molecules, only and specifically, onto the SWNTs is important for two reasons. Firstly, the pyrene units in the pyrenecyclodextrins are an organic semiconductor,[14] a property which could cause device leakage through the pinholes of the SiO_2 dielectric. (The self-assembly of the pyrenecyclodextrin molecules, only and specifically, onto the SWNTs by means of π–π stacking interactions avoids the leakage problems associated with the transistors after decorating the SWNTs with these molecules.) Secondly, the sensing sites in the hybrids are the open cavities of the β-CD rings in the pyrenecyclodextrin derivative. The self-assembly of the pyrenecyclodextrin molecules, only and specifically, onto the SWNTs – and not onto the SiO_2 – will increase the sensitivity of the system.

In order to investigate the sensing behavior of the pyrenecyclodextrin-SWNT hybrids, the SWNT/FET devices were fabricated – using CVD-grown SWNT networks as the channels – on silicon wafers with a 500 nm thick SiO_2 dielectric. The density of the network was predetermined to be 1.5 tubes μm^{-2}, that is, just above the percolation threshold to avoid too many conduction paths through the metallic SWNTs; a situation which would reduce the ON/OFF ratio of the transistor.[15] The lift-off lithography process[15a] was used to pattern the e-beam-deposited Pd contact pads on top of the SWNTs network. Oxygen plasma was employed to etch away the SWNTs outside the source-drain channels. Since the channel is 200 μm long and 1000 μm wide, that is, approximately 100 times longer than the SWNTs, the network resistance, rather than the contact resistance between Pd and network, dominates the overall

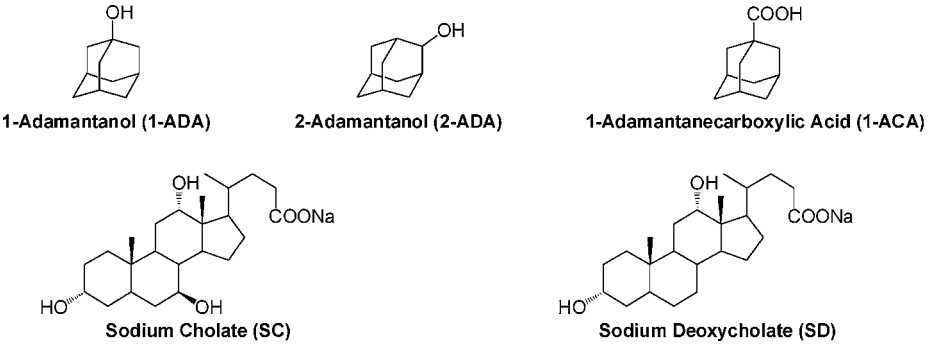

Figure 2. Structural formulas of the organic compounds (guests) that can be sensed in aqueous solution by pyrenecyclodextrin-SWNT/FET devices.

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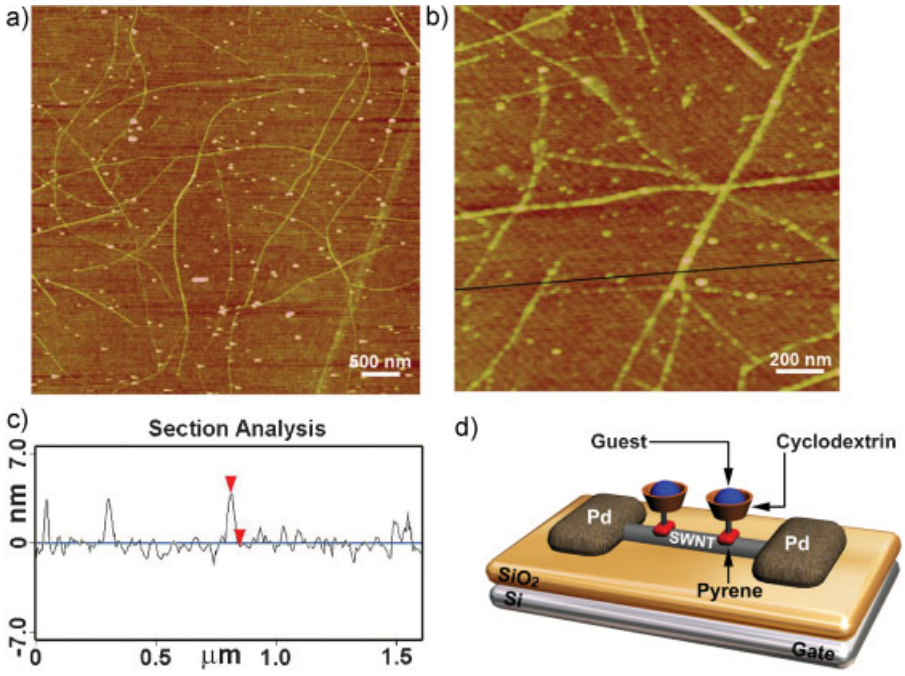

