

Bioinspired Detection of Light Using a Porphyrin-Sensitized Single-Wall Nanotube Field Effect Transistor

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ABSTRACT

Single-wall carbon nanotube (SWNT) field effect transistors (FETs), functionalized noncovalently with a zinc porphyrin derivative, were used to directly detect a photoinduced electron transfer (PET) within a donor/acceptor (D/A) system. We report here that the SWNTs act as the electron donor and the porphyrin molecules as the electron acceptor. The magnitude of the PET was measured to be a function of both the wavelength and intensity of applied light, with a maximum value of 0.37 electrons per porphyrin for light at 420 nm and 100 W/m². A complete understanding of the photophysics of this D/A system is necessary, as it may form the basis for applications in artificial photosynthesis and alternative energy sources such as solar cells.

Porphyrin, the light-absorbing chromophore in chlorophyll, plays a central role in photosynthesis. The uniqueness of porphyrins is, to a large extent, their long-lived intermediate electronic state that is accessed upon their irradiation by visible light. It is this photoexcited porphyrin state that initiates an electron-transfer process within the grana of the chloroplast. Nature's process of electron transport has been mimicked in the form of an electron donor/acceptor (D/A) pair utilizing porphyrin derivatives combined with a complementary electron-accepting species. Charge-separated states have been studied by forming composites between porphyrin derivatives and carbon-based nanostructures such as C₆₀^{1–4} and, more recently, single-wall nanotubes (SWNTs).⁵ These states have extremely long lifetimes with reported durations in excess of 300 μ s for porphyrin/fullerene⁶ and 10 μ s for porphyrin/SWNT⁷ dyads. A variety of spectroscopic studies performed in solution indicate^{8,9} that a photoinduced electron transfer (PET) occurs from the porphyrin to the carbon-based species.

The photophysical properties of porphyrin/fullerene dyads make them strong candidates for applications as nanostructured photovoltaic devices. Dyads based on porphyrin/C₆₀, self-assembled on an indium tin oxide (ITO) electrode, show¹⁰ high photocurrent generation efficiencies, and have

also shown promise either as artificial photosynthetic devices¹¹ or as power supplies for molecular machines.¹² Recently, reports on porphyrin/SWNT hybrids have established¹³ their ability to serve as the active layer in solar cell devices. For use in photovoltaic devices, noncovalent functionalization^{14,15} of SWNTs with porphyrin derivatives has been an attractive approach since it does not destroy the desirable electronic properties of SWNTs. As such, understanding the dynamics of the PET occurring within D/A composites is essential for the full realization of their potential as photosynthetic materials. In the present report, we used field-effect transistors to directly monitor the interactions between a zinc(II) metalloporphyrin/SWNT system upon irradiation with visible light (Figure 1a).

There is an extensive body of work^{16,17} describing the response of SWNT field effect transistors (FETs) to various analytes. Those analytes noncovalently attached to the surface of a SWNT are expected to have two effects that can change the SWNT conductivity. First, there may be a charge transfer between the analyte and the nanotube, changing the carrier concentration (n). Second, the analyte may act as a randomly distributed scattering potential, changing the mobility (μ) of the charge carrier. Since conductivity is defined by $\sigma = ne\mu$ (where e is the electron charge), a measurement of the conductivity alone cannot distinguish between a change in the carrier concentration and a change in the mobility of the electrons. Transistor measurements of the transfer characteristics, however, can distinguish between these two mech-

