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Article

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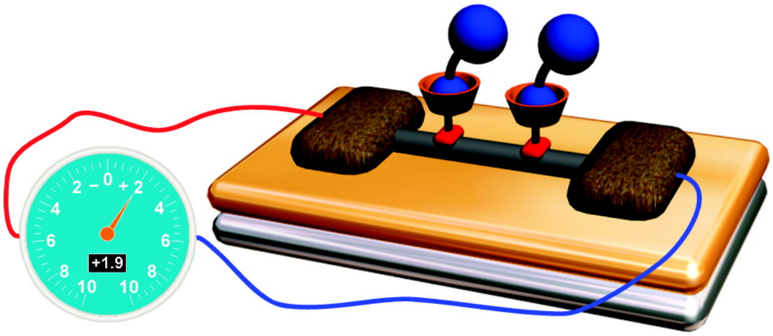

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A Tunable Photosensor

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Abstract: A pyrene-modified β-cyclodextrin (pyrenecyclodextrin)-decorated single-walled carbon nanotube (SWNT) field-effect transistor (FET) device was fabricated, which can serve as a tunable photosensor to sense a fluorescent adamantyl-modified Ru complex (ADA−Ru). When the light is on (I = 40 W m^{-2} and λ = 280 nm), the transfer curve of the pyrenecyclodextrin-SWNT/FET device shifts toward a negative gate voltage by about 1.6 V and its sheet resistance increases quickly, indicating a charge-transfer process from the pyrenecyclodextrins to the SWNTs. In contrast, the transfer curve of the pyrenecyclodextrin-SWNT/FET device in the presence of the ADA−Ru complex shifts toward a positive gate voltage by about 1.9 V and its sheet resistance decreases slowly when the light is on (I = 40 W m^{-2} and λ = 490 nm), showing a charge-transfer process from the pyrenecyclodextrin-SWNT hybrids to the ADA−Ru complex. Because these photoresponse processes are recoverable following the removal of the light, the present photosensor exhibits a promising application in the area of tunable light detection.

Introduction

Increasing the selectivity, response speed, and sensing ability of sensors for chemical and biological analytes has generated a lot of interest[1] recently. Because single-walled carbon nanotubes (SWNTs) possess the advantages of biocompatibility, size appropriateness, and sensitivity toward minute electrical perturbations, they have already exhibited[2,3] considerable promise for the electronic detection of biological species, as well as simple gases. The insolubility[4] of the SWNTs in the most organic solvents and the difficulties of handling these highly intractable carbon nanostructures, however, restrict real-life applications of SWNTs to a considerable extent. To improve upon the properties of the SWNTs, low cost and industrially feasible approaches to their modification have been much sought after[2a,f,5−8] in recent years. Among the approaches, noncovalent supramolecular modifications[6−8] of the SWNTs can do much to preserve the desired properties of the SWNTs, while remarkably improving their solubilities. For example, Guldi and Prato et al.[2f,7c,e,f] have reported that the noncovalent combination of the SWNTs with pyrene and porphyrin derivatives leads to novel electron donor−acceptor nanohybrids, which, upon photoexcitation, undergo fast electron-transfer, followed by the generation of microsecond-lived charge-separated species. Moreover, success in the noncovalent functionalization of the SWNTs has provided a further opportunity to employ these entities[8] as chemical and/or biological sensors. In these sensors, 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, and, on the other hand, to sense particular biomolecules, thus permitting their detection with FET devices.

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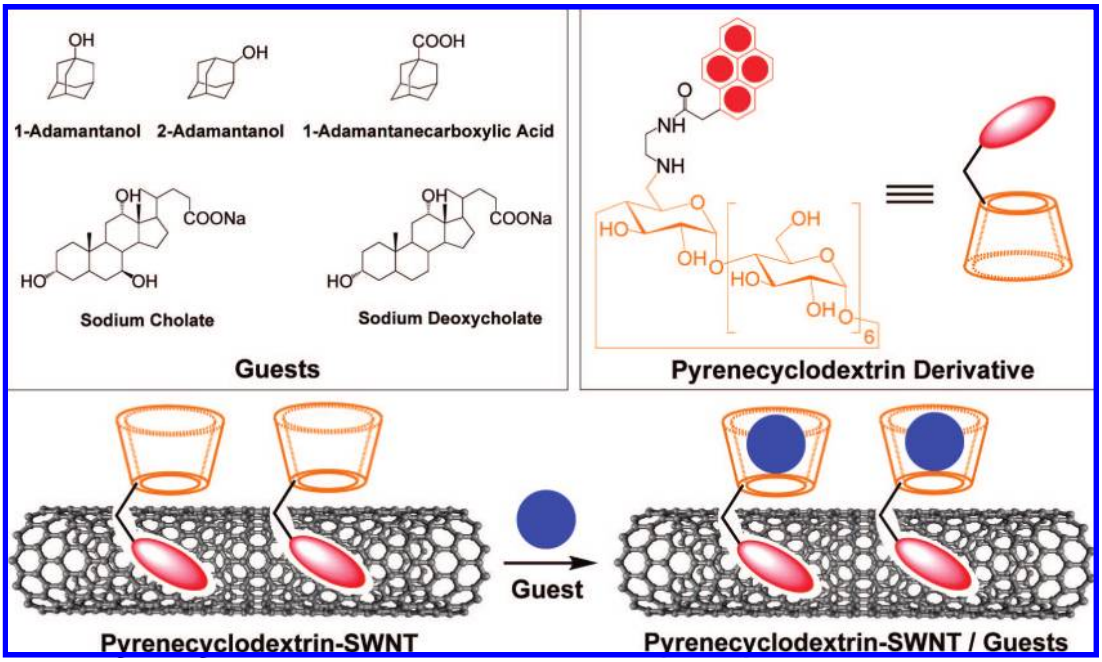
Scheme 1. Schematic Representation of the Pyrenecyclodextrin-Decorated SWNT Hybrids, How They Interact with Guest Molecules When They Are Being Sensed in an FET Device, and Five Guest Molecules, 1-Adamantanol, 2-Adamantanol, 1-Adamantanecarboxylic Acid, Sodium Cholate, and Sodium Deoxycholate



