Effects of molecular environments on the electrical switching with memory of nitro-containing OPEs

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An oligo(phenylene ethynylene) (OPE) molecule with a nitro side group has exhibited electrical switching with memory and thus has potential for use in molecular electronic devices. However, different research groups have reported different electrical behaviors for this molecule. In addition to variations among test structures, differences in local molecular environments could be partially responsible for the differences in the reported results. Thus, we tested four variations of a nitro-OPE/dodecanethiol monolayer in the same type of nanowell test device to study how the environment of the nitro-OPE affects the observed electrical behavior. We found that the density of the nitro-containing molecules in the device altered the observed electrical switching behavior. Further, we found a positive correlation between the disorder of the monolayer and the observed electrical switching behavior. This correlation is consistent with suggestions that nitro molecule switching may depend on a conformational change of the molecule, which may be possible only in a disordered monolayer. © *2006 American Vacuum Society.* [DOI: 10.1116/1.2208994]

I. INTRODUCTION

Since memory behavior was first reported for the nitro-oligo(phenylene ethynylene) (referred to as the nitro-OPE) [Fig. 1(a)],[1] other researchers have reported various combinations of electrical switching, memory, and/or negative differential resistance (NDR).[2–4] These reports employed test structures that differed in the number of nitro-OPE molecules simultaneously contacted as well as in the local molecular environments. Some reports describe devices that contact thousands of molecules,[1,3] while other devices contact just a few.[2,4] In our previous work, we used our nanowell test device to address a possible correlation between contacting a large area of nitro molecules and observing memory behavior.[5]

However, that previous work only considered the type of molecules and not the ordering of the nitro-OPE monolayer's environment. A recent report indicates that this environment may correlate strongly with the rate of electrical switching for the nitro-OPEs.[4] The literature, as well as our own scanning tunneling microscope (STM) images, suggests that when molecules of nitro-OPEs are inserted into a preformed monolayer of alkanethiols, the alkanethiol monolayer remains ordered.[6] In contrast, a homogeneous monolayer of nitro-OPEs is disordered.

To test for correlations between the environment of the nitro-OPE molecules (including the type and ordering of the surrounding molecules) and observations of electrical switching with memory, we have tested four different types of monolayers in the nanowell test device. The first was a monolayer of solely dodecanethiols [Fig. 1(b)]. The second was a monolayer comprised solely of nitro-OPEs. The third was an "inserted" monolayer where nitro-OPE molecules were inserted into an ordered dodecanethiol monolayer following procedures established by Cygan *et al.*[6] The fourth was a "coassembled" monolayer where a disordered monolayer was formed by simultaneously assembling molecules of nitro-OPEs and dodecanethiols [Figs. 1(a) and 1(b), respectively].[6]

In the same type of nanowell device, we observed different electrical behavior from each of these four different monolayers. We observed simple exponential current-voltage characteristics without switching for the dodecanethiol monolayer and switching with memory behavior for the disordered monolayer of nitro-OPEs. The ordered inserted monolayer of nitro-OPEs in dodecanethiols showed mostly simple exponential behavior with no electrical switching. The disordered coassembled monolayer of nitro-OPEs and dodecanethiols showed reversible nonlinear behavior as well as switching with memory behavior. However, the switching with memory behavior observed from the disordered coassembled monolayer differed from that of the disordered

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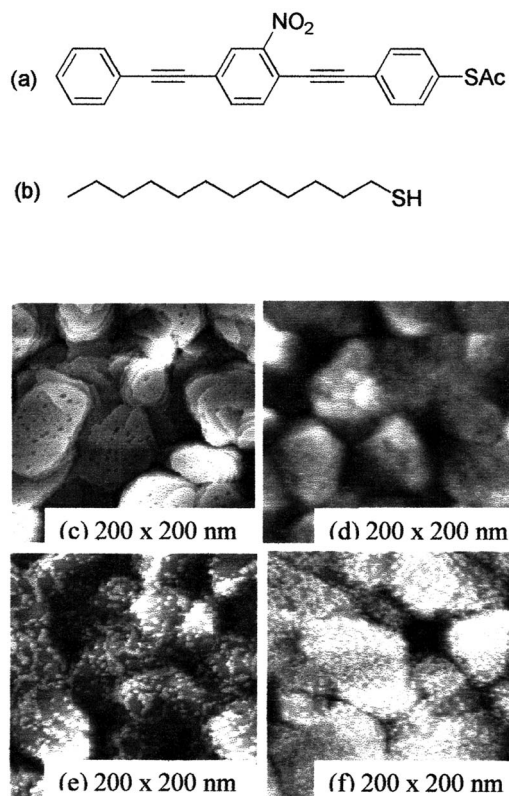[a]Electronic mail: john-bean@virginia.edu

