

The Electrical Behavior of Nitro Oligo(Phenylene Ethynylene)'s in Pure and Mixed Monolayers

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In order to realize molecular electronic devices, molecules with electrically interesting behavior must be identified. One molecule that has potential for use in devices is an oligo(phenylene ethynylene) (OPE) molecule with nitro sidegroup(s). These “nitro” molecules have been reported to show electrical switching with memory behavior, as well as negative differential resistance (NDR). However, different research groups testing the nitro molecules in different test beds have observed different electrical behaviors. In this work, we assembled two different nitro monolayers: one completely composed of nitro molecules and the second a mixed matrix where nitro molecules were separated by dodecanethiol molecules. We used scanning tunneling microscopy to image each of the monolayers and observed that the nitro molecules were effectively inserted into the ordered dodecanethiol monolayer. We tested the electrical behavior of the pure monolayer, as well as the mixed monolayer, in our nanowell test device. The nanowell devices were fabricated on micron-size gold lines patterned on oxide-coated silicon wafers. The gold lines were covered with a silicon dioxide layer, through which a nanometer size well was milled. This nanowell device was filled with a self-assembling monolayer of organic molecules, and capped with titanium and gold. The nanowell electrical results showed switching with memory for the pure nitro monolayer, but not for the mixed monolayer. This switching behavior consisted of a molecule starting in a high conductivity state and switching to a low conductivity state upon application of a threshold voltage. The high conductivity state could only be returned by application of an opposite threshold voltage.

Key words: Oligo molecule, nitro oligo(phenylene ethynylene) (OPE), electrical behavior

INTRODUCTION

In order to build electronic circuits using organic molecules, it is essential to identify molecules with suitable electrical behavior that can be combined and integrated with conventional materials to perform logical functions. In the recent past, an oligo(phenylene ethynylene) (OPE) molecule with a “nitro” side group, commonly referred to as the nitro molecule, has been used to demonstrate electrical switching with memory, a feature that may have potential device applications.^{1,2} However, not all re-

search groups testing the nitro molecule have observed electrical switching with memory behavior. Some groups have observed only reversible negative differential resistance (NDR),^{3,4} and others have observed electrical switching without memory.^{5,6} A review of the literature reveals that groups testing the nitro molecule in devices that contacted and supplied voltage through molecule assemblies composed of thousands of molecules have observed switching with memory behavior.^{1,2} Others, who have used devices that contacted and supplied a voltage to just a few molecules or that consisted of nitro molecules inserted in an alkanethiol matrix, did not observe

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memory effects.³⁻⁶ Additionally, Allara et al. tested individual nitro molecules as well as groups of self-assembled molecules and found that the magnitude of molecular conduction varied depending on the environment around the molecule.⁷ Thus, it may be possible that the environment of the nitro molecule affects conduction and that electrical switching with memory behavior is a phenomenon that only occurs when a large group of nitro molecules is present in a pure monolayer. To investigate such a possibility, we tested a monolayer of nitro molecules, as well as a monolayer of nitro molecules inserted in an alkanethiol matrix, in our nanowell test device.⁸ In this work, we will refer to the monolayer composed solely of nitro molecules as the “pure nitro layer” and the monolayer of nitro molecules inserted into the alkanethiol monolayer as the “mixed monolayer.”

When we tested each of the two monolayers in our nanowell test device, we observed electrical switching with memory from the pure nitro monolayer, but not from the mixed monolayer. The absence of switching behavior in the current-voltage (I-V) characteristics of the mixed monolayer indicates that this behavior may not be an intrinsic characteristic of individual nitro molecules, but possibly a result of interactions among thousands of nitro molecules in a pure assembly. Although there are other reports of switching with memory behavior/NDR/switching without memory¹⁻⁶ observed from the nitro molecules, to our knowledge, this is the first report of using the same type of test structure to test two different configurations of monolayers and observe two different behaviors. One configuration consisted of a monolayer of pure nitro molecules and exhibited the switching behavior. The other configuration consisted of individual nitro molecules inserted into an alkanethiol monolayer. This mixed monolayer of nitro molecules and alkanethiol molecules did not exhibit any switching behavior. Thus, the switching with memory behavior may be dependent on the local environment of the molecule. Although the origin of the observed switching behavior is not yet clear, our experimental results may help the research community in understanding the underlying cause of the observed switching behavior and reconciling the various behaviors reported by different groups.