To carry out quantitative investigations on the sensitivities offered by noncovalently functionalized SWNT/FET devices to provide the interfaces that are selective toward the sensing of a wide range of analytes, we have described the fabrication of the FET devices (Scheme 1) in a recent work[9] using the hybrids of pyrene-modified β-cyclodextrin (pyrenecyclodextrin)-decorated SWNTs, which serve as chemical sensors to detect nonfluorescent organic molecules selectively, based on the concept of molecular recognition. In the presence of certain molecules, the transistor characteristics of the pyrenecyclodextrin-decorated SWNT/FET devices shift toward negative gate voltage, exhibiting the following sequence of sensing abilities for the guest molecules: 1-adamantanol > 2-adamantanol > 1-adamantanecarboxylic acid > sodium deoxycholate > sodium cholate. The results indicate that the electrical conductance of the device is highly sensitive to certain organic molecules and varies significantly with changes in the surface adsorption of these molecules. Satisfyingly, the magnitude of the transistor characteristic movements in the pyrenecyclodextrin-SWNT/FET devices in the presence of the organic molecules depends linearly on the magnitudes of the complex formation constants (K_S) exhibited by the pyrenecyclodextrin derivative with these molecules, a fact that demonstrates that the pyrenecyclodextrin-decorated SWNT/FET devices serve as chemical sensors for the detection of organic molecules in aqueous solution, not only selectively but also quantitatively.

Because the photosensing process[2i] is usually rapid and clean, and can be executed at an electrode surface even in the solid state, we have given particular attention to fabricating the photosensitive SWNT-based FET devices, which are able to

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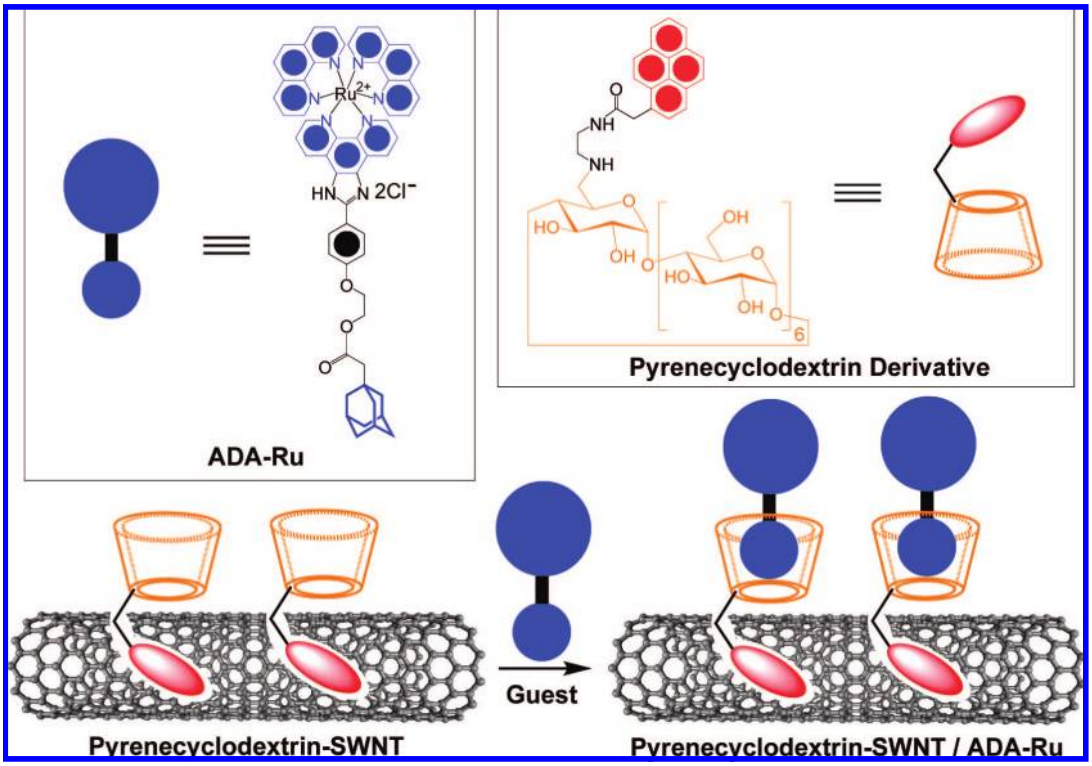
Scheme 2. Schematic Representation of the ADA−Ru Complex and How the Pyrenecyclodextrin-Decorated SWNT Hybrids Interact with the ADA−Ru Complex When They Are Being Sensed in an FET Device