FIG. 1. (a) Oligo(phenylene ethynylene) (OPE) molecule with a nitro side group (referred to as a nitro-OPE), which had its acetate moiety removed with acid during the assembly process of the free thiol, (b) a dodecanethiol molecule, (c) constant current STM topographic images of a homogeneous monolayer of dodecanethiol on Au with a tip bias of 0.1 V and tunneling current of 200 pA, (d) A homogeneous monolayer of nitro-OPEs on Au with a tip bias of 1 V and tunneling current of 10 pA, (e) an "inserted" monolayer of nitro-OPEs into a dodecanethiol monolayer on Au with a tip bias of 1 V and tunneling current of 5 pA, and (f) a "coassembled" monolayer of nitro-OPEs and dodecanethiols on Au with a tip bias of 1 V and tunneling current of 5 pA.

monolayer comprised solely of nitro-OPEs. Thus, the behavior of the nitro-OPEs seems to be dependent on both the type and order of the molecules' environment.

II. EXPERIMENT

We used the nanowell device to electrically characterize molecular monolayers. The nanowell device consists of a small well in silicon dioxide [formed using focused ion beam (FIB)] with a gold bottom where a monolayer is self-assembled and then capped with titanium and gold. This nanowell test device is described in greater detail elsewhere.[7]

Figures 1(a) and 1(b) shows the molecules that were used to form the monolayers tested in this study. The homogeneous monolayer of the nitro-OPE molecules was formed solely of the nitro-OPEs [Fig. 1(a)] (after liberation of the free thiol using published synthetic and deprotection protocols).[8] The dodecanethiol molecule shown in Fig. 1(b) was used in both the inserted and coassembled monolayers and was purchased from Sigma-Aldrich.

Prior to self-assembly of the molecules, the nanowells were cleaned with piranha solution (30% hydrogen peroxide

added to 66% sulfuric acid in a ratio of 1:3). The solution of nitro-OPE molecules was prepared in an inert atmosphere of nitrogen gas by dissolving 2 mg of molecules in 10 mL of ethanol and then treating the solution with 120 μL of sulfuric acid to remove the protective acetyl group.[9] For the coassembled monolayer, 80 μL of dodecanethiol was added to the solution of nitro-OPEs after deprotection.[8] The chips were then immersed in the thiol solution for 16 h. For the inserted monolayer, the chips were immersed in a solution of 120 μL of dodecanethiol in 10 mL of ethanol for 24 h. They were then rinsed with dichloromethane and transferred to a deprotected solution of nitro-OPE molecules (2 mg of molecules in 10 mL of ethanol deprotected with 120 μL of sulfuric acid) and were left for 16 h. The methods of preparing coassembled and inserted monolayers were previously established and tested by Cygan *et al.*[6]

After removal from solution, the nanowell chips were rinsed with tetrahydrofuran (THF) and a top metal contact bilayer of titanium and gold was grown by sequential evaporations. The titanium and gold were evaporated at the rates of 1 and 10 Å/s, respectively at chamber pressures of approximately 10^{-6} Torr. No additional heating or cooling of the substrate was performed during the evaporations. After evaporation, the devices were probed with a HP 4145B parameter analyzer to establish the electrical characteristics.