EXPERIMENTAL SECTION

Figure 1a shows a schematic of the layout of the substrate where the nanowell devices were built. Micron size gold lines were patterned on an oxide-coated silicon wafer (3.3 mm × 3.3 mm). Each of the gold lines started at 200-micron size square pad and extended to the center of the chip where the lines were separated by 2–3 microns spacing. The substrate was covered with silicon dioxide layer, except the 200-micron size pads, which were used for probing, and another gold line from the top corner pad that made contact with the top evaporated gold contact. Each nanowell device was built on one of the gold lines at the center of the substrate. The final

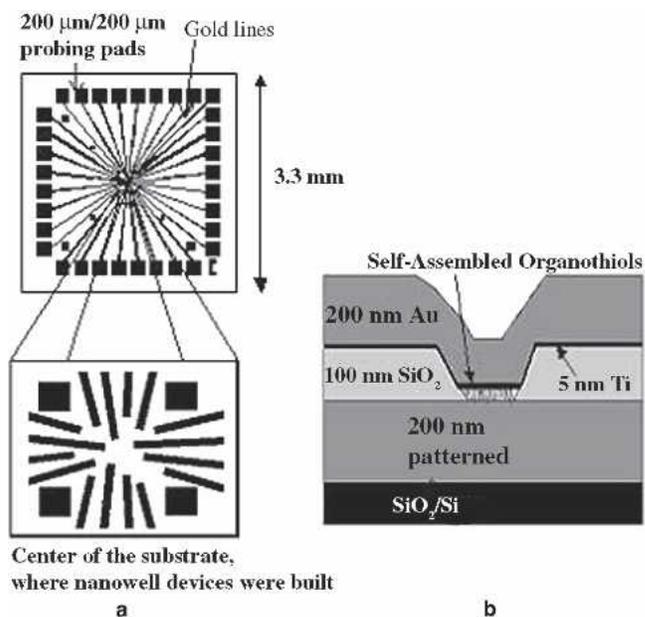


Fig. 1. (a) A diagram of the substrate where the devices are fabricated. (b) A cross section of the nanowell device.

nanowell device (shown in Fig. 1b) consisted of an approximately 50-nm-wide well in silicon dioxide with a gold bottom, where a monolayer of the desired molecules was self-assembled and then capped with titanium and gold. The nanowell device was first proven effective by testing with self-assembled alkanethiol molecules and comparing measured electrical characteristics with their established characteristics.⁸

Prior to the self-assembly of the nitro molecules, the nanowells were formed. Focused ion beam was used to mill holes through the silicon dioxide on pre-patterned substrates to expose approximately 50-nm size holes on gold lines. The substrates with the newly formed nanowells were then cleaned with piranha solution (30% hydrogen peroxide added to 66% sulfuric acid in a ratio of 1:3) to remove organic contamination. Once the substrates were clean, the millimolar solutions of molecules for assembly were prepared.

Figure 2 shows the molecules used to form the monolayers tested in the nanowell device. The pure monolayers tested were formed using only Molecule

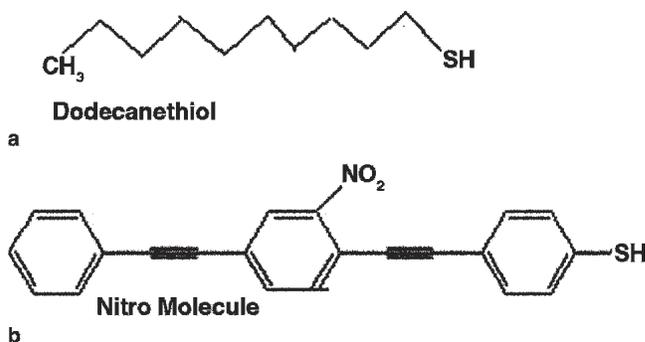


Fig. 2. The chemical structures of (a) the nitro molecule and (b) the dodecanthiol molecule.