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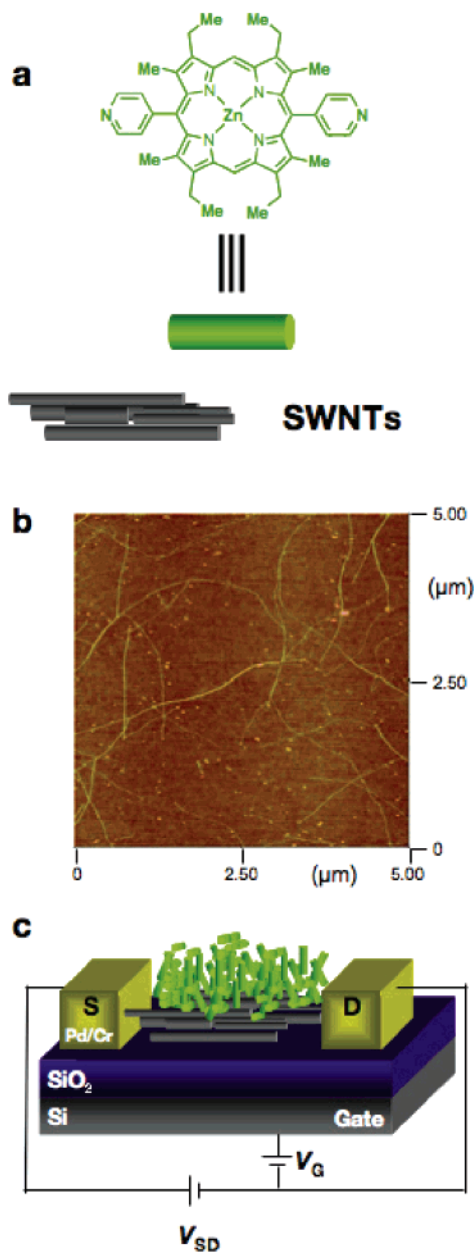


Figure 1. (a) Zinc(II) metalloporphyrin used to coat a SWNT FET device. (b) atomic force microscopy image of CVD grown SWNTs used. Average SWNT length $\sim 3 \mu\text{m}$, average tube diameter $\sim 1.5 \text{ nm}$. (c) Schematic of the device used for transistor measurements. A layer of the porphyrin was cast from a solution of *N,N*-dimethylformamide on top of SWNTs grown by CVD on a silicon wafer.

anisms. Extensive experimentation has established that, in SWNT network devices, changes in n lead to shifts of the threshold voltage (the voltage where the device first turns on). For example, previous studies have shown^{18–20} that the binding of electron-accepting molecules (NO_2 , F_4TCNQ) to a SWNT leads to a threshold voltage shift toward positive gate voltages, while the binding of electron-donating molecules (NH_3 , PEI) leads to a shift toward negative gate voltages. In another example, studies were done on the interaction between monosubstituted benzene compounds and SWNTs; it was found that the shift of the transfer curve is proportional to the Hammett values of the substituents.²¹

Since these shifts correlated well with the Hammett parameter, it is their conclusion that the shifts observed are due to charge transfer between the aromatic compound and the SWNTs. In contrast, a change in the mobility μ leads to a change in the device transconductance called the tilt (defined as the ratio of the slope of the I_{VG} curve to its initial slope, where both slopes are measured at zero gate voltage). A decrease in the device mobility can be caused by geometric deformations introduced along the nanotube by the analyte, by randomly charged scattering centers, or by changes occurring at the tube–tube interface. Our previous investigations of protein binding to nanotubes using a FET have demonstrated²² the importance of distinguishing between a change in mobility and a change in carrier concentration.