For *ex situ* imaging of the monolayer structure, a STM (Model: PicoPlus, Molecular Imaging Inc, USA) was used. The samples for the STM study were assembled by a routine similar to the one described above, on $\sim 1 \times 1$ cm^2 evaporated Au(100 nm)/Ti(5 nm)/Si substrates.

III. RESULTS AND DISCUSSIONS

A. Scanning tunneling microscopy results

Figures 1(c)–1(f) and 2(a)–2(f) show STM images taken in air with Pt/Ir tips, at a tip bias of 1 V and tunneling current of 5–10 pA. All STM images were taken in constant current mode. In the low magnification STM images in Fig. 1, differences can be observed between the images of the homogeneous monolayer of dodecanethiols on Au (c), a homogeneous monolayer of nitro-OPEs on Au (d), an inserted monolayer of nitro-OPE molecules in dodecanethiols on Au (e), and a coassembled monolayer of nitro-OPEs and the dodecanethiols on Au (f). Fig. 1(c) shows flat terraces with substrate vacancy sites. Figure 1(d) shows similar terraces (due to the grains of the polycrystalline gold surface). Figures 1(e) and 1(f) show "white" spots that are interpreted to be molecules (or groups of molecules) that are taller than their surrounding monolayer. These spots are approximately the same size as those identified as individual OPE molecules in an alkanethiol monolayer by Cygan *et al.*[6] Thus, the white spots in Figs. 1(e) and 1(f) are thought to be the nitro-OPE molecules inserted into the alkanethiol background layer. The presence or absence of alkanethiol ordering in the surrounding dodecanethiol monolayer cannot be
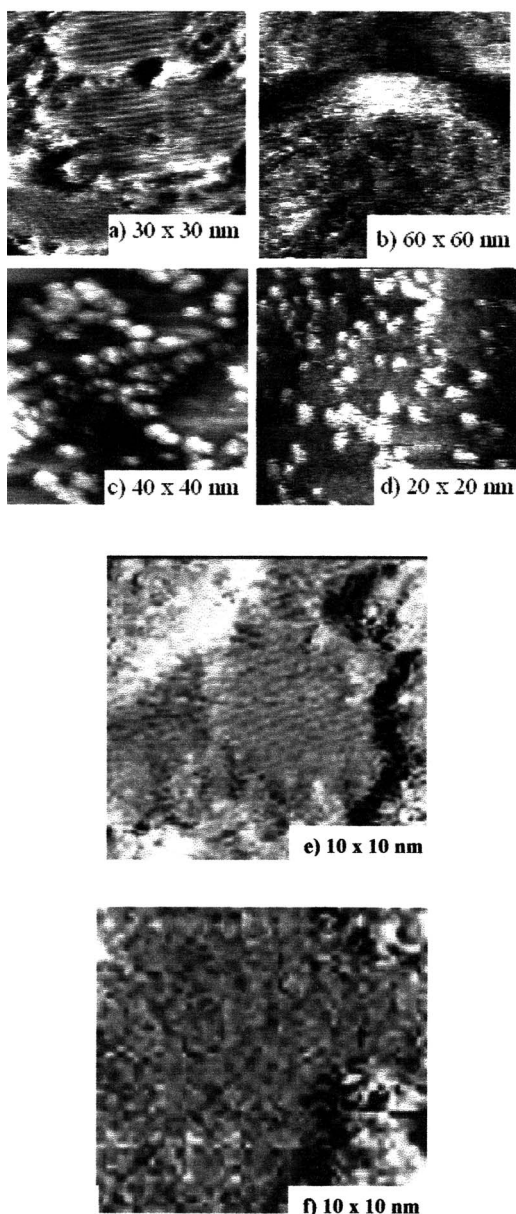
FIG. 2. (a) Dodecanethiol monolayer on Au with a tip bias of 1 V and tunneling current of 5 pA, (b) a homogeneous monolayer of nitro-OPEs on Au with a tip bias of 1 V and tunneling current of 10 pA, (c) an "inserted" monolayer of nitro-OPEs in a dodecanethiol monolayer on Au with a tip bias of 1 V and tunneling current of 5 pA, (d) a "coassembled" monolayer of nitro molecules and dodecanethiols on Au with a tip bias of 1 V and tunneling current of 5 pA, (e) a higher magnification image of Fig. 2(c), and (f) a higher magnification image of Fig. 2(d).

observed from these images [Figs. 1(c)–1(f)], but could be seen in higher magnification current images and is discussed below.