2(b). Molecule 2(b) was synthesized at Rice University using standard protocols.⁹ The millimolar solution for self-assembly of the pure nitro monolayer was prepared in an inert atmosphere of nitrogen gas by dissolving the molecule in ethanol and then treating the solution with sulfuric acid to remove the protective acetyl group.¹⁰ Once the solution had been prepared and deprotected, the nanowell devices were left in the nitro solution for 48 h in a nitrogen atmosphere. Cyclic voltammetry was performed using an EG&G Model 273A Potentiostat (Oak Ridge, TN) on macroscopic Au surfaces coated with nitro monolayers to ensure that the desired dense monolayers had formed.¹⁰ After the nanowell substrates were removed from the nitro solution, they were rinsed with tetrahydrofuran (THF), and then transferred to the electron beam evaporator where 5 nm of titanium followed by 200 nm of gold was evaporated to form the top device contact. The titanium and gold metals were evaporated at the rate of 1 Å/s and 10 Å/s respectively. The specified source to substrate distance for our evaporating system is 17.5 in. During the evaporation of the top metal, no additional heating or cooling of the substrate was performed. The temperature of the substrate inside the evaporator was not expected to exceed the desorption temperature¹¹ (120°C) of the alkanethiol monolayer. To assemble the mixed monolayer in the nanowell device, dodecanethiol (C12) molecules were first assembled by immersing the nanowell chips in a millimolar solution of Molecule 2(b) for 24 h.¹² The chips were then rinsed with dichloromethane and transferred to a freshly prepared solution of nitro molecules.^{10,12} This method of inserting nitro molecules into an alkanethiol matrix was previously established and tested by Weiss et al.¹² After 16 h in the nitro solution, the nanowell substrates were rinsed with THF and transferred to the electron beam evaporator where the top metal contact was deposited.

RESULTS AND DISCUSSION

Scanning Tunneling Microscopy Images

Figures 3 and 4 show scanning tunneling microscopy (STM) images taken in air using a Molecular Imaging PicoPlus SPM (Tempe, AZ) with Pt/Ir tips, at a tip bias of 1 V and tunneling current of 5–10 pA for the molecules and 200 pA for bare gold surface. The samples used for STM studies were prepared by growing the monolayers on a 1 cm × 1 cm plain gold substrate. The gold substrate was prepared by evaporating 5-nm Ti (used as an adhesion layer) followed by 200-nm gold on silicon (100) substrates. In the low-magnification STM images in Fig. 3, morphological differences between the plain Au substrate 3a, pure alkanethiol monolayer 3b, pure nitro monolayer 3c, and the mixed monolayer 3d can be observed. Atomically flat terraces with approximate dimensions of 20 nm are observed on the Au surface (Fig. 3a). Holes appear on the gold grains in 3b that are not present on the grains in 3a. These holes are likely to be the defects in the alkanethiol monolayer