Figure 3. a) AFM image of chemical vapor deposition (CVD)-grown SWNTs with a diameter of 1.5 nm. b) AFM image of the pyrenecyclodextrin-decorated SWNTs. c) Cross-sectional analysis of (b). The height of the pyrenecyclodextrin-decorated SWNTs is estimated to be about 4.0 nm, indicating an average height for the pyrenecyclodextrin coating of around 2.5 nm. d) Model of the pyrenecyclodextrin-decorated SWNT/FET device showing how the pyrenecyclodextrin molecules interact with the SWNT and, at the same time, bind with guest molecules.

resistance.[15a] The pyrenecyclodextrin was self-assembled onto the SWNT networks according to the scheme illustrated in Figure 1. The silicon wafers with the SWNT networks were soaked in a DMF solution of the pyrenecyclodextrin (1.13×10^{-3} mol L^{-1}) overnight, washed quickly with H_2O, and then blown to dryness with N_2. Devices fabricated by using this self-assembly procedure did not suffer from a leakage problem since the pyrenecyclodextrin molecules only self-assemble on the SWNTs. The configuration of the SWNT/FET device used for making the transistor measurements is illustrated in Figure 3d.

The transfer characteristics (I_{sd} vs. V_g) of the transistor were measured by applying 100 mV and sweeping the gate voltage between +20 and −20 V in steps of 0.5 V. Figure 4 illustrates the transfer curves of the SWNT/FET device before and after the self-assembly of pyrenecyclodextrins. After pyrenecyclodextrin molecules coat the surfaces of the SWNTs, the OFF current of the SWNTs does not change while the ON current decreases by 40%. The calculated motilities for the SWNTs and the pyrenecyclodextrin-SWNTs are 2.52 and 2.74 cm^2 S^{-1} V^{-1}, respectively. The threshold voltage of the pyrenecyclodextrin-SWNT/FET device shifts towards a negative gate voltage by about 9.4 V as compared with bare SWNTs. At a given gate voltage, the conductance of the SWNT network decreases after the decoration with pyrenecyclodextrin molecules.[16] The decrease of the SWNT network conductance, after the decoration by the pyrenecyclodextrin molecules, can be attributed to either (i) the fact that the SWNTs are *p*-type semiconductors where the shift of the threshold voltage to the left indicates that electron transfer[17] possibly occurs from the pyrenecyclodextrin molecules to the SWNTs, causing a decrease of the carrier density (n) in the SWNTs; or (ii) the fact that the adsorption of the pyrenecyclodextrin molecules on the SWNTs[7] induces the scattering potential and decreases the mobility (μ) of holes in SWNTs.

Next, the pyrenecyclodextrin-SWNT/FET device was soaked in an aqueous solution of the organic compound (guest) for 1 h, washed briefly with H_2O thereafter, and finally blown to dryness with N_2. The pyrenecyclodextrin molecules coating the surfaces of the SWNTs act as hosts and recognize various guest molecules.[12] When these guest molecules are included in the cavities of the pyrenecyclodextrin hosts, the threshold voltage of the pyrenecyclodextrin-SWNT/FET device shifts even more towards a negative gate voltage. Control experiments were conducted to demonstrate that the threshold voltage of bare SWNT/FET devices, that is, devices without the coat of pyrenecyclodextrin molecules, did not show any appreciable change in the presence of the guests under exactly the same conditions. These results can be accounted for by the fact that, as the guest molecules become included in the cavities of the pyrenecyclodextrin hosts, two possible phenomena can come into play: (i) the guest molecules included in the β-CD cavities will cause a rearrangement in the charge distribution of the pyrenecyclodextrin, which, in turn, will induce a change in the