Figures 2(a)–2(d) show STM images of the same samples as in Fig. 1, but at higher magnifications. Figures 2(e) and 2(f) show even higher magnification images of Figs. 2(c) and 2(d). Figure 2(a) shows striping that is consistent with that reported elsewhere for an alkanethiol monolayer assembled on Au.[10] Figure 2(b) shows the homogeneous monolayer of nitro-OPEs; no such striping or ordering was observed at any

area of these samples. Other groups also have failed to observe ordering from monolayers of similar OPE molecules using STM.[6] Figure 2(c) shows the topographic images of the inserted monolayer of nitro-OPEs in dodecanethiols. This image matches what others have reported for similar molecules inserted into a dodecanethiolate monolayer.[6] The striping that indicates order in the surrounding monolayer is evident in the higher magnification image of Fig. 2(e). The pitch of the stripes matches that expected for a monolayer of ordered dodecanethiol molecules in an upright ordered configuration.[10] Although striping has been observed from other groups for molecules that are "lying down" on the substrate surface, the interstripe pitch expected for lying down dodecanethiol molecules is at least 30 Å (which is wider than the stripes we observe).[10] Figure 2(d) is the topographic image of the coassembled monolayer, which is similar to the image from the inserted monolayer [Fig. 2(c)]. However, no striping can be observed in the higher magnification image [Fig. 2(f)] of the surrounding dodecanethiol monolayer. Thus, STM images confirm that the procedure described is adequate for inserting or coassembling the nitro molecules in an alkanethiol matrix.

B. Electrical behavior of the homogeneous dodecanethiol monolayer

Once it was established that the four different types of monolayers (homogeneous dodecanethiol, homogeneous nitro, ordered inserted monolayers of nitro-OPEs in dodecanethiols, and disordered coassembled monolayers of dodecanethiols and nitro-OPE molecules) could be formed, the monolayers were assembled in the nanowell test device[7] and electrical measurements were performed. A homogeneous monolayer of dodecanethiols was first tested in the nanowell device. The current-voltage characteristics for this molecule are shown in Fig. 3(a). The *I-V* characteristics of the alkanethiols showed irreversible breakdown for applied voltages greater than approximately $|2|$ V. This electrical breakdown resulted in characteristics that indicated either an irreversible electrically "open" device (less than 10 pA of current at 1 V) or an irreversible electrically "short" device (milliamperes of current). This behavior was very different from that of the nitro-OPEs (see Secs. III C, III D, and III E), which showed reversible "switching" between two conductivity states. Of the 128 devices tested with this molecule, 6% showed the reversible exponential behavior of Fig. 3(a). The remainder of this set showed electrical opens or shorts.