SWNT FETs were fabricated using a chemical vapor deposition (CVD) process where the SWNT networks were grown on silicon wafers (5000 Å of oxide), with a network density just above the percolation threshold ($1.6 \text{ tubes}/\mu\text{m}^2$, Figure 1b).²³ With an average tube length of $3 \mu\text{m}$ and an average tube diameter of 1.5 nm , the surface coverage is 0.72% . The networks were contacted by thermally evaporated Pd/Cr source–drain electrodes. We then used a lithography step, followed by an oxygen plasma etch, to define nanotube channels of known length and width between the source and drain electrodes. The channel length (L) was $500 \mu\text{m}$ and the channel width (W) was $1000 \mu\text{m}$. By working with such long channels ($L \approx 300$ times greater than the SWNT length), we are operating in a regime where the contact resistance arising from the presence of Schottky barriers is small compared to the resistance of the nanotube network itself. On top of the SWNTs, $1 \mu\text{L}$ of porphyrin dissolved in DMF ($1.2 \times 10^{-6} \text{ M}$) was added and dried in vacuum. This method of drop-casting a photoactive compound onto a SWNT network has been reported previously²⁴ to provide a strong enough interaction to show evidence of charge transfer upon illumination with light. Care was taken to apply the porphyrin only to the middle two-thirds of the SWNT channel, such that no porphyrin was within $100 \mu\text{m}$ of the contacts. Therefore, any change in the device characteristics should be attributed to resistance changes occurring along the SWNT channel and not in the Schottky barrier at the contacts. Figure 1c shows a schematic of the transistor device.

The transistor characteristics of the device were measured by applying a 15 mV bias between the source–drain electrodes while sweeping the gate voltage between $\pm 6 \text{ V}$ at 250 mHz (gate amplitude and sweep rate optimized to minimize hysteresis). Figure 2a shows the transfer curve for a SWNT FET, both before and after the addition of porphyrin, and two distinct changes are noticeable. First, and most apparent, is a suppression of the source–drain current for all gate voltages. This is most likely the result of the addition of charged scattering sites (porphyrin molecules) distributed randomly along the nanotube, thus decreasing the hole mobility, and is in broad agreement with previous reports of a porphyrin-coated SWNT FET.²⁵ Another possible cause for the drop in mobility is that the porphyrin is affecting the inter-SWNT contacts, which could easily disrupt the current through a network that is close to the percolation