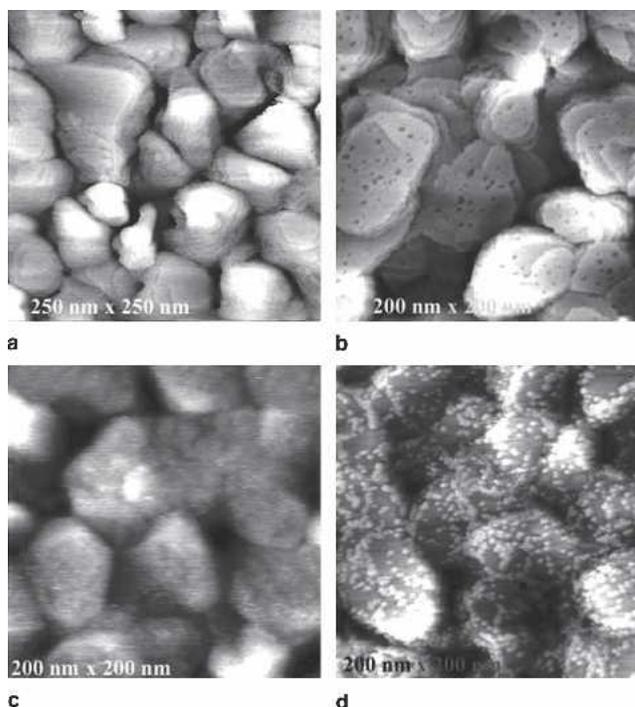


Fig. 3. (a) Constant current STM topographic images of bare Au with a tip bias of 0.1 V and tunneling current of 200 pA, (b) C12 monolayer on Au with a tip bias of 1 V and tunneling current of 5 pA, (c) pure nitro monolayer on Au with a tip bias of 1 V and tunneling current of 10 pA, and (d) a mixed monolayer of nitro molecules inserted in C12 on Au with a tip bias of 1 V and tunneling current of 5 pA.

that can be seen at the higher magnification in Fig. 4b. These holes do not appear in 3c, and are replaced by bright spots that are probably the nitro molecules inserted in the alkanethiol monolayer^{4,12} in Fig. 3d. Whether these bright spots are individual or groups of nitro molecules is unclear; however, most of the bright spots in Figs. 3d and 4d are approximately the same size as bright spots identified as individual OPE molecules by Weiss et al.¹²

Figure 4 shows STM images of the same samples as in Fig. 3, but at higher magnifications. The higher resolution image of the alkanethiol matrix in Fig. 4b shows not only the defect sites, but also striping that is consistent in period and geometry with what is expected for C12 alkanethiols on Au.^{12,13} Figure 4c of the pure nitro monolayer does not show any molecular ordering; it is unclear whether ordering is present and could not be resolved, or if the monolayer is not ordered. Ordering of nitro molecules at atomic scale resolutions has been observed by other groups using atomic force microscopy.¹⁰ However, Weiss et al. also did not observe ordering from monolayers of similar OPE molecules using STM.¹² Figure 4d shows the mixed monolayer at a higher resolution. The striping of the alkanethiol monolayer may not be clearly seen in Fig. 4d. The height scale for image 4b shows a height of 5 Å for the maximum brightness, whereas the height scale for image 4d shows a height of 20 Å for the maximum brightness of the image. The high contrast due to the nitro molecules in 4d may make the striping difficult to re-

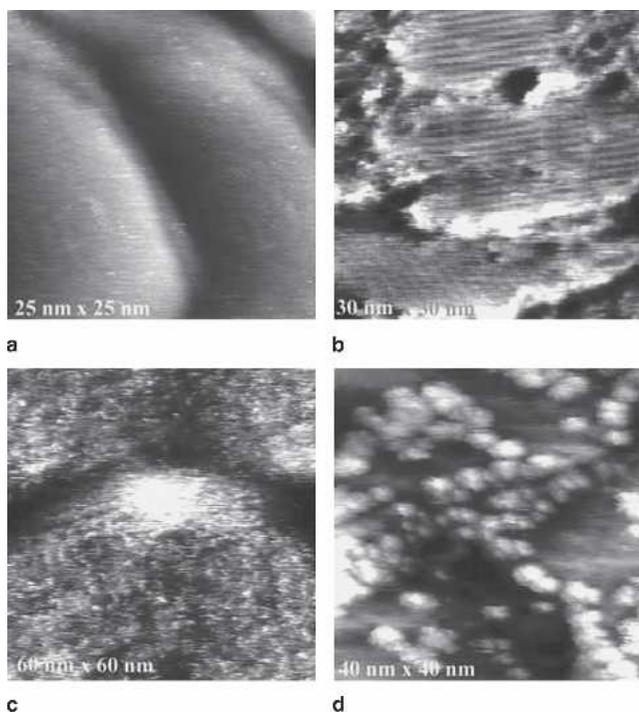


Fig. 4. (a) Constant current STM topographic images with scan areas of bare Au with a tip bias of 0.1 V and tunneling current of 200 pA. (b) C12 monolayer on Au with a tip bias of 1 V and tunneling current of 5 pA. (c) Pure nitro monolayer on Au with a tip bias of 1 V and tunneling current of 10 pA. (d) A mixed monolayer of nitro molecules inserted in C12 on Au with a tip bias of 1 V and tunneling current of 5 pA.