C. Electrical behavior of the homogeneous nitro-OPE monolayer

The homogeneous monolayer of nitro-OPE molecules showed electrical switching with memory behavior.[11] The graph in Fig. 3(b) shows an example of the switching with memory. One can observe that when the applied voltage is scanned to −3 V, the current switches from a high conductivity state to a low conductivity state at approximately −1.75 V and then continues on a lower conductivity path. We labeled −1.75 V in Fig. 3(b) as $-V_t$ to signify that this is
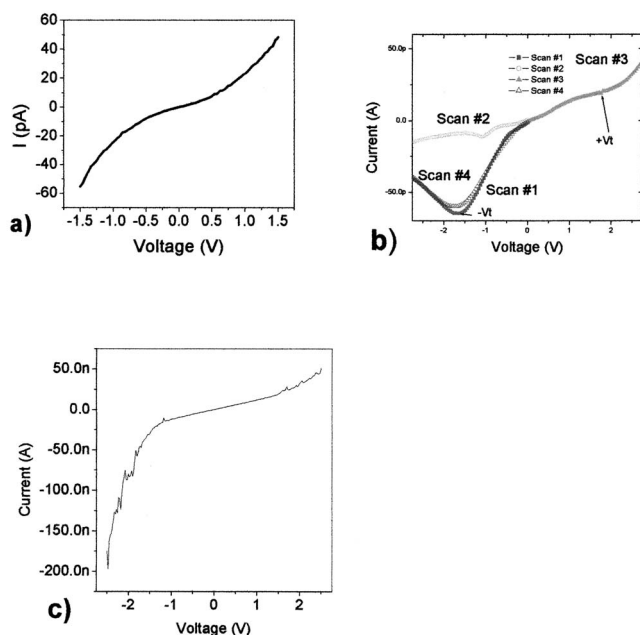
FIG. 3. (a) *I-V* characteristics of a nanowell device with a homogeneous monolayer of dodecanethiol and (b) *I-V* characteristics of the electrical switching with memory observed from the homogeneous monolayer of nitro-OPEs in the nanowell device. (c) The most common behavior observed from the nanowell devices with the "inserted" monolayer of nitro-OPEs in dodecanethiol.

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 low to high conductivity state is only possible after the opposite threshold voltage $+V_t$ is applied, as shown during scan 3. In scan 3, one can observe a change in the slope of the *I-V* curve around +1.75 V on the forward bias. This increase in current marks the transition 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 a negative voltage scan again being applied where the device again starts in the high conductivity state and switches to a low conductivity state. We were able to continue switching this device in this manner. In about 50% of the devices that showed the switching behavior, the switching could be repeated before the device exhibited an irreversible electrical break down. This switching behavior, including device statistics, is described in greater detail elsewhere.[11]

For this work, the term switching describes a change in conductivity with the application of a threshold voltage. A device was not deemed to "switch" unless it was observed to change from one conductivity state to the opposite state with an applied threshold voltage, and it was then observed to return to the original conductivity state with the application of the opposite threshold voltage. In addition, all switching devices exhibit "memory" behavior. In other words, the device will experience a change in its conductivity state upon the application of a particular threshold voltage (i.e., switch at V_t) and will hold (or "remember") this state until the required opposite threshold voltage is applied. For example, in

Fig. 3(b), this device switches in that in the first scan it changes from high to low conductivity (evident by the change in current between the first and second scans). It exhibits memory in that once it is switched to the low state (in the first scan), it remains in the low state (evident by the second scan) until $+V_t$ is applied with the third scan and it switches to a higher conductivity state (which is confirmed by the high conductivity in the fourth scan). This behavior looks similar to electrical hysteresis, but because the voltage was scanned in only one direction on each voltage side, we refer to it as switching

The switching with memory behavior was observed in 17% of the "working" nanowell devices (devices that did not show electrical opens or shorts). Similar switching behavior was observed in the remaining 83% of the devices, but in this case 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.

D. Electrical behavior of the "inserted" monolayer of nitro-OPE molecules in a dodecanethiol monolayer

We also tested the electrical characteristics of a monolayer of nitro-OPEs inserted into a monolayer of alkanethiols in our nanowell device. The specifics of this behavior have been reported in more detail elsewhere.[5] Out of the 208 devices tested, 86% were electrical opens or shorts. The rest of the devices showed one of four different behaviors. Figure 3(c) shows the *I-V* characteristics for the most common behavior (observed in 48% of the working devices). The *I-V* curve is reversible, exponential, asymmetric, and does not show any switching behavior between −2.5 and 2.5 V. The median current at −1 V for these devices was 9 nA. The asymmetry might have resulted from an energetic asymmetry between the Au bottom contact and Ti/Au top contact. 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.

