

Reversible Switching in Molecular Electronic Devices

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This manuscript compares the conductance when molecules connecting single-walled carbon nanotubes (SWNTs) change their states of conjugation. We use electrodes made by excising a nano-scale section from an individual SWNT, having shown previously that this is a general method to wire a small number (<10) of molecules into electrical circuits (Figure 1A).^{1–3} These SWNT molecular devices can be made sensitive to pH,¹ electron deficient aromatics,² and protein/substrate binding.³ Here we incorporate diarylethenes that are well-known to switch between open (non-conjugated) and closed (conjugated) states.⁴ We show that the thiophene-based device can be switched from the insulating open form to the conductive closed form but not back again, while the pyrrole-based device does cycle between the open and closed states.

The design of the molecular switches follows previous studies^{5–7} in solution, where the thiophene- and pyrrole-based molecules are known to switch from an open, non-conjugated form to a closed, conjugated form (Figure 1B). Previously these molecules have been investigated in self-assembled monolayers (SAMs) on gold surfaces,⁸ SAMs on particles,⁹ and switched ex situ and inserted into devices,¹⁰ but there are no reversibly switchable, single molecule devices.¹¹ It has been hypothesized that when they are wired to gold electrodes the thiophene-based devices do not switch because of the overlap of the excited-state of the open form of the molecule with the plasmon bands of the gold electrodes.^{11,12} Since we have developed SWNTs as easily and generally derivatizable electrodes, we were eager to see whether the fundamentally different band structure of the SWNT electrodes and/or the covalent attachment of the organic conductor to the carbon electrode would yield a switchable system.

We fabricated devices by a method that has been described previously, in which we grow individual SWNTs,¹³ place metal electrodes on the tubes through a stencil, and then oxidatively cut the nanotubes through a lithographic mask defined with an electron beam.^{1–3} Using this method we can create gaps that are of molecular size. The oxidative cutting functionalizes the ends of these carbon-based electrodes with carboxylic acids. This functionality allows a smooth introduction of the molecular bridge through formation of amide bonds (Figure 1A). We synthesized the diamines **1** and **2**.¹⁴ In solution, as expected, the photocyclization requires UV light (365 nm), and the photoreversion occurs with visible light (>500 nm). The UV-vis spectra for **1** and **2** are in the Supporting Information (Figure S1).

Amide bond formation between the amines of **1** and **2** and the carboxylic acids that terminate the electrodes provides the chemical attachment to span the gap and forms a molecular switch. In all cases, the rejoined SWNTs recover their original general electrical behavior (either metallic or semiconducting), albeit at reduced current values relative to the starting SWNT. The yield and fidelity of this connection reaction were determined by a method that has been previously described.^{1,3} Similar to these previous studies with molecular wires,^{1,3} the yield is ~3% for the connection of **1** (from 140 devices) and for the connection of **2** (from 96 devices). Figure 2A displays the electrical characteristics for a *metallic* SWNT

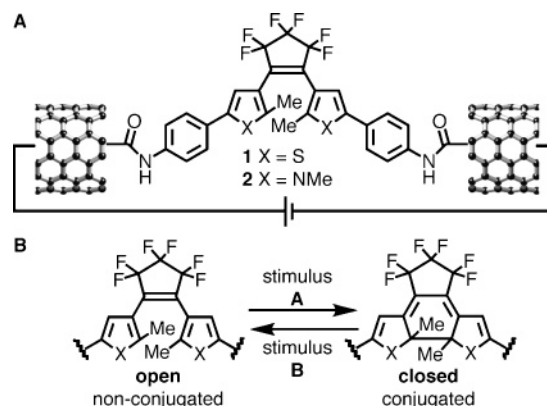


Figure 1. (A) Molecular bridges between the ends of an individual SWNT electrode. (B) Switching between conjugated and non-conjugated molecular structures.

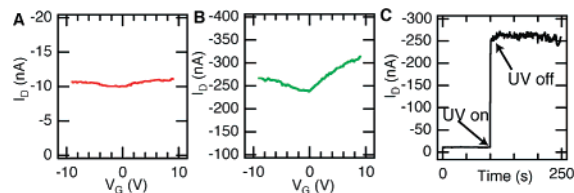


Figure 2. (A) Individual SWNT device connected with open-1. (B) Device from (A) after UV irradiation to form closed-1. (C) Drain current as a function of time. $V_{SD} = -50$ mV. $V_G = -9$ V.

connected with the molecular bridge open-1; these are similar to data obtained previously except the current levels for open-1 are generally lower than for other molecular wires.^{1–3} This is expected because the molecules in their open state have the pathway of conjugation broken.

When this cut tube that had been reconnected with open-1 was irradiated with a low-intensity (23 W) handheld UV source (365 nm), there was a 25-fold increase in the conductance of the device (Figure 2B). The UV-sensitivity of the open state of these devices is remarkable. The reason for this may be that when an open molecule bridges the gap it will be in a conformation that is primed to cyclize.⁴ When the light is extinguished, the current through these devices remains at the higher level (Figure 2C). We saw no change in the conductance over several weeks. We observe the same phenomenon when we employ a semiconducting SWNT instead of a metallic one. Table S1 summarizes similar behavior for several different devices using both metallic and semiconducting devices.

