Study of the room temperature molecular memory observed from a nanowell device

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We tested the electrical characteristics of an oligo(phenylene ethynylene) (OPE) molecule with one nitro side group, an OPE with two nitro side groups, and an OPE with no nitro side groups in our nanowell device. The OPE molecule with nitro side group(s) showed switching behavior with memory as well as nonreversible negative differential resistance (NDR). Current-voltage (*I-V*) characteristics showed a high conductivity state that switched to a low conductivity state upon the application of a threshold voltage. This low state held until the opposite threshold voltage was applied and the device switched back to the high conductivity state. The OPE with no nitro side groups did not show memory or NDR. In this work, we report the complete switching behavior observed including the device yield, average threshold voltage, and the average high to low current ratios. © *2005 American Vacuum Society.* [DOI: 10.1116/1.1931687]

I. INTRODUCTION

Researchers are debating whether the electrical switching behavior observed from some molecular devices can be attributed exclusively to the molecules.[1] An oligo(phenylene ethynylene) (OPE) molecule with at least one nitro side group, commonly referred to as a nitro molecule, has shown switching behavior with memory as well as negative differential resistance (NDR)[2] and may have the potential for use in memory devices.[2,3] However, not all research groups have observed molecular memory from the nitro molecule.[4,5] There is also the question as to whether or not the observed NDR is independent from the observed switching behavior.

This work confirms earlier reports of switching with memory,[2,3] but adds data showing that the switching device yield is low and that a number of variations in *I-V* characteristics are observed. We report the total device yield, percent of devices showing switching with memory, average threshold voltage, and the average high/low current ratios for nitro molecules. For this work, we tested OPE molecules with one and two nitro side groups [Molecule 1 and Molecule 2 in Fig. 1(b), used after *in situ* acetate removal to produce the free thiol] in our nanowell device[6] [Fig. 1(a)]. The current-voltage (*I-V*) characteristics of the nitro molecules show two distinct conductivity states. The current starts in the high conductivity state and switches to the low state when a large enough voltage is applied. This switch from high to low conductivity looks like negative differential resistance (NDR), but is not reversible. The low conductivity state holds until the opposite voltage is applied and the de-

vice switches back to the high conductivity state. Neither memory nor switching behavior were seen when we tested a simple conjugated molecule without a nitro group (Molecule 3). Thus, we can attribute the memory/switching behavior of the nitro molecules to the nitro side groups.

II. EXPERIMENT

We used the nanowell device to electrically characterize monolayers of nitro molecules. The nanowell device is shown in Fig. 1 and consists of a well milled using a focused ion beam in silicon dioxide with a 10–50 nm gold bottom. A monolayer of molecules is self-assembled in the well and capped with 5 nm of titanium and 200 nm of gold. The top titanium and gold layers are evaporated using direct electron beam evaporation at room temperature. The nanowell was first proven effective by testing with the commonly used control molecules, alkanethiols, as well as with conjugated molecules with well-established electrical results.[6] Our electrical results agreed with those reported in the literature by other groups.[7,8]

Prior to self-assembly of the nitro molecules, the nanowells were cleaned with piranha solution (30% hydrogen peroxide added to 66% sulfuric acid in a ratio of 1:3). Molecule 1 and Molecule 2 were synthesized at Rice University following established protocols.[9] Molecule 3 was synthesized at the University of Virginia. The milli-molar solution of molecules was prepared in an inert atmosphere of nitrogen gas by dissolving the molecules in ethanol and then treating the solution with sulfuric acid to remove the protective acetyl group.[10] The chips were left in the solution for at least 48 h to ensure adequate time for the self-assembly of the monolayer. Next, the top metal layer was evaporated and the de-