serve as photosensors using the light-controlled charge-transfer (CT) principle. Specifically, the photosensitive SWNT/FETs have promising applications as the essential components of light-emitting diodes (LEDs) or photovoltaic devices (PVDs). However, research that introduces luminescent metal complexes during the fabrication of photosensitive carbon nanotube hybrids, or photosensitive carbon nanotube-based FET devices, has been the subject of very few reports[10] to date. Herein, we describe our recent results obtained with pyrenecyclodextrin-decorated SWNT/FET devices as tunable photosensors. In such SWNT/FET devices (Scheme 2), the pyrenecyclodextrin derivatives on the surfaces of the SWNTs serve as the sensing host. A ruthenium complex with an adamantyl tether (ADA−Ru) as the sensing guest can be immobilized by binding the adamantyl group into the cavity of the pyrenecyclodextrin derivative in aqueous solution. It is this molecular recognition event that renders the CT between the ADA−Ru guest and the pyrenecyclodextrin-decorated SWNT hybrids practicable.

Results and Discussion

Fabrication and Characterization. The pyrenecyclodextrin derivative was synthesized[9] by the condensation of mono(6-aminoethylamino-6-deoxy)-β-cyclodextrin (β-CD) with 1-pyreneacetic acid in *N*,*N*-dimethylformamide (DMF) solution, and the hybrids of the pyrenecyclodextrin-decorated SWNTs were prepared[9] according to a previous report. The pyrene units attached to β-CD rings associate with the surfaces of the SWNTs by means of $\pi-\pi$ stacking interactions.[11] The synthesis of the ADA−Ru complex, the sensing guest, is outlined in Scheme 3. In the procedure, 1,10-phenanthroline-5,6-dione (**7**) was formed by oxidation of 1,10-phenanthroline (**6**). This dione was transformed into an imidazo[4,5-*f*]-1,10-phenanthroline derivative (**8**) by reacting it with an adamantyl-modified benzaldehyde (**5**). Reaction of **8** with (1,10-phenanthroline)$_2$RuCl$_2$ (**9**) afforded the ADA−Ru complex in a yield of 71%. The fact that the adamantyl group of the ADA−Ru complex can be included in the cavity of the β-CD ring is demonstrated by a ^{1}H NOESY experiment. Because the aqueous solubility of pyrenecyclodextrin is too low to perform the ^{1}H NOESY experiment, we pursued the ^{1}H NOESY experiment using β-CD with ADA−Ru complex in D$_2$O at 25 °C. NOE crosspeaks (A−C) between the protons of the adamantyl group and the H3 and H5 protons on the inside of the β-CD ring are observed [Figure S1 in the Supporting Information] in the ^{1}H NOESY spectrum. These observations indicate that the adamantyl group of the ADA−Ru complex is included in the hydrophobic cavity of the β-CD ring as illustrated in Scheme 2.

The SWNT/FET device was fabricated, using CVD-grown SWNT networks as channels, on silicon wafers with a 500 nm thick silicon dioxide (SiO$_2$) dielectric (see a detailed procedure for the fabrication of the SWNT/FET device in the Experimental Section).[12] The device with the SWNT networks was soaked in a DMF solution of pyrenecyclodextrin (1.13 mM) overnight,

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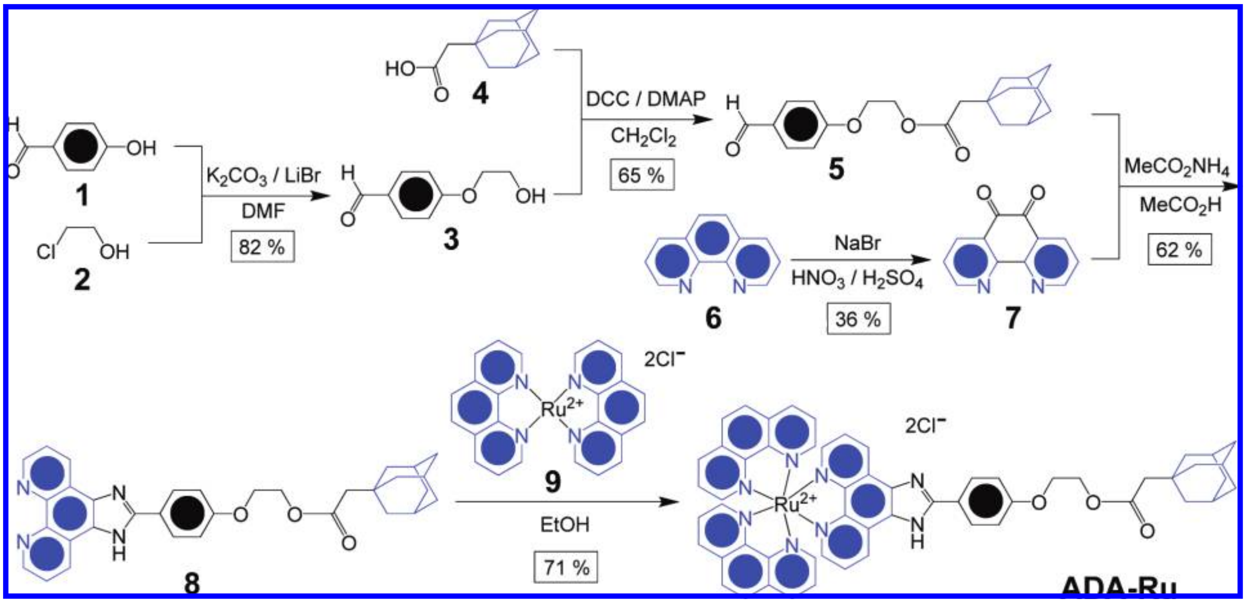
Scheme 3. Schematic Representation of the Preparation of the ADA−Ru Complex