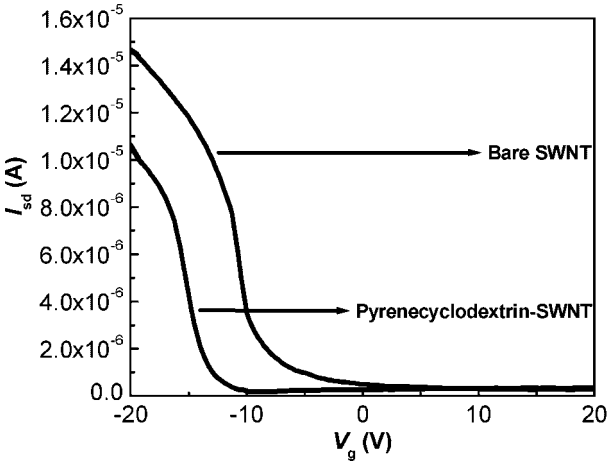

Figure 4. Transfer curves obtained from the SWNT/FET device before and after coating with pyrenecyclodextrin molecules dissolved in a DMF solution at a concentration of 1.13×10^{-3} mol L^{-1}.

charge transfer[17] from the pyrenecyclodextrin molecules to the SWNTs, that is, causing a change in the charge carrier density (n) in the SWNTs; or (ii) the guest molecules included in the β-CD cavities could bring about a further decrease in the charge mobility (μ) either by altering the scattering potentials of the pyrenecyclodextrin molecules or by causing the further deformation of the SWNTs.[18] We observe this latter phenomenon for all the guest molecules we tested. The change in the transistor characteristics for the pyrenecyclodextrin-SWNT/FET device reaches a maximum value in relation to the shift and the tilt of the transfer curves in the presence of guest molecules under the experimental conditions already described. The shifts of the transistor characteristics (Table 1) for the five compounds, however, were of different magnitudes, that is, the left-shift values turned out to be ca. 4.0 V for 1-ADA, ca. 2.8 V for 2-ADA, ca. 1.9 V for 1-ACA, ca. 1.2 V for SD, and ca. 0.7 V for SC. The typical transfer curves of the pyrenecyclodextrin-SWNT/FET devices before and after binding the SD (3.93×10^{-3} mol L^{-1}) or 1-ADA (3.98×10^{-3} mol L^{-1}) guest are illustrated in Figure 5.

Because the guest molecules are included inside the cavities of the pyrenecyclodextrin hosts as a result of immersing the pyrenecyclodextrin-SWNT/FET device into an aqueous solution of guest molecules, the number of the included guests will depend directly on their binding abilities towards the β-CD ring. In order to make a quantitative assessment of the inclusion complexation behavior of the pyrenecyclodextrin with these guests, fluorescence titration experiments were performed at 25 °C in an aqueous phosphate buffer (pH = 7.0). In these experiments, the fluorescent maximum intensity of the pyrenecyclodextrin at 396 nm decreased gradually upon addition of known amounts of guests, and was accompanied by a hypsochromic shift (5–10 nm) for the peak of maximum intensity in the emission spectrum. Typical fluorescent spectral changes for the pyrenecyclodextrin with 1-ADA are described in the Supporting Information. Using the nonlinear least-squares curve fitting method,[19] the complex formation constants (K_S) can be obtained for each host–guest combination, assuming a 1:1 stoichiometry in aqueous buffer. The K_S and ($-\Delta G^\circ$) values obtained for the complexation of the pyrenecyclodextrin with the five different guests are listed in Table 1. The K_S values for the complexation of the pyrenecyclodextrin with the different guests listed in Figure 2 exhibit the following sequence of binding abilities: 1-ADA > 2-ADA > 1-ACA > SD > SC. The pyrenecyclodextrin affords the highest complex formation constant up to (44200 ± 2000) M^{-1} upon complexation with 1-ADA and the lowest one of (4370 ± 200) M^{-1} upon complexation with SC. Remarkably, the complex formation constants (K_S) of the pyrenecyclodextrin host with these guests correlate with the magnitudes of the transistor characteristic shifts of the pyrenecyclodextrin-SWNT/FET device before and after binding of these organic molecules. The correlation is performed by plotting the complex formation constants (K_S) versus the shift values of the transistor characteristics using a limited data set. A good straight line (Fig. 6) with a correlation coefficient (r) of 0.995 was obtained by the linear-fitting method. This correlation between the molecular recognition ability of the pyrenecyclodextrin and the transistor characteristic shifts of the pyrenecyclodextrin-SWNT/FET indicates that the FET