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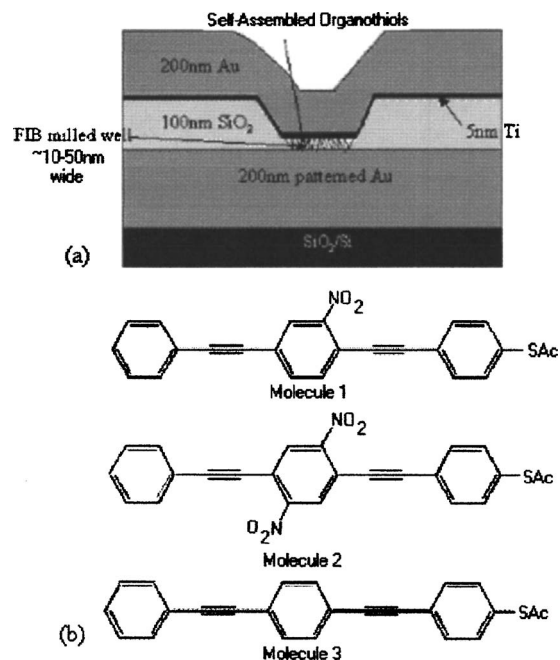[a]Author to whom correspondence should be addressed; electronic mail: jcb6t@virginia.edu

FIG. 1. (a) Nanowell device. (b) Three different molecules tested in the nanowell test device. Molecule 1 is an OPE molecule with one nitro side group. Molecule 2 is an OPE molecule with two nitro side groups. Molecule 3 is an OPE molecule with no nitro side groups. The acetate moieties were removed by acid treatment to produce the free thiols for assembly.

vices were electrically probed. Room temperature probing was performed with a HP 4145 B semiconductor parameter analyzer. Cyclic voltammetry performed on uncapped monolayers was carried out in 1 mM $K_4Fe(CN)_6$ in 0.03 M NaCl and 0.07 M $NaClO_4$, at a scan rate of 100 mV/s.

III. RESULTS AND DISCUSSIONS

A. Cyclic voltammetry

First, we used cyclic voltammetry (CV) to characterize single uncapped monolayers of Molecule 1 on gold chips to ensure our procedures produced adequate nitro monolayer coverage. Results are shown in Fig. 2 and compare well to results obtained by other groups for similar monolayers.[10] CV was also performed on Au surfaces not exposed to nitro
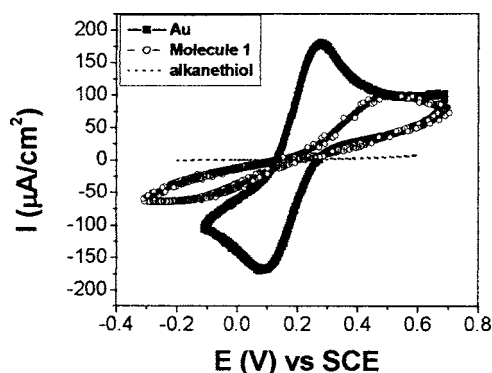

FIG. 2. Cyclic voltammograms for different monolayers on gold: bare Au, Molecule 1, and an alkanethiol.
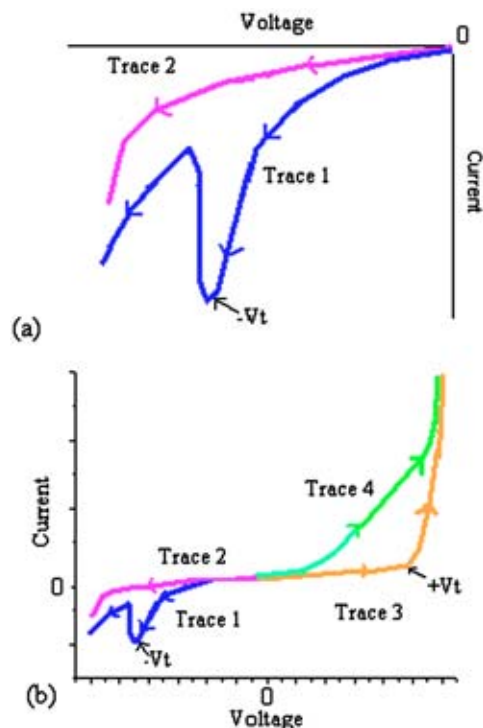