Although the behavior seen in Fig. 3(c) was the most commonly observed behavior for the monolayer with the inserted monolayer, three other behaviors were also observed. The first of these behaviors was nonreversible NDR (7% of working devices). The second behavior observed was similar to that of Fig. 3(c), but lower in current (10% of working devices). These lower current *I-V* plots showed currents at 1 V in the range of tens of picoamperes, which is a similar current scale as observed for homogeneous monolayers of

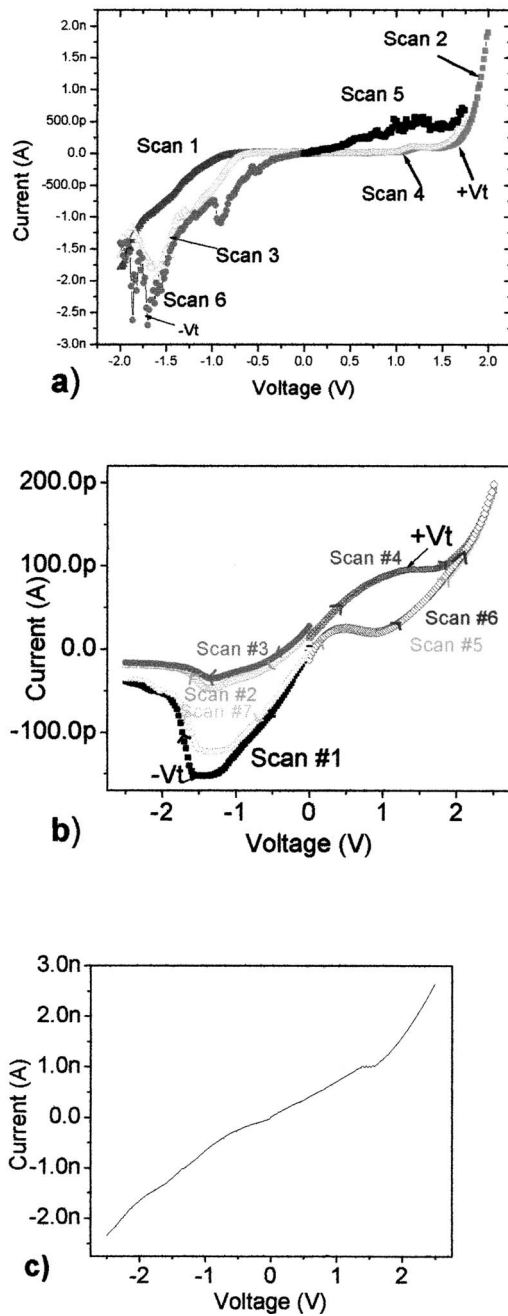## E. Electrical behavior of the "coassembled" monolayer of nitro-OPEs and dodecanethiols

Of the 96 disordered coassembled nitro-dodecanethiol monolayer devices that were tested, 30% were not electrical opens or shorts. These working devices showed various electrical behaviors including: two types of electrical switching, exponential behavior with nonreversible (NDR), and simple nonlinear behavior. One of the observed behaviors showed switching that was similar to that of the homogeneous monolayer of nitro-OPEs, but with the current starting in a low rather than a high conductivity state. This behavior was observed from 23% of the working devices and is shown in Fig. 4(a). Scan 1 is a scan from 0 to −2.0 V and shows current that starts in a low conductivity state. Scan 2 is a scan from 0 to +2 V and shows the current switching from the low to a "high" conductivity state at approximately 1.75 V $(+V_t)$. This high state is held until the current is scanned to −1.75 V (V_t) in scan 3 where the current switches to the low conductivity state again. Then, when the voltage is again scanned to $+V_t$ on the fourth scan, the current switches back to the high conductivity state. A subsequent positive voltage scan (scan 5) shows that the device remains in the high conductivity state until $−V_t$ is applied on scan 6. In this manner the current could be switched back and forth between the low and high conductivity states by applying the positive threshold and negative threshold voltages, respectively. The average positive switching threshold for this behavior was 1.5±0.07 V and the average negative switching threshold for this behavior was −1.7±0.21 V. The high/low current ratios for these ranged from 6:1 to 113:1.