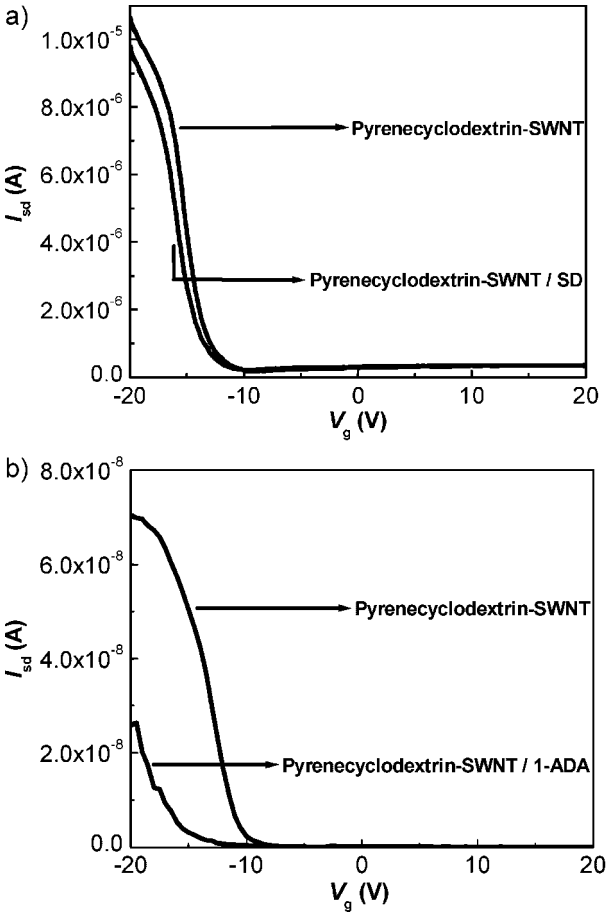

Figure 5. a) The transfer curves of the pyrenecyclodextrin-SWNT/FET devices before and after binding of the SD guest dissolved in aqueous solution at a concentration of 3.93×10^{-3} mol L^{-1} and b) the transfer curves of the pyrenecyclodextrin-SWNT/FET before and after binding of the 1-ADA guest dissolved in aqueous solution at a concentration of 3.98×10^{-3} mol L^{-1}. Both experiments were carried out at room temperature.

Table 1. Shift values of the transistor characteristics (I_{sd}–V_g curves) associated with the pyrenecyclodextrin-SWNT/FET device, reflecting its sensing towards different organic molecules compared with the complex formation constants (K_S) and Gibbs free energy changes ($-\Delta G^\circ$) when pyrenecyclodextrins form complexes with these organic molecules in aqueous buffer (pH = 7.0) at 25 °C.

Guest	FET shift value [V]	K_S [M^{-1}]	$-\Delta G^\circ$ [a] [cal mol^{-1}]
1-ADA	4.0	44200 ± 2000	6330 ± 30
2-ADA	2.8	32870 ± 1600	6170 ± 30
1-ACA	1.9	18760 ± 900	5830 ± 20
SD	1.2	8620 ± 200	5380 ± 20
SC	0.7	4370 ± 200	4970 ± 20

[a]1 cal = 4.184 J.

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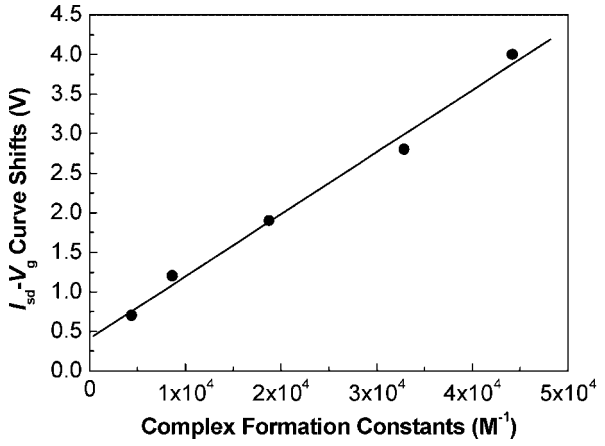

Figure 6. Plot of the curve shift values for the transfer characteristics of the pyrenecyclodextrin-SWNT/FET device, after binding different organic molecules in aqueous solution, against the K_S values for the pyrenecyclodextrin with these same organic molecules in aqueous buffer (pH = 7.0) solution.

device can be used to sense organic molecules quantitatively. The stronger the binding between the hosts and the guests, the larger the amounts of the guest that are included inside the cavities of the hosts simply because the inclusion process is a dynamic one in solution. The more guest molecules included in the host cavities, the larger is the change in the carrier concentration or the carrier mobility, or both, and these changes are reflected in the shifts of the FET characteristics. We expect that other similar organic molecules (guests), which can be included inside the cavities of β-CD and display moderate binding constants, and do not have any obvious interactions with the SWNTs, will follow a linear relationship in the pyrenecyclodextrin-SWNT/FET devices.