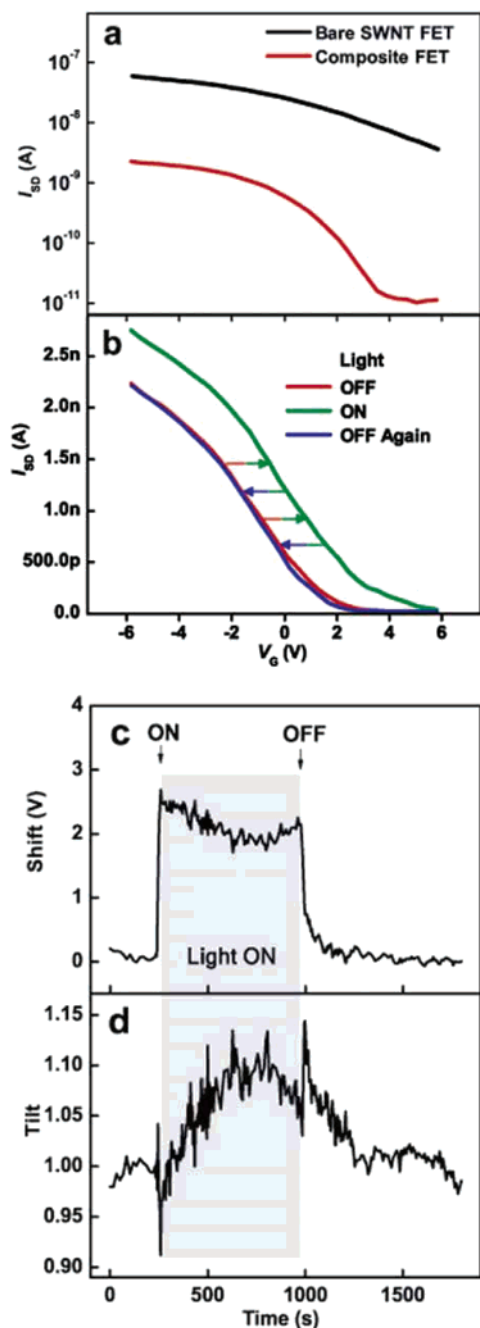


Figure 2. (a) Transfer curve of SWNT FET (250 mHz gate sweep rate, 15 mV gate sweep amplitude), before (black) and after (red) addition of $1 \mu\text{L}$ of 1.2×10^{-6} M porphyrin in DMF. The FET device ($W = 1000 \mu\text{m}$ and $L = 500 \mu\text{m}$) was measured in the dark for both curves. Up and down sweeps have been averaged. (b) Transfer curve of device before (red) and after (green) illumination by 100 W/m^2 (420 nm peak at 15 nm fwhm) light supplied by an LED. Light was left on for 1000 s in an otherwise dark room. The blue line shows transfer curve after light has been turned off, showing full device recovery. The green curve shows ~ 2 V shift of the transfer curve toward positive gate voltages (indicating enrichment of holes along the nanotube) while under illumination. (c, d) Fits to the data obtained in (b) show the shift and the tilt of the transfer curve as a function of time (data point taken every 4 s). Light is on during times indicated by the shaded box.

threshold. The second change in the transfer curve is the presence of an “off” state in the device coated with porphyrin that is not present in the bare device for the gate voltage

range used. This indicates that the addition of porphyrin introduces a shift in the threshold voltage toward negative gate voltages; however, because there is no well-defined “off” state in the bare SWNT device, it is difficult to determine the magnitude of this shift. The shift introduced by adding porphyrin to the SWNT FET could be caused by either (a) the ground-state charge transfer of electrons from the porphyrin to the SWNTs or (b) the displacement of oxygen molecules from the surface of the SWNTs.²⁶ These two distinct changes (shift and tilt) become more pronounced at high porphyrin concentrations, as more SWNTs become coated with porphyrin molecules. The device characteristic shown in Figure 2a has reached the saturation value of shift and tilt, indicating full porphyrin coverage of the two-thirds of the SWNT network channel that was coated.

The photoresponse of the porphyrin-coated FET was investigated by its illumination with an LED centered at 420 nm (15 nm full width/half max), which approaches the center wavelength of the porphyrin Soret band (416 nm). The LED was placed 1 cm from the device and calibrated such that $50 \mu\text{W}$ of light falls on the device area of $5 \times 10^{-7} \text{ m}^2$ (100 W/m^2). Figure 2b shows the transfer curve of the device in the dark (red curve), illuminated by light (green curve), and again in the dark (blue curve). The response of the device to the light is a shift of the threshold voltage toward positive voltages, indicating hole doping of the SWNTs.²⁷ Thus, photoexcitation of the device causes a transfer of electrons from the SWNTs to the porphyrin. By contrast, if the light was modifying the intertube contact resistance, the result would be a change in device mobility, indicated by a tilt in the transfer curve, and not the shift that we have observed. The photoresponse is fully recoverable after removal of the light, indicating complete recovery of the transferred electrons. The direction of the threshold voltage shift indicates that the process transfers electrons from the SWNTs to the porphyrin, which is quite surprising since porphyrins are thought to be electron donors.^{7,8,28} An explanation for this discrepancy is that the direction of the PET may depend on several factors: (a) the orientation of the porphyrin molecule along the SWNTs, (b) the functionalization method of SWNTs (covalent or noncovalent), and (c) the molecular structure of the particular porphyrin derivative used. Since there was initially a ground-state transfer of electrons to the SWNTs upon addition of porphyrin, the PET simply indicates at least partial recovery of these transferred electrons. In other words, upon photoexcitation of the porphyrin, some of the electrons that had been transferred to the SWNT in the ground-state are transferred back to the porphyrin molecule in the excited state. Therefore, the porphyrin molecule may remain an overall electron donor in the excited state, albeit a much weaker one than it was in the ground state.