washed with H_2O briefly thereafter, and blown with N_2 gas to dryness. Atomic force microscopy indicates[9] that the average height of the pyrenecyclodextrin layer on the surfaces of the SWNTs is ca. 2.5 nm. We have observed that the pyrenecyclodextrin molecules are coated uniformly only onto the surfaces of the SWNTs and do not stick to the SiO_2 surfaces. Because the pyrene unit in the pyrenecyclodextrin is an organic semiconductor,[13] it may cause the SWNT device to leak through the pinholes of the SiO_2 dielectric if the pyrenecyclodextrin molecules stick to the SiO_2 surfaces. The self-assembly of the pyrenecyclodextrin molecules, only and specifically, onto the SWNTs by means of $\pi-\pi$ stacking interactions avoids the leakage problems associated with the transistors after decorating the SWNTs with these molecules, a benefit that increases the sensitivity of the system. This method of casting a photoactive compound onto a SWNT network has been reported[3k] previously to provide a strong enough interaction to reveal evidence for CT upon illumination. Any changes in the device characteristics can be attributed to resistance changes occurring along the SWNT channel and not in the Schottky barriers at the contacts. The device configuration we have employed for transistors and resistance measurements is illustrated in Figure 1.

Sensing Process. The conductance transfer characteristics (I_{sd} versus 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 2a illustrates the transfer curves of the SWNT/FET device before (black curve) and after (red curve) the self-assembly of pyrenecyclodextrin molecules in the dark. The threshold voltage of the pyrenecyclodextrin-SWNT/FET device shifts toward a negative gate voltage by about 9.4 V, as compared to bare SWNTs. Because the excitation wavelength (λ_{ex}) of pyrenecyclodextrin is 274 nm (see Figure S2 in the Supporting Information), an LED with an intensity (I) of 40 W m^{-2} and excitation wavelength (λ_{ex}) of 280 nm is used as a light source for the FET device. After the LED has been switched on for 5 min, the transfer curve of the pyrenecyclodextrin-SWNT/FET device shifts further to the left (from the red curve to the blue one in Figure 2a) by about 1.6 V. Note that the conductance of the transistor is given by $G = n\mu e$, where n is the carrier concentration, μ is the carrier mobility, and e is the elementary charge of an electron. The barrier concentration (n) and the carrier mobility (μ) on the SWNTs remain unchanged whether the light is on or off. Therefore, there should be a CT, associated with e, from the pyrenecyclodextrins to the SWNTs when the light is on, causing the transfer curve to shift even further to the left. In DMF solution, the fluorescence intensity (see Figure S3 in the Supporting Information) of the pyrenecyclodextrin solution (4.30×10^{-4} mol L^{-1}) decreases on the stepwise addition of a SWNT solution ($(0 - 1.44) \times 10^{-3}$ g L^{-1}) at 25 °C. Strong fluorescence emission of the pyrenecyclodextrin was observed from 370 to 425 nm. Under these conditions, the competitive light absorption by the SWNTs was too low to be determined and can be ignored in the fluorescence experiments.[14] The dependence of fluorescent quenching around 412 nm on the SWNT concentration implies[3k,12c,15] that a CT process exists in the pyrenecyclodextrin-SWNT system, an implication that supports perfectly the result of the FET device investigation. In such hybrid systems, the light generates electron−hole pairs. The generated excitons tend to combine;

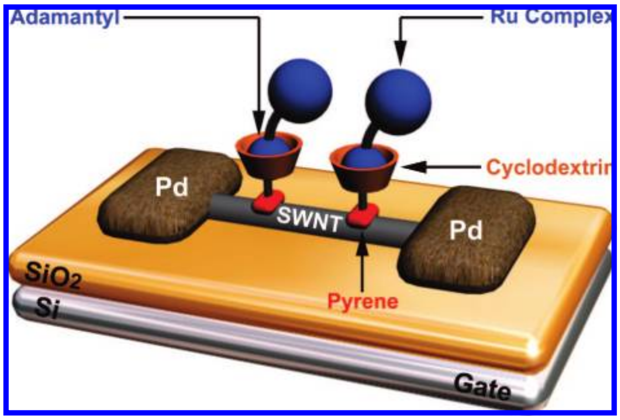


Figure 1. A model of the pyrenecyclodextrin-decorated SWNT/FET device showing how the pyrenecyclodextrin molecules interact with the SWNT and, at the same time, bind with guest molecules.