We are confident that the increase in conductance was a result of the behavior of the molecular bridge. We used two different molecular bridges that cannot switch and found that UV irradiation had a negligible effect (Figure S2). To rule out artifacts from the association of the amine-rich compounds on the surface of the carbon nanotubes, we have incorporated **1** and **2** into SWNTs that were only partially cut and found little effect when the devices were irradiated with UV or visible light (Figure S3). We have tested

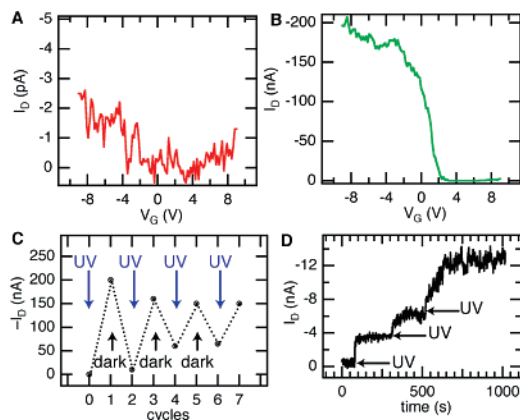


Figure 3. (A) Individual semiconducting SWNT device connected with open-2. (B) Device from (A) after UV irradiation to form closed-2. (C) Drain current as a function of the switching cycle for the device is irradiated with UV light and then left in the dark for 12 h. For (A)–(C) the $V_{SD} = -50$ mV and $V_G = -9$ V. (D) Steps in the conductance for a device reconnected with 2 when the UV light is pulsed. $V_{SD} = -50$ mV and $V_G = -1$ V.

pyrene-tethered photoswitches on an uncut tube and saw no change when they were irradiated. We cut gaps too large to be spanned by either diamine, treated these gaps with either 1 or 2, and saw no analogous jumps in conductance in the SWNTs when irradiated with UV light. We synthesized a monobenzamide of 1 and coupled it to either partially cut tubes or to fully cut tubes.¹⁴ These devices showed no measurable change in current after UV irradiation in either partially cut or fully cut tubes (Figures S4 and S5).

The essential point is that the opposite phenomenon occurs in the devices reported here when compared to ones made from gold-electrode break junctions with dithiolated molecules.¹¹ In the SWNT-molecule junctions, we were unable to photochemically switch devices bridged with 1 from closed to open state. In the gold-break junctions, the molecules switch from a cyclized form to an uncyclized form but cannot revert.¹¹ We hypothesize that in the present case the electrode dissipates the energy generated in the excited-state of closed-1 but not in open-1. This result is not wholly unexpected; Irie and co-workers have shown that increasing the length of π -conjugation on the termini of such switches decreases the quantum yield for opening.^{4,15} The nanotube is the ultimate extension of this conjugation.

To test whether the excited-state of closed-1 was responsible for the inability to switch, we synthesized the pyrrole-based molecular switch, 2. As expected,¹⁶ we found that the bis-benzamide of closed-2 is able to revert to its open state thermally. In solution, the half-time for opening of the bis-benzamide is 23 min as monitored by UV-vis spectroscopy. DFT calculations¹⁴ show that the thiophene-based switch closed-1 is only ~ 10 kcal/mol higher in energy than open-1, while the closed-2 is higher than open-2 by ~ 28 kcal/mol. Thus while the conrotatory ring-opening is thermally forbidden in each case, the barrier should be significantly smaller for 2.

Figure 3 shows the electrical behavior of an individual semiconducting device bridged with 2. The cut tube is initially reconnected with open-2, and the source-drain current through the device is very low (~ 2 pA) and there is only a slight increase as the gate bias voltage is increased. With UV irradiation the bridge cyclizes, and the on-state current of this semiconducting device increases by more than 5 orders of magnitude (Figure 3B). Irradiation with visible light did not restore the initial, low-conductance state; however, the low-conductance state reappeared when the device aged at room temperature overnight. The on/off cycle can be toggled many times. Of the many molecular wires we have incorporated into these devices, these are the only ones that

consistently have conductances that are similar to the original uncut, carbon nanotubes.^{1–3} Our quantum chemical calculations indicate that the orbital energies of closed-2 should produce a more conductive molecular bridge than closed-1.¹⁷

The high conductance for closed-2 may also be a consequence of multiple bridges forming between the ends of the SWNTs. The diameter of the tube measured with AFM (~ 2.4 nm) is large enough to incorporate as many as eight molecular bridges. Data in Figure 3D suggest the presence of multiple molecular bridges. We pulse the UV-light source three times. Subsequent to each pulse there is an increase in conductance and then a plateau. After the last molecule is triggered, there is a slow process that further increases the current through the device. The junction may be reorganizing to accommodate the steric difference between the open and closed forms of the molecule.

We have compared the device conductance when constituent molecules, diarylethenes, switch between states of conjugation. The thiophene-based molecular bridge can be switched from the open form to the closed form but not back again; the pyrrole-based photoswitch can cycle between the open and closed states.

Acknowledgment. We thank Philip Kim, Stephen O'Brien, Limin Huang, and Matthew Myers. We acknowledge financial support from the Nanoscale Science and Engineering Initiative of the National Science Foundation under NSF Award Number CHE-0117752 and by the New York State Office of Science, Technology, and Academic Research (NYSTAR). We thank the MRSEC Program of the National Science Foundation under Award Number DMR-0213574 and NYSTAR for financial support for MLS.

Supporting Information Available: Details of the methods used for the synthesis of the photoswitchable molecules, device fabrication/testing, DFT calculations, and control experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- We find that the HOMOs for closed-1 and closed-2 are very similar in size and shape. They are composed predominantly of π orbitals in the conduction path. The energy of the HOMO in closed-1 is ~ 10 kcal/mol lower than that of closed-2.

JA073127Y