The time dependence of the change in carrier concentration (shift) and the change in device transconductance (tilt) was further analyzed. Shown in parts c and d of Figure 2 is the time dependence of the response as the light source was turned on and left on for a period of just over 10 min before being shut off. Transfer curve sweeps were recorded every 4 s and fitting algorithms were used to extract the shift and

tilt for each curve. Figure 2c shows a quick (time scale <1 ms) shift of the transfer curve in response to irradiation by light, followed by a slow tilt (Figure 2d) that occurs on the order of several minutes. We interpret these time scales to indicate that the shift is a consequence of the initial excitation of porphyrin electrons, followed by a transition of electrons from the SWNTs to the porphyrin, creating a charge-separated species. The much longer process indicated by the tilt most likely arises from a spatial rearrangement of the resulting charged porphyrin along the surface of the SWNTs, thus altering the geometry of the scattering sites and slightly increasing the device mobility.

From the measured value of the shift (Figure 2c), the number of electrons transferred per porphyrin molecule can be extracted. Before the porphyrin/electron conversion efficiency was calculated, the following assumptions were made: (a) there is full coverage of two-thirds of the SWNT network by porphyrin molecules and (b) only those porphyrins that are in contact with a SWNT will contribute to the charge-transfer process. The formula $C \times V = Q$ allows the calculation of the number of electrons transferred from the SWNT network. The capacitance C of the FET is estimated from the total capacitance of each individual nanotube. The analytical formula for the capacitance per unit length (C/L) of a metal cylinder above an infinite conducting plane, lying in a dielectric medium is $C/L = 2\pi\epsilon\epsilon_0/\ln(2h/r)$.²⁹ For a nanotube of radius (r) ≈ 1.5 nm, a dielectric thickness (h) of 5000 Å and dielectric constant (ϵ) of 4.1, we approximate that $C/L \approx 350$ fF/cm³⁰ for an individual tube. Using the average density of 1.6 tubes/ μm^2 , average tube length of 3 μm , and device area of $5 \times 10^5 \mu\text{m}^2$ leads to a device capacitance of ≈ 84 pF. Substitution of the device capacitance and the threshold voltage shift of 1.7 V (lowest value of shift in Figure 2c) into $C \times V = Q$ and solving for the charge Q leads to a transfer of 8.9×10^8 electrons from the SWNTs. The number of porphyrin molecules that contribute to this PET is calculated by dividing the total active area of the SWNTs in our device by the area of each porphyrin molecule (~ 1 nm²). This calculation leads to approximately 2.4×10^9 porphyrin molecules in contact with the SWNTs. Thus, we estimate a transfer of $8.9 \times 10^8 / 2.4 \times 10^9 \approx 0.37$ electrons/porphyrin molecule. By comparison, previous studies on NH₃/SWNTs have revealed¹⁶ that 0.04 electrons per NH₃ molecule are transferred.

The magnitude of the PET was found to be a function of the intensity of light used. The intensity dependence of the PET was indirectly measured by monitoring the resistance of a SWNT FET device (at zero gate voltage) coated with porphyrin in response to light of fixed wavelength but variable intensity. Although we do not evaluate the shift and tilt separately for this measurement, the data shown in Figure 2c,d already indicate that the resistance change is dominated by the shift for short time scales and the tilt for long time scales. A 420 nm LED was used to illuminate a device coated with porphyrin (a different device than that used in Figure 2 was used for this experiment), and the resistance was monitored over time (60 s) using varying light intensities (Figure 3a). We found that the device responded in the same