In conclusion, we have fabricated pyrenecyclodextrin-decorated SWNT/FET devices to sense particular organic molecules based on the concept of molecular recognition. In the presence of certain molecules, some of which are included inside the cavities of cyclodextrins with moderate binding constants, and do not have appreciable interactions with the SWNTs, the transistor characteristics of the pyrenecyclodextrin-decorated SWNT/FET device shift towards negative gate voltage. The magnitudes of the shifts for these organic molecules depend highly on their complex formation constants (K_S) with the pyrenecyclodextrin and follow a linear relationship. The mechanism is postulated to involve either the change of the carrier concentration as a result of the change in the charge transfer from the pyrenecyclodextrins to the SWNTs in the pyrenecyclodextrin-decorated SWNT/FET, or because of the change in the carrier mobility resulting from differences in the scattering potential as a consequence of deformation of the SWNTs. Current experimental results indicate that the electrical conductance of the pyrenecyclodextrin-decorated SWNTs is highly sensitive to certain organic molecules and varies significantly with changes in the surface adsorption of these molecules. Thus, the pyrenecyclodextrin-SWNT/FET device can indeed serve as a chemical sensor to detect organic molecules, not only selectively, but also quantitatively, an outcome which augurs well for real-life applications.

Experimental

Pyrenecyclodextrin: The mono(6-aminoethylamino-6-deoxy)-β-CD (1.18 g, 1.0 mmol) and *N*,*N*′-dicyclohexylcarbodiimide (DCC; 0.21 g, 1.0 mmol) were dissolved in DMF (30 mL) in the presence of a small amount of 4 Å molecular sieves under an atmosphere of Ar. A DMF solution (10 mL) of 1-pyreneacetic acid (0.26 g, 1.0 mmol) was then added dropwise. The mixture was stirred for 2 days in an ice bath and then for another 2 days at room temperature, before being left to stand for 5 h until no more precipitate deposited. The precipitate was removed by filtration, and the filtrate was poured into Me_2CO (150 mL). The precipitate formed in Me_2CO was collected by filtration. The crude product was dissolved in H_2O (20 mL) and kept at room temperature for 1 day. The precipitate which formed was collected by filtration and washed with Me_2CO (2×10 mL) and H_2O (2×10 mL) to give a pure compound (0.80 g, 56%) as a colorless solid. ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 25 °C, TMS, δ): 3.17–1.19 (m, 4H, NCH_2CH_2N), 3.35–3.65 (m, CD–H2-6), 4.21 (s, 2H, CH_2CO), 4.46–4.60 (m, 6H, CD–OH6), 4.84–4.90 (m, 7H, CD–H1), 5.70–5.79 (m, 14H, CD–OH2/3), 8.01–8.38 ppm (m, 9H, Pyrene-H); ^{13}C NMR (125 MHz, $(CD_3)_2SO$, 25 °C, TMS, δ): 39.6, 48.1, 49.3, 63.7, 68.6, 73.4, 74.2, 76.1, 80.5, 102.7, 120.2, 123.4, 125.3, 126.7, 128.4, 134.5, 139.2, 172.2 ppm; MS (HR-MALDI): *m*/*z* (%): Calcd for $C_{62}H_{86}N_2O_{35}$ 1418.5011, found 1418.0878 [*M*], 1441.2023 $[M + Na]^+$, 1455.9979 $[M + K]^+$.

Hybrids of Pyrenecyclodextrin-SWNT: The pyrenecyclodextrin-SWNT hybrids were prepared by two methods. (i) The DMF solution (5 mL) of the pyrenecyclodextrin (20.0 mg, 1.4×10^{-5} mol) was added dropwise to a DMF suspension (15 mL) of the SWNTs (5.0 mg). The resulting mixture was then sonicated at room temperature for 5 h. The solution was filtered to remove any precipitated material. The filtrate was then concentrated under a reduced pressure, followed by the centrifugation. The precipitate was washed thoroughly with H_2O to remove excess of free pyrenecyclodextrin and dried to give the pyrenecyclodextrin-SWNT hybrids. (ii) The SWNT-coated silicon wafers were immersed in a DMF solution (1.13×10^{-3} mol L^{-1}) of the pyrenecyclodextrin overnight, before being thoroughly washed briefly with H_2O and then blown dried.

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