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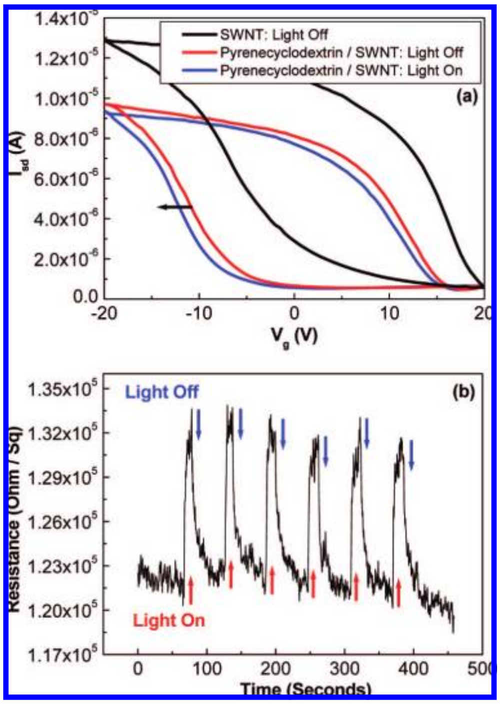

Figure 2. (a) The $I_{sd}-V_g$ curves of SWNT/FET before (black) and after (red) assembling the pyrenecyclodextrin (1.13 mM) in the dark and the $I_{sd}-V_g$ curve of the pyrenecyclodextrin-SWNT/FET when the light is on (blue), $\lambda = 280$ nm and $I = 40$ W m^{-2}. (b) The resistance of the pyrenecyclodextrin-SWNT/FET device vs time monitored under zero gate voltage, $\lambda = 280$ nm and $I = 40$ W m^{-2}.

meanwhile, the electrons or holes are transferred partially to the SWNTs, depending on the distance and the energy barriers between the pyrenecyclodextrin and the SWNTs. In other words, the formation of the pyrenecyclodextrin-SWNT hybrids favors the transfer of electrons or holes from the pyrenecyclodextrin (donor) to the SWNTs (acceptor), such that the exited electrons or holes enter the SWNTs.

We also measured the network resistance of the pyrenecyclodextrin-SWNT/FET device between the source and drain with zero-gate voltage. The resistance measurement was carried out by applying a 100 mV bias with a Keithley 2400 apparatus. The network resistance responds (Figure 2b) quickly to the turning on and off of the LED, where $I = 40$ W m^{-2} and $\lambda = 280$ nm. When the light is on, the sheet resistance increases and stays high until the removal of the light. The data in the sharp-increase region were enlarged and shown to fit well to an exponential equation, producing a time constant of 5.1 s. The photoresponse is fully recoverable after removal of the light, indicating complete recovery of the CT. To eliminate the possibility that the change of the resistance was a result of the response of the SWNT network itself, we carried out a control experiment on the SWNT network without the coating of pyrenecyclodextrins and did not observe any detectable resistance change. The light wavelength dependence of the pyrenecyclodextrin-SWNT/FET was investigated by monitoring the changes in resistance of the device upon illumination by light of different wavelengths with a fixed intensity ($I = 40$ W m^{-2}). Light was applied in wavelength intervals of 20 nm from 260 to 420 nm. Each specific wavelength of light was left on for 10 s and off for 50 s to allow the device to recover. The results show that the resistance of the device increases when it is exposed to light and decreases when the light source is removed, an observation that is consistent with the data presented in Figure 2b. The changes in resistance of the pyrenecyclodextrin-SWNT/FET in response to light of varying wavelengths yet of constant intensity are shown in Figure S4 in the Supporting Information, overlaid with the absorption spectrum of the pyrenecyclodextrin (5.64×10^{-5} mol L^{-1}) recorded in DMF solution at 25 °C. The clear correlation between the magnitude of the changes in resistance of the pyrenecyclodextrin-SWNT/FET and the absorption spectrum of the pyrenecyclodextrin provides direct evidence that the light-induced change of the pyrenecyclodextrin's electronic structure is coupled to the CT process through the SWNT network.[3k]

Next, the pyrenecyclodextrin-SWNT/FET device was soaked in an aqueous solution of the ADA−Ru guest for 2 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 the hosts and recognize the guest molecules. When the guest molecules are included in the cavities of the pyrenecyclodextrin hosts, the threshold voltage of the pyrenecyclodextrin-SWNT/FET device shifts even more toward a negative gate voltage by about 4.1 V in the dark, that is, from the red curve to the orange one in Figure 3a. The change in the transistor characteristic for the pyrenecyclodextrin-SWNT/FET device reaches a maximum value in relation to the shift and

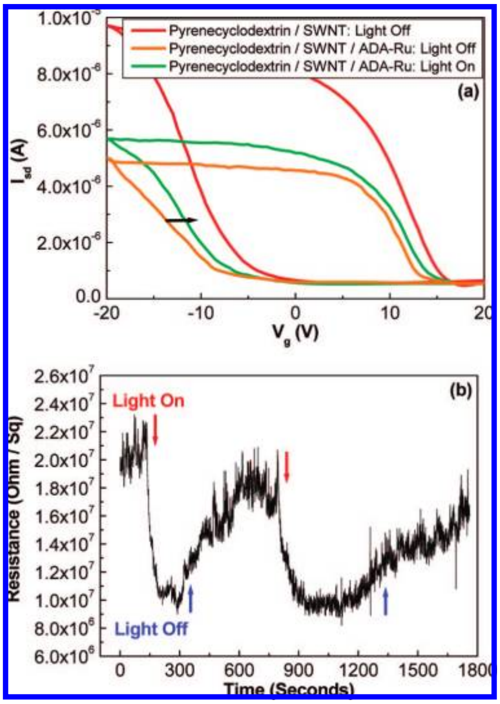

Figure 3. (a) The $I_{sd}-V_g$ curves of the pyrenecyclodextrin-SWNT/FET before (red) and after (orange) binding the ADA−Ru complex (2.20 mM) in the dark and the $I_{sd}-V_g$ curve of the ADA−Ru-pyrenecyclodextrin-SWNT/FET when the light is on (green), $\lambda = 490$ nm and $I = 40$ W m^{-2}. (b) The resistance of the ADA−Ru-pyrenecyclodextrin-SWNT/FET device vs time monitored under zero gate voltage, $\lambda = 490$ nm and $I = 40$ W m^{-2}.