solve in the alkanethiol matrix surrounding the nitro molecules. However, this striping was observed when viewing the same area of the mixed monolayer using STM in current imaging mode rather than topographic imaging mode. Yet, from the STM image, it appears that the nitro molecules fill in defects existing in the alkanethiol monolayer, as well as insert along the grain boundaries of the gold surface. Scanning tunneling microscopy images thus confirm that the procedure described for forming the matrix is adequate for inserting the nitro molecules in an alkanethiol matrix.

Electrical Characteristics

The electrical behaviors of the pure nitro molecules, as well as the mixed monolayer, were tested in the nanowell test device. The monolayer of pure nitro molecules showed electrical switching with memory behavior.¹⁴ The graph in Fig. 5 shows an example of the switching with memory. For electrical measurements, the top contact was grounded and the forward bias (positive voltage) or reverse bias (negative voltage) was applied to the bottom contact. Thus, on the forward bias, electrons were injected from the top contact into the molecule, and on the reverse bias, electrons were injected from the chemisorbed contact into the molecule. Scan 1 in Fig. 5 shows the first reverse bias scan between 0 and -3 V. One can observe that at about -2.3 V, the current switches from a high conductivity state to a low conductivity state and then continues on a lower

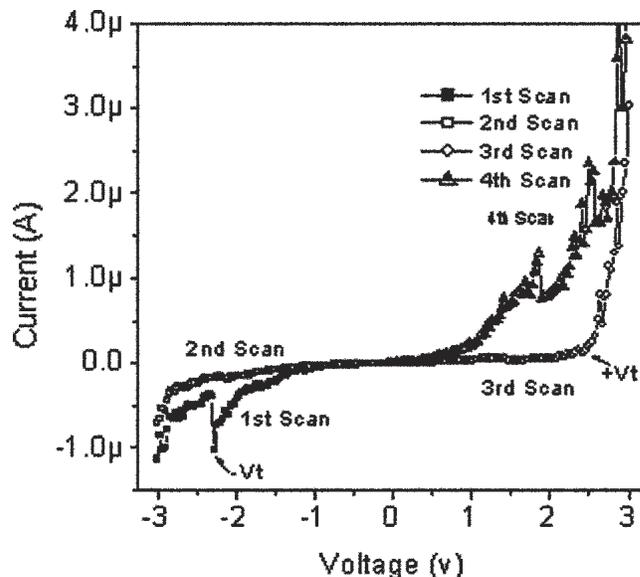


Fig. 5. I-V characteristics of pure nitro molecule monolayer showing switching with memory behavior.

conductivity path. We labeled -2.3 V in Fig. 5 as $-V_t$ to signify that this is the switching point, or threshold voltage. In Scan 2, the voltage is again applied from 0 to -3 V and the current remains in the low conductivity state. Switching from the low to high conductivity state is only possible after the opposite threshold voltage, $+V_t$, is applied during Scan 3. In Scan 3, one can observe a change in the slope of the I-V curve around $+2.5$ V on the forward bias. This sudden increase in current marks the change from the low conductivity state to the high conductivity state; we call this the forward bias threshold voltage or $+V_t$ point. Scan 4 shows that as the forward bias is applied from 0 V to $+3$ V again, the device remains in the high conductivity state until the reverse bias threshold voltage, $-V_t$, is applied. In about 50% of the devices, this switching behavior could be repeated before the device exhibited an irreversible electrical break down.