FIG. 3. (a) Plot of current vs negative voltage for a typical nitro device. Trace 1 shows a high conductivity state (the arrows indicate that the trace is occurring from 0 V outward on the negative voltage side) that then switches to a low conductivity state at −Vt. During Trace 2, the current remains in this low conductivity state. (b) A plot of current vs positive and negative voltage for a typical nitro device: Once the current is traced to +Vt in Trace 3, the current switches back to a high conductivity state. Trace 4 shows a repeat sweep of the positive voltage side after the switch to high conductivity, where the current holds the high conductivity state. The current will remain in the high conductivity state until the opposite threshold voltage, −Vt, is applied.

molecules, but exposed to all of the solutions that were used in the assembly of nitro molecules (labeled Au in Fig. 2). Figure 2 shows that the ferrocyanide peak for the Au surface with a nitro monolayer (Molecule 1) is shifted by approximately +0.35 V and reduced by a factor of 3 in peak height when compared to the Au surface with no monolayer. This reduction in current along with the positive shifting of the peak demonstrates that the monolayer significantly reduces the transport of $Fe^{III}(CN)_6^{4-}$ to the Au surface, and thus, confirms that the monolayer assembly procedure used in this work resulted in the formation of a relatively dense monolayer. Slight differences in ferrocyanide peak heights and voltages between our work and that of others[10] may be due to differences in the scan rate (100 mV/s in this study versus 20 mV/s in prior study) and the conductivity of the electrolyte (0.03 M NaCl and 0.07 M $NaClO_4$ in this study versus 100 mM KNO_3 in prior study).

B. General switching behavior/NDR observed

The OPE molecules with one or two nitro sidegroups (Molecule 1 and Molecule 2, respectively) each showed molecular memory when tested in the nanowell. Figure 3(a) shows the typical behavior observed from the nitro mol-

ecules. When first applying the negative voltage from 0 to
−3 V, we saw a high current, high conductivity state [Trace
1 in Fig. 3(a)]. When the voltage reached a high enough
voltage value, the "threshold voltage" [labeled −Vt in 3(a)],
the current switched to a low conductivity state. Once the
current had been switched to the low conductivity state, it
stayed in this state, even with consecutive traces [Trace 2 in
Fig. 3(a)]. The high conductivity state was returned only by
applying the opposite polarity threshold voltage of +Vt.

Figure 3(b) shows an example of a complete switch be-
tween states. Once the current was applied at a high enough
positive voltage value, +Vt, the current switched back to a
high conductivity state [Trace 3 in Fig. 3(b)]. After this
switch to high conductivity, the device stayed in the high
conductivity state [Trace 4 in Fig. 3(b)] until the opposite
threshold voltage, −Vt, was applied.

In this manner, we were able to switch the devices back
and forth between high and low conductivity states. The de-
vices held their state until the required threshold voltage was
applied. We refer to this electrical behavior as "switching
with memory." Additionally, we observed that although the
state always began in the high conductivity state, the high to
low switch occurred on whichever voltage side the threshold
voltage value was first applied.

Recently, there have been reports of switching behavior in
molecular devices that can be attributed to metal filaments
forming between the contacts. The observation of voltage
induced filament formation between contacts to a thin film
was described as early as 1977.[11] However, the switching
behavior observed from our nanowell device does not match
that reported for classic filament formation. First, with fila-
ment formation, the current starts in a low state and then
switches to a high state when enough voltage is applied to
form a filament.[11] This high state holds until the voltage is
increased to the point where the filament is destroyed and the
current returns to the low state.[11] As Fig. 3(b) shows, the
nitro molecules in the nanowell start in the high state, not the
low state that is associated with filament formation. Also, if
the high state were due to filament formation, and if the
voltage-induced switch from the high to low state were due
to the destruction of the filament, the destroyed filament
should reform as the voltage is again increased; however,
after our device has switched from a high to a low state, it
holds the state even with increased voltage. Thus, the switch-
ing *I-V* curves that have been observed for the nanowell do
not agree with the theory of filament formation.