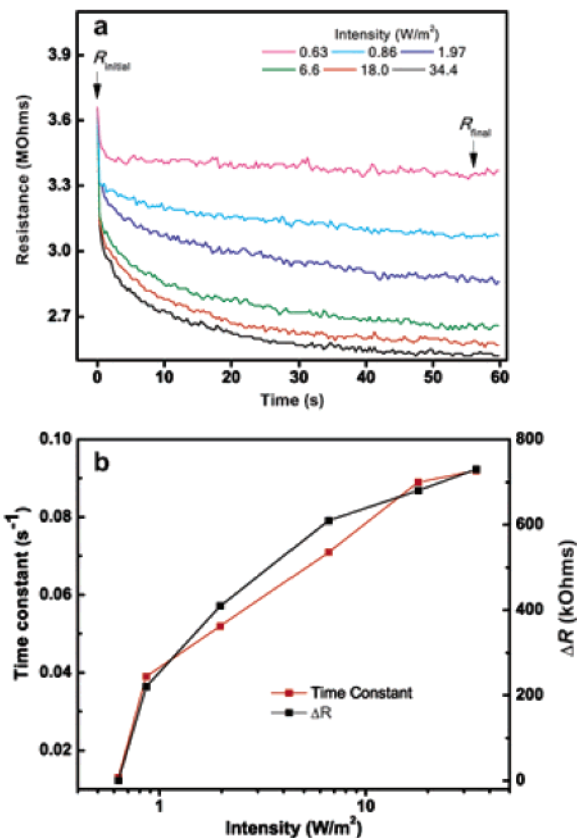


Figure 3. (a) Resistance vs time of porphyrin-coated SWNT FET at zero gate voltage, upon illumination by light of various intensities. The SWNT channel is 1 mm wide and 100 μm long. Contact to device made with Pd/Cr contacts and a probe station. Resistance measured using a Keithley 2400 multimeter in a two-point probe setup (500 mV bias). Light supplied by LED (420 nm peak/15 nm fwhm). (b) Parameters extracted from fits to first few seconds of curves in (a) using $y = R_{\text{final}} + R_2 e^{-y/t_1}$ where t_1 is the time constant and ΔR is the initial resistance minus R_{final} .

direction (decreasing resistance) for all intensities used, but the saturation value of the device resistance varied. This indicates that the FET curve shifts to the right for all intensities (electrons transferred from the SWNTs to the porphyrin molecules) but that the magnitude of the shift is a function of the light intensity. The response recorded for the first few seconds was fitted to the equation $y = R_{\text{final}} + R_2 e^{-y/t_1}$ and two parameters were extracted: (1) the time constant, t_1 , and (2) the change in resistance, ΔR , which is defined by the initial resistance (R_{initial}) minus R_{final} . Since the change in resistance is dominated by the shift for short time scales, and the IV_g curve is linear at zero gate voltage, the parameter ΔR is proportional to the magnitude of the shift of the transfer curve. These two parameters are plotted for each intensity in Figure 3b. We observed that (a) both t_1 and ΔR vary as a function of applied light intensity and (b) both t_1 and ΔR approach a saturation value. The fact that the ΔR value is a function of light intensity gives clear indication that the porphyrin excited and ground states exist in dynamic equilibrium. The PET in this D/A system is governed by the rate of porphyrin electron excitation to an intermediate state by absorbed photons and by the rate at which these photoexcited electrons decay back to the ground

state. The rates of these two processes exist in dynamic equilibrium. Note that in the absence of a relaxation process back to the ground state, one would find a saturation at the same resistance for all intensities, yet one would approach this limiting value with a different time constant. Further analysis of the data including the temperature dependence of the dynamics will be reported later.