The switching with memory behavior was observed in 17% of the nanowell devices tested that did not show clear electrical opens or shorts. Electrical shorts were observed when the top metal penetrated through the defects in the monolayer and made contact with the bottom gold. Variations in the underlying gold, such as in grain size and roughness, may have made monolayers in some devices more susceptible to electrical shorts than in others. Similar switching behavior was observed from the other 83% of the devices, but electrical breakdown occurred before a complete cycle of switching from a high to a low state and back to a high state was observed. Additionally, there were variations in threshold voltage values and high/low ratios among devices that showed switching with memory. The average threshold voltage for switching from high to low conductivity was $|2.3| \pm 1.27$ V, and the average threshold voltage for switching from low to high conductivity was $|2.5| \pm 1.06$ V. The current ratios for

a switch from a high state to a low state ranged from 3:1 to 111:1, and the current ratios for a switch from a low state to a high state ranged from 1:1 to 1:9. The variations in on-off current among devices may be due to differences in nanowell sizes. The nanowell sizes were found to vary between 10 nm and 50 nm in diameter.⁸ However, the current density in our nanowell device was found to vary from pAs to μ As. If current scaled linearly with the number of molecules in the device, or if one expected the nitro molecules to act as molecular “wires,” the large range of current densities would not be expected. However, there is evidence that current may not scale linearly with the number of molecules in the device.¹⁵ Additionally, the source of the switching behavior is unknown, but there are simulations that suggest that the switching may be due to charging and discharging of the strong dipole nitro groups on the molecules.^{16,17}

We also tested the electrical characteristics of a mixed monolayer of nitro molecules inserted into a dodecanethiol matrix in our nanowell device. Out of the 208 matrix devices tested, 86% were clear electrical opens or shorts. The rest of the devices showed one of the four different behaviors. Figure 6a shows the I-V characteristics for the most common molecular behavior observed from the mixed monolayer. This behavior was seen from 48% of the devices that were not opens or shorts. The I-V curve is reversible, exponential, slightly asymmetric, and does not show any switching behavior between -2.5 V and 2.5 V. The current at -2.5 V was approximately 4 times higher than the current at $+2.5$ V. This asymmetry might have resulted from an energetic asymmetry between the bonded and nonbonded ends of the molecule.¹⁸ However, not all curves with this behavior showed this asymmetry. When voltage was increased beyond ± 2.5 V, the current increased exponentially before the device broke down irreversibly. At no point was any switching behavior observed from the mixed matrix tested in the nanowell. This type of exponential and reversible behavior observed from the matrix and shown in Fig. 6a has not been observed from the pure nitro monolayer in our nanowell device.

Figure 6b shows a plot comparing the current versus voltage for a nitro/alkanethiol mixed monolayer, a C12 monolayer, and the “on” and “off” states of a nitro monolayer tested in the nanowell device. The I-V plots from 0 to $+1$ V show that the current magnitude of the mixed monolayer is between the current magnitudes of the pure nitro monolayer and of the pure alkanethiol monolayer. The current magnitude of the mixed monolayer is observed to be about 100 times larger than that of pure C12 monolayer tested in the same test device. However, the current magnitude of the mixed matrix is smaller than that of the pure nitro monolayer in either the on or the off state. These results are expected because nitro molecules are more conductive than alkanethiols, and the mixed monolayer consists of a lower number of nitro mol-