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the tilt of the transfer curve in the presence of guest molecules. A control experiment was conducted to demonstrate that the threshold voltage of bare SWNT/FET device, that is, the device without the coat of pyrenecyclodextrin molecules, did not show any appreciable change in the presence of the ADA−Ru guests under exactly the same conditions because the ADA−Ru guests without the binding of attached pyrenecyclodextrins are not immobilized on the surfaces of SWNTs. These results can be explained by the fact that, as the guest molecules become included in the cavities of the pyrenecyclodextrin hosts, two possible phenomena can come into play: one is that 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 ground-state CT from the ADA−Ru guests to the pyrenecyclodextrin-SWNT hybrids, that is, causing a change in the charge carrier density (n) in the SWNTs, or the other is that 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[16] of the SWNTs.

As the maximum excitation wavelength (λ_{ex}) of the ADA−Ru guest is 490 nm (see Figure S5 in the Supporting Information), an LED with an intensity (I) of 40 W m^{-2} and excitation wavelength (λ_{ex}) of 490 nm is used as a light source for the FET sensing device. The fluorescence of the pyrenecyclodextrin is too weak to be determined and can be ignored under this excitation wavelength with the same conditions.[17] Interestingly, after the LED has been switched on for 5 min, the transfer curve of the pyrenecyclodextrin-SWNT/FET device shifts back to the right (from the orange curve to the green one in Figure 3a) by about 1.9 V in the presence of the ADA−Ru guest. The response of the device to the light is a shift of the threshold voltage toward positive voltages, indicating hole-doping of the SWNTs.[3k] Thus, photoexcitation of the device causes a CT from the pyrenecyclodextrin-SWNT hybrids to the ADA−Ru complex. An explanation for this process is that the direction of the photoinduced CT may depend on several factors including (i) the orientation of the guest molecules along the SWNTs, (ii) the functionalization method (covalent or noncovalent) to derivatize the SWNTs, and (iii) the structure of the particular guest molecule used. Because there was initially a ground-state CT to the pyrenecyclodextrin-SWNT hybrids upon addition of the ADA−Ru guest, the photoinduced CT simply indicates at least partial recovery of these transferred charges. In other words, upon photoexcitation of the ADA−Ru guest, some of the charges that had been transferred to the pyrenecyclodextrin-SWNT hybrids in the ground state are transferred back to the ADA−Ru molecule in the excited state.

To provide further support for our conclusions, we performed some investigations in solution. We determined the fluorescent change of the pyrenecyclodextrin in the presence of the ADA−Ru guest with an excitation wavelength (λ_{ex}) of 274 nm at 25 °C. In aqueous solution, the fluorescence intensity (Figure 4) of the pyrenecyclodextrin solution (3.10 × 10^{-6} mol L^{-1}) decreases on the stepwise addition of an ADA−Ru solution ((0 − 4.65) × 10^{-6} mol L^{-1}). The competitive light absorption of the ADA−Ru guest was too weak to be determined and can be ignored in the fluorescence experiments under this condition. This fluorescent quenching phenomenon suggests (i) because the decreased fluorescence intensity can be rationalized[18] by the decreased microenvironmental hydrophobicity of the β-CD cavity and/or steric deshielding around the fluorophore (the pyrene unit in the pyrenecyclodextrin) arising from the inclusion complexation between the β-CD cavity (host) and the adamantyl moiety of the ADA−Ru complex (guest), the fluorescent group (the pyrene unit) of the host can be attacked efficiently by the deactivating water molecules through the formation of the host−guest inclusion complex, which consequently contributes to the fluorescence decrease of the host, and/or (ii) a CT process exists from the pyrenecyclodextrin to the ADA−Ru guest in the system because the ADA−Ru complex can act as an electron acceptor. Because we treated the pyrenecyclodextrin-decorated SWNTs as single entities in the FET sensing device, this observation is consistent with the conclusion that there is a CT process from the pyrenecyclodextrin-SWNT hybrids to the ADA−Ru complex in the FET device when the light is on.

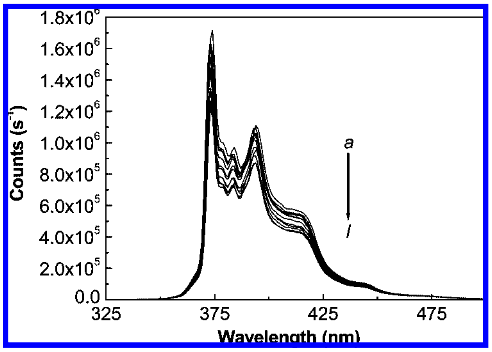

Figure 4. Fluorescence spectral changes of the pyrenecyclodextrin (3.10 × 10^{-6} mol L^{-1}) upon addition of ADA−Ru (0, 0.42, 0.85, 1.27, 1.69, 2.11, 2.54, 2.96, 3.38, 3.81, 4.23, and 4.65 × 10^{-6} mol L^{-1} from a to l) in aqueous solution at 25 °C, λ_{ex} = 274 nm.