The second type of switching behavior was observed in 8% of the working disordered coassembled devices and is shown below in Fig. 4(b). The switching for this device was similar to that observed from the homogeneous nitro-OPE monolayer device, but the high to low conductivity switching occurred on the positive as well as on the negative voltage sides. For this device, the current started in the high conductivity state and then switched to the low conductivity state when the threshold voltage $(−V_t)$ was applied (scan 1). In scans 2 and 3, this voltage is retraced and the current remains in the low state. However, the high state returns as soon as the voltage is scanned on the positive voltage side to $+V_t$ (scan 4). This low state holds as the voltage is rescanned on the same side (scans 5 and 6). The current again goes to a high conductivity state when a slightly negative voltage value is applied (scan 7). This switching at a voltage just beyond 0 is similar to the behavior observed for another molecule with nitro groups tested by Szochmacher Blum *et al.*[12] The average positive switching threshold voltage for these devices is 1.3±0.12 V and the average negative switching threshold voltage is −1±0.33 V. The on/off ratios ranged from 1.7:1 to 8.6:1. The scans in Figs. 4(a) and 4(b) show that the current at 0 V is not zero for the scans. This indicates some charging and discharging of the device, which was not observed for the homogeneous monolayer of nitro-OPEs.

FIG. 4. (a) Electrical switching with memory observed from the "coassembled" monolayer of nitro molecules and dodecanethiols in the nanowell device-showing current starting in low state, (b) electrical switching with memory observed from the "coassembled" monolayer in the nanowell device-showing current starting in a high state, and (c) reversible current-voltage characteristics observed from the coassembled monolayer in the nanowell device.

dodecanethiol molecules. The parameter values from fitting to Simmons equation for these curves also matched the values found for the homogeneous monolayers of dodecanethiol.[5] Thus, these devices may have had few to nitro-OPE molecules participating in the conduction. The third observed behavior was an early electrical device breakdown that occurred before any reversible results could be observed (35% of working devices).

The differences between the switching with memory behavior observed for the homogeneous monolayer and the coassembled monolayer could be due to interactions between the nitro-OPE molecules. These molecular interactions may be dependent on the spacing of the molecules. For example, it has been postulated that the two conductivity states may be observed due to conformational changes of the molecules (the center rings twisting in space) caused by charging of the nitro group.[13] Because this charging would not occur for molecules without the nitro side group, they would not experience this conformational change.[13] It is unclear how the ordered coassembled monolayers kept the nitro-OPEs from exhibiting switching behavior. One possibility is that the ordered monolayers limited the ability of the nitro molecules to conform in space. Other groups have also shown that the local environment affects the observed molecular behavior.[14–16]

The coassembled monolayer also showed two additional types of behavior other than switching with memory. These included an exponential behavior with small nonreversible NDR peaks (not shown in Fig. 4 and observed for 10% of the working devices) and a simple exponential currnet-voltage dependence that occurred for 59% of the working devices [Fig. 4(c)]. The NDR consisted of small peaks in an otherwise exponential curve, but were at most once reversible and would disappear on consecutive scans. The simple exponential devices showed a median current value of 431 pA at -1 V, which is more than an order of magnitude higher than the median current observed for homogeneous dodecanethiol monolayers of 15 pA at 1 V. Thus, we believe that the nitro molecule participated in the electron transport.

IV. CONCLUSIONS

Four variations of nitro-OPEs/dodecanethiol monolayers, each tested in the same type of nanowell device, exhibited different electrical behaviors. The observed electrical switching with memory behavior, a behavior with possible device applications,[1] depended on the type of molecule in the surrounding monolayer and the order of the surrounding monolayer. Neither the homogeneous dodecanethiol monolayer nor the heterogeneous inserted nitro-OPE monolayer showed any switching with memory behavior. The disordered homogeneous nitro-OPE monolayer and the disordered coassembled monolayer showed different switching with memory behaviors. Thus, there appears to be a correlation between having nitro molecules surrounded by a disordered monolayer and observing electrical switching with memory. Additionally, the specifics of the switching with memory behavior (such as the threshold voltages and the initial switching state) depend on the intermolecular spacing of the nitro-OPEs. These findings highlight the influence of the molecular environment on the observed electrical characteristics of the nitro-OPE molecule.

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