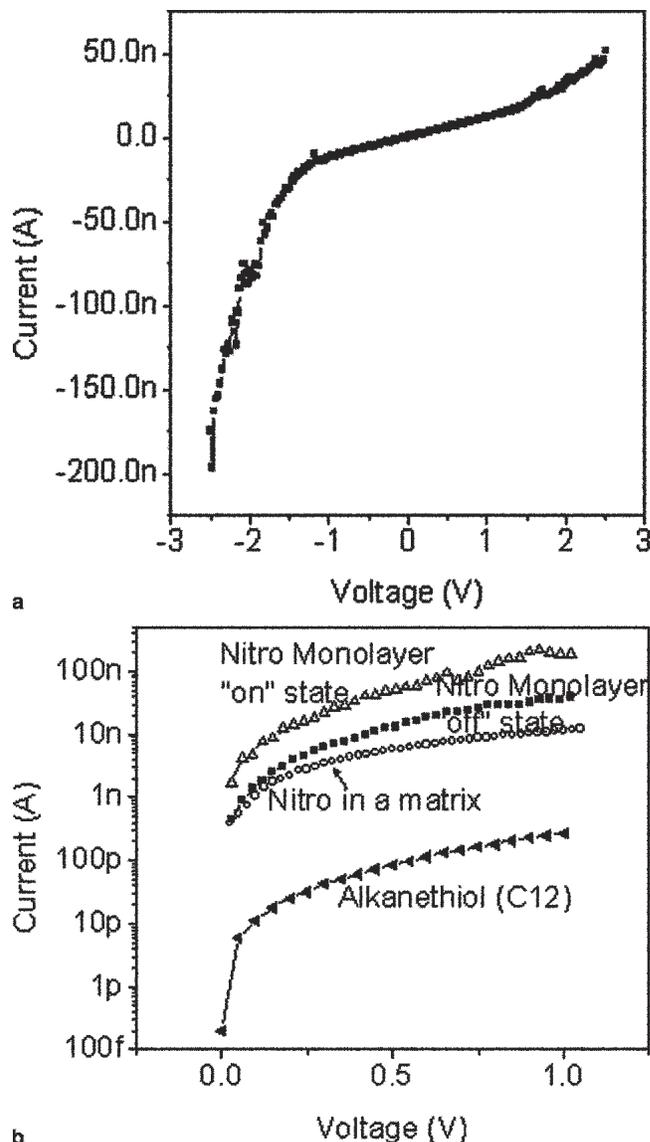


Fig. 6. (a) I-V characteristics of the most common behavior observed from the mixed monolayer; current magnitudes of a monolayer of alkanethiol (C12) molecules, a mixed monolayer, and (b) a pure nitro monolayer in each of the on and off states.

ecules than the pure nitro monolayer, and, thus, should show conductivity intermediate between the two.

Although the behavior seen in Fig. 6a was the most commonly observed behavior for the alkanethiol/nitro matrix, three other behaviors were additionally observed. The first behavior is NDR. Mayer et al. also observed reversible NDR peaks from nitro molecules inserted in a matrix of C16 molecules.³ However, the NDR observed by us was not reliably reversible. Additionally, our NDR was observed in only 7% of the matrix devices tested that were not electrical opens or shorts. As can be seen in Fig. 7a, the NDR occurs during the first scan at around -2.7 V, and then occurs again at -3.3 V of the second scan. This NDR did not occur on the third scan or following scans. When we tested the pure nitro monolayer devices, NDR-like behavior was