Because we do not observe any appreciable threshold voltage change in bare SWNT/FET device, the device without the coat of pyrenecyclodextrin molecules, in the presence of the ADA−Ru complex as demonstrated above, we performed the fluorescent experiments on the ADA−Ru complex with the SWNTs in solution to get some insight for the interaction between them. Significantly, the fluorescence intensity (see Figure S6 in the Supporting Information) of the ADA−Ru aqueous solution (3.76 × 10^{-6} mol L^{-1}) increases on the stepwise addition of a SWNT DMF solution ((0−0.67) × 10^{-3} g L^{-1}) with an excitation wavelength (λ_{ex}) of 490 nm at 25 °C. Similar fluorescent enhancement behavior of the ADA−Ru aqueous solution (3.76 × 10^{-6} mol L^{-1}) with the stepwise addition of a pyrenecyclodextrin aqueous solution ((0−6.58) × 10^{-6} mol L^{-1}) can be observed under an excitation wavelength (λ_{ex}) of 490 nm at 25 °C. Under these conditions, the competitive light absorption of the SWNTs or pyrenecyclodextrin was too low to be determined and so can be ignored in the fluorescence experiments. The fluorescent enhancement of the ADA−Ru complex upon the addition of the SWNTs or the pyrenecyclodextrin supports[3k,12c,15] firmly the fact that a CT process from the pyrenecyclodextrin-SWNT hybrids to the ADA−Ru complex happens when the light is on in the FET device.

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Furthermore, the network resistance of the pyrenecyclodextrin-SWNT/FET device in the presence of ADA−Ru was also measured by turning on and off of the LED ($I = 40$ W m^{-2} and $\lambda = 490$ nm). When the light is on, the sheet resistance (Figure 3b) decreases and stays low position until the removal of the light. The photoresponse is almost recoverable after removal of the light, indicating the recovery of the CT. The resistance responds to the turning on and off of the LED more slowly, as compared to that of the pyrenecyclodextrin-SWNT/FET device. The data in the decrease region were enlarged and shown to fit well to an exponential equation, producing a time constant of 65.0 s. This long time constant, measured from the resistance, may not reflect[19] the CT dynamics from the pyrenecyclodextrin-SWNTs to the ADA−Ru guests, simply because of the fact that the charge reconfiguration over the entire network lasts until it reaches an equilibrium state.

Conclusion

We have demonstrated that the pyrenecyclodextrin-SWNT/FET device can serve as a tunable photosensor for sensing a luminescent Ru complex, backed up by fluorescent spectroscopic experiments in solution. When the light is on ($I = 40$ W m^{-2} and $\lambda = 280$ nm), the transfer curve of the pyrenecyclodextrin-SWNT/FET device shifts toward a negative gate voltage by about 1.6 V and its sheet resistance increases quickly, indicating a CT process from the pyrenecyclodextrins to the SWNTs. In contrast, the transfer curve of the pyrenecyclodextrin-SWNT/FET device in the presence of the ADA−Ru guest shifts toward a positive gate voltage by about 1.9 V and its sheet resistance decreases slowly when the light is on ($I = 40$ W m^{-2} and $\lambda = 490$ nm), showing a CT process from the pyrenecyclodextrin-SWNT hybrids to the ADA−Ru guests. These photoresponse processes are recoverable after removal of the light. The results reveal the SWNT/FET sensing devices can be tailored to meet specific needs using rationally designed approaches to analyte sensing. They raise the prospect of promising applications in the area of tunable light detection, as in artificial eyes and PVDs.

Experimental Section

General. All reagents, including β-CD, 1-adamantaneacetic acid (**4**), ruthenium(III) chloride hydrate, 4-hydroxybenzaldehyde (**1**), and 1,10-phenanthroline (**6**), are commercially available and were used without further purification. SWNTs were purchased from Carbon Solutions Inc. and used without further purification. 4-(2-Hydroxyethoxy)benzaldehyde (**3**), 1,10-phenanthroline-5,6-dione (**7**), and (1,10-phenanthro-line)$_2$RuCl$_2$ (**9**) were prepared as described previously.[20−22] Pyrenecyclodextrin and pyrenecyclodextrin-decorated SWNT hybrids were synthesized according to our previous report.[9] Nuclear magnetic resonance (NMR) spectra were recorded on Brüker Avance 500 and 600 spectrometers at 25 °C. Chemical shifts were reported in parts per million (ppm) downfield from the Me$_4$Si resonance, which was used as the internal standard when recording ^{1}H NMR spectra. Electrospray ionization (ESI) mass spectra were measured on an IonSpec FT-ICR mass spectrometer. Fluorescence spectra were recorded on LPS-220B fluorescence spectrometer (Photon Technology International) with lamp power supply at 25 °C.