The wavelength dependence of the porphyrin/SWNT PET was also investigated by monitoring the change in resistance of the device upon illumination by light of different wavelengths, but fixed intensity. For this experiment, we used a device consisting of a layer of SWNTs coated with porphyrin, with a macroscopic channel size (1 cm^2), enabling us to attach wires to the device with silver epoxy and place it in a spectrofluorimeter. Using the tunable, narrow ($\sim 3\text{ nm}$) light source of the spectrofluorimeter, we applied light of fixed intensity (5 W/m^2), but variable wavelength to the device, and monitored the change in resistance at each wavelength. Light was applied in wavelength intervals of 20 nm from 710 to 370 nm . Each specific wavelength of light was left on for 5 s and off for 55 s to allow the device to recover. We found that the resistance of the device decreased when it was exposed to light and increased when the light source was removed (inset in Figure 4). This is consistent with the data from Figure 2b, indicating the removal of electrons (addition of holes) to the already p-type SWNTs in response to light, and the subsequent recovery of those electrons in the dark. It has been reported³¹ that a bare SWNT device exhibits a higher resistance upon irradiation with UV–vis light. This response is believed to arise from the photoinduced desorption of oxygen molecules from the SWNT surface, thus depleting the holes and lowering the device conductance. However, in our device, the PET between the porphyrin/SWNTs dominates the photoinduced oxygen desorption, at least in the wavelength ranges tested. Figure 4 shows a plot of the change in resistance of the device for the time that the light was switched on, at each particular wavelength, overlaid with the absorption spectrum of the porphyrin molecule in solution. The clear correlation between the magnitude of the change in resistance and the porphyrin absorption spectrum provides direct evidence that the light-induced change of the porphyrin's electronic structure is coupled to the charge transport through the nanotube network. The process of electron transfer back to the SWNTs in the dark (Figure 4 inset) has a longer time constant than the initial electron transfer of electrons from the SWNTs in the light, in broad agreement with reports³² on the photoresponse of a ruthenium complex/SWNT composite.

We have demonstrated that a porphyrin derivative can be combined with SWNTs to mimic part of the natural process of photosynthesis or, more specifically, the use of a light harvesting material to initiate an electron transfer. However, unlike photosynthesis, in our system the absorption of light initiates the transfer of holes rather than electrons from the porphyrin. We suspect that the direction and magnitude of the PET in these systems may be controllable, and as such, we are currently investigating different porphyrin derivatives

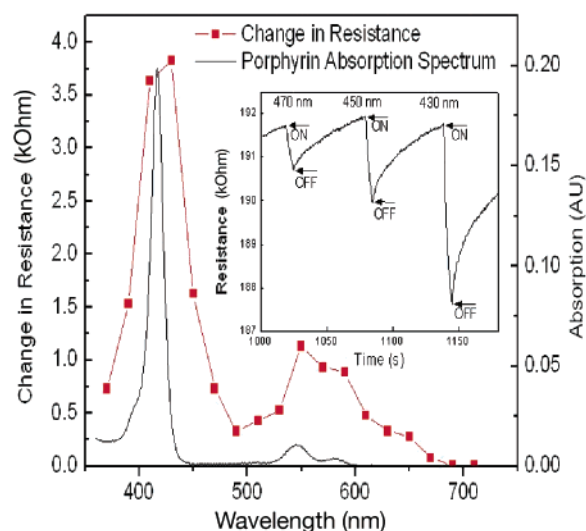


Figure 4. Change in resistance of device coated with porphyrin in response to light of varying wavelengths but constant intensity. The device was irradiated with a source of wavelength between 710 and 370 nm varied in intervals of 20 nm . All wavelengths used were adjusted to be 5 W/m^2 . Resistance was measured using a Keithley 2400 in a two-point probe setup (100 mV bias). Light was left on for 5 s , and off for 55 s . The time dependence of the resistance is shown in the inset for three different wavelengths as the light was cycled on and off. The larger graph shows the change in resistance of the device at each wavelength in response to the light being on for 5 s . Also included is the absorption spectra of the porphyrin molecule. The plot shows a correlation between the porphyrin absorption spectrum and the change in device resistance.

and SWNT functionalization methods. The rate and magnitude of the PET process were found to depend both on the wavelength and on the intensity of the light used, reaching a maximum value of 0.37 electrons/porphyrin molecule. The combination of a light-absorbing molecule having tunable absorption bands with a complementary material having high mobility can potentially act as a photosensitive wire able to move photoexcited charges away from the recombination centers. Such a device that exhibits these properties has promising applications in tunable light detection as in artificial eyes and, in the near future, as a photovoltaic device.

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