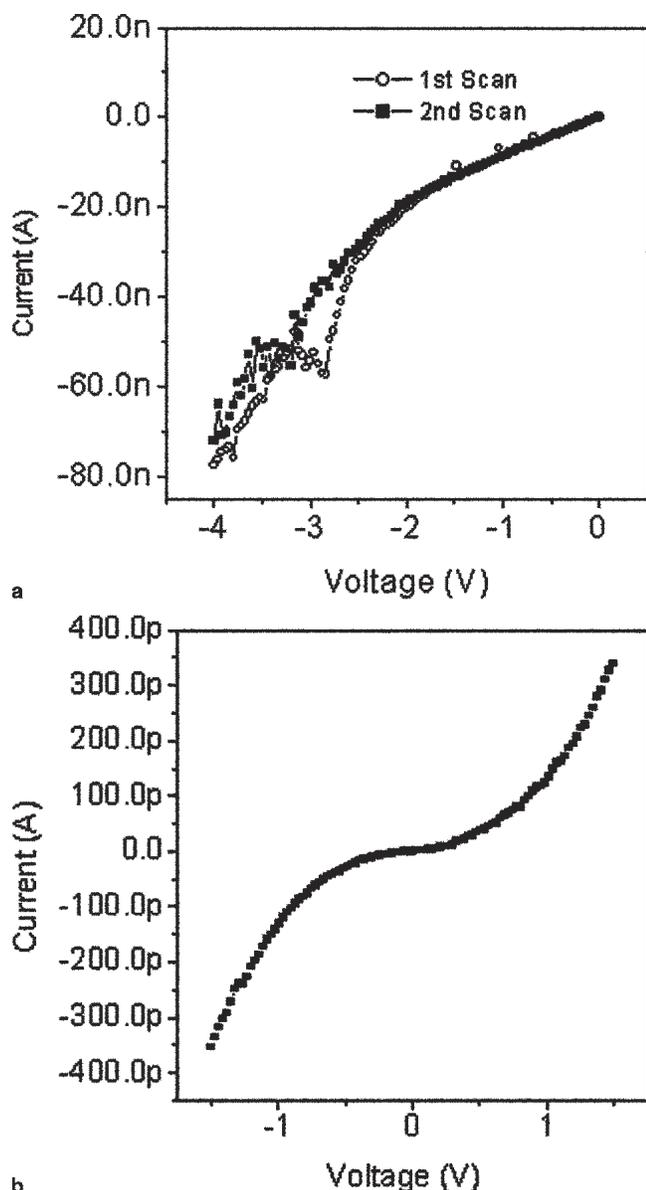


Fig. 7. Electrical characteristics that were observed occasionally from the mixed monolayer tested in the nanowell device (a) NDR and (b) pA of current.

only observed during a switch from high to low conductivity and was not reversible.¹⁴

The second behavior was similar to that shown in Fig. 6a, but significantly lower in current. These I-V characteristics were exponential and symmetric and were observed from approximately 10% of the devices that did not show electrical opens or shorts. The current magnitude of the curve in Fig. 7b is similar to what has been observed for C12 molecules in our device.⁸ Additionally, when these curves were fit to the Simmons equation,¹⁹ fitting parameters matched the expected values for C12.^{19–21} Thus, these devices may have had few to no nitro molecules participating in the conduction. The STM images in Figs. 3 and 4 show that the nitro molecules are inserted at the grain boundaries and defect sites in the C12 monolayer. If a nanowell is located on an

area of the alkanethiol monolayer that has few to no interstitial defect sites, nitro molecules may not be inserted, resulting in a mostly or all alkanethiol device and current in the pA range. The third observed behavior was an early electrical device breakdown that occurred before any reversible results could be observed. This early breakdown behavior was observed in approximately 35% of the devices that were not obvious electrical opens or shorts.

We observed switching with memory from the pure nitro molecules. However, a mixed monolayer of the nitro molecules inserted in a monolayer of alkanethiol molecules did not show the switching behavior. Therefore, the switching behavior may be dependent on the interaction between nitro molecules in a group. Previously reported simulation results suggested that the switching behavior may be caused by the change in conductivities due to the conformational change or charging of nitro molecules under an applied bias.^{16,17} If the switching behavior were caused solely due to the charging of the nitro molecule, the mixed monolayer would have exhibited the same behavior. Thus, it may be possible that the switching is also dependent on a conformational change of the molecules that does not occur in the mixed monolayer. There may be two reasons why the conformational change does not occur in a mixed monolayer. First, a group interaction between nitro molecules may be essential to assist an individual molecule to change and hold its conformation. This interaction may be dependent on the size of the group of nitro molecules. Second, the order of the surrounding matrix may have an influence on the behavior of individual nitro molecules. Since the STM image of the pure monolayer did not show any ordering but the image of a mixed monolayer did, it may be possible that an ordered matrix inhibited the conformational change of the nitro molecules.

In summary, we have tested the nitro molecule in two different monolayer environments in the same nanowell test device. We observed switching with memory while testing the pure nitro monolayer, but did not observe any switching behavior from a mixed monolayer of nitro molecules in a matrix of C12 alkanethiols. An exponential reversible I-V curve with nanoamps of current was observed most often from the mixed monolayer. The STM images of the mixed monolayer confirm that the nitro molecules were inserted in the alkanethiol matrix. Because the nitro molecules in the matrix did not show the switching with memory observed from a pure monolayer of the same nitro molecules in the same device, the switching with memory behavior may be dependent on contacting a large area of pure nitro molecules.

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