SWNT/FET. The FET device was fabricated using CVD-grown SWNT networks as the channels on silicon wafers with a 500 nm thick silicon dioxide (SiO$_2$) dielectric.[12] The density of the network was chosen to be 1.5 tubes μm^{-2}, just above the percolation threshold to avoid too many conduction paths through the metallic SWNTs, a situation that would reduce the ON/OFF ratio of the transistor characteristics. The lift-off lithography process was used to pattern the *e*-beam deposited Pd contact pads on top of the SWNTs network. Oxygen plasma was used to etch away the SWNTs outside the source-drain channels. Because the channel is 200 μm long and 1000 μm wide, approximately 100 times longer than the SWNTs, the network resistance, rather than the contact resistance between Pd and network, dominates the overall resistance. During the sensing process, three independent measurement experiments were performed to afford self-consistent parameters, the changes of the threshold voltages and the resistances, and give the averaged values.

5: A mixture of 4-(2-hydroxyethoxy)benzaldehyde **3** (1.16 g, 7.0 mmol), 1-adamantaneacetic acid **4** (1.27 g, 6.5 mmol), DCC (1.44 g, 7.0 mmol), and DMAP (10.0 mg, 0.1 mmol) in CH_2Cl_2 (50 mL) was stirred for 5 h at room temperature in an atmosphere of Ar. The resulting suspension was filtered, the filtrate was evaporated, and the residue was subjected to column chromatography (SiO_2, CH_2Cl_2 eluent) to give compound **5** (1.46 g, 65%) as a colorless solid. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C, TMS): δ 1.64−1.72 (m, 12H, ADA−H), 1.95−1.97 (m, 3H, ADA−H), 2.13 (s, 2H, CO−CH$_2$−ADA), 4.29−4.31 (m, 2H, OCH$_2$), 4.45−4.47 (m, 2H, OCH$_2$), 7.05−7.07 (d, $J = 8.5$ Hz, 2H, Ar−H), 7.86−7.88 (d, $J = 8.6$ Hz, 2H, Ar−H), 9.91 (s, 1H, CHO). ^{13}C NMR (125 MHz, CD_2Cl_2, 25 °C): δ 28.6, 30.4, 32.6, 36.5, 42.1, 48.6, 61.6, 66.2, 114.6, 130.2, 131.6, 163.3, 171.1, 190.3.

8: 1,10-Phenanthroline-5,6-dione **7** (0.80 g, 4.2 mmol) and ammonium acetate (5.86 g, 133 mmol) were dissolved in hot glacial MeCO$_2$H (10 mL). While the mixture was stirred, a solution of **5** (1.43 g, 4.2 mmol) in glacial MeCO$_2$H (10 mL) was added dropwise to the mixture. The mixture was heated at 90 °C for 3 h and was then poured into H_2O (200 mL). The solution was neutralized with ammonia to pH 7, before being cooled to room temperature. The precipitate was filtered off and washed with large portions of H_2O. The product was dried to afford compound **8** (1.38 g, 62%) as a dark red solid. ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 25 °C, TMS): δ 1.46−1.56 (m, 12H, ADA−H), 1.85−1.87 (m, 3H, ADA−H), 2.04 (s, 2H, CO−CH$_2$−ADA), 4.21−4.26 (m, 2H, OCH$_2$), 4.33−4.37 (m, 2H, OCH$_2$), 7.13−7.14 (d, $J = 8.6$ Hz, 2H, Ar−H), 7.81−7.86 (m, 2H, Ar−H), 8.17−8.19 (d, $J = 8.6$ Hz, 2H, Ar−H), 8.85−8.87 (d, $J = 8.0$ Hz, 2H, Ar−H), 8.97−8.98 (d, $J = 7.6$ Hz, 2H, Ar−H), 13.5 (s, NH). ^{13}C NMR (125 MHz, CD_2Cl_2, 25 °C): δ 28.5, 32.8, 36.7, 43.2, 48.7, 62.1, 66.2, 112.5, 114.8, 121.6, 122.9, 124.3, 125.4, 126.6, 130.0, 132.5, 135.3, 150.1, 153.1, 154.4, 159.7.

ADA−Ru: **8** (0.15 g, 0.3 mmol) and **9** (0.15 g, 0.3 mmol) were dissolved in absolute EtOH (100 mL). The solution was heated under reflux for 6 h and was then filtered to remove unreacted starting materials. The filtrate was concentrated under vacuum and then poured into Et$_2$O (30 mL). The solution was filtered, and the obtained solid was washed with Et$_2$O. The product was dried to give compound (0.21 g, 71%) as a magenta solid. ^{1}H NMR (500 MHz, D_2O, 25 °C, TMS): δ 1.31−1.43 (m, 12H, ADA−H), 1.67−1.69 (m, 3H, ADA−H), 1.91 (s, 2H, CO−CH$_2$−ADA), 4.26−4.34 (m, 4H, OCH$_2$CH$_2$O), 7.32−7.34 (d, $J = 8.5$ Hz, 2H, Ar−H), 7.54−7.66 (m, 6H, Ar−H), 7.94−8.04 (m, 6H, Ar−H), 8.20−8.28 (m, 6H, Ar−H), 8.50−8.62 (m, 6H, Ar−H). MS (ESI): $m/z = 496.7$ $[M - 2Cl]^{2+}$.

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Supporting Information Available: ^{1}H NOESY NMR spectrum and figures of the fluorescent and UV−vis experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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