Although switching was observed from the nitro mol-
ecules (Molecule 1 or Molecule 2), the only NDR we ob-
served was in the form of a peak, such as in Trace 1 of Fig.
3(a) where the current state switches from high to low. Since
this peak is simply an indication of a change from a high to
a low conductivity state, it does not occur in Trace 2, and is
not reversible without the application of +Vt. For this reason,
nitro molecules may not be suitable for classic NDR circuits
(e.g., Goto pairs[12,13]). The cause of the NDR/switching with
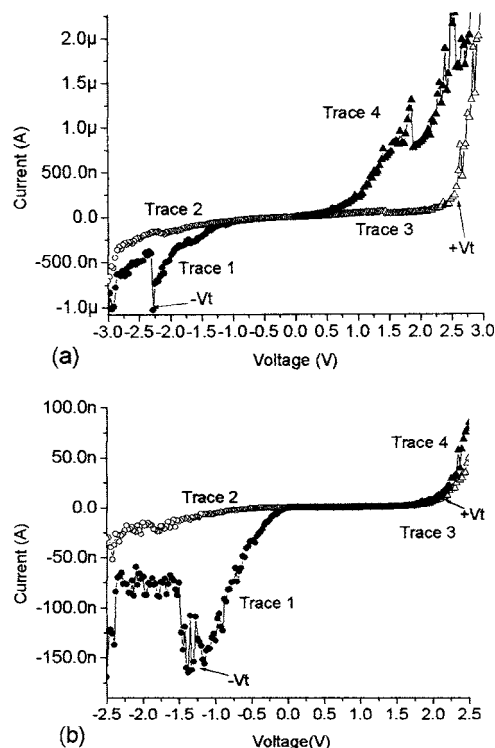memory is still not clear, but simulations have attributed the

FIG. 4. (a) Plot of current vs voltage for Molecule 1. Trace 1 shows voltage
applied from 0 to −3 V where the current switches from a high to a low
conductivity state at −Vt. Trace 2 is from 0 to −3 V and holds the low
conductivity state. Trace 3 shows a trace from 0 to +3 V where the current
switches from low to high conductivity at +Vt and is followed by a repeat
trace from 0 to +3 V (Trace 4) that holds the high conductivity state. (b)
Additional *I-V* results for Molecule 1. Trace 1 shows voltage applied from 0
to −2.5 V where a switch from high to low conductivity can be observed at
+Vt. This trace is followed by the repeat trace from 0 to −2.5 V (Trace 2)
that holds the low conductivity state. Trace 3 shows a trace from 0 to +2.5 V
where a change to the high conductivity state occurs at −Vt. Trace 4 shows
a repeat trace from 0 to +2.5 V where the high conductivity state is held.

behavior to conformational changes of the nitro molecules
that occur due to charging and discharging of the nitro side
group(s).[14,15]

Additionally, the yield of switching devices observed was
low. Of the 592 devices tested with nitro molecules (Mol-
ecule 1 or Molecule 2), 13% showed behavior other than
classic electrical open or short circuits. This percentage is
consistent with results we have observed for alkanethiol mol-
ecules tested in the nanowell. Of the 81 devices that did not
show open or short characteristics, 19% showed switching
with memory. The other 81% showed permanent electrical
breakdown before a complete switch from a high state to a
low state and back to a high state was observed. This low
yield of working devices may be an obstacle to realizing
molecular devices with nitro molecules.

C. Electrical characteristics of the OPE with a single nitro group (Molecule 1)

The graph in Fig. 4(a) shows an example of the switching
with memory observed from an OPE molecule with a single
nitro group (Molecule 1). Figure 4(b) shows additional re-
sults from testing Molecule 1 in the nanowell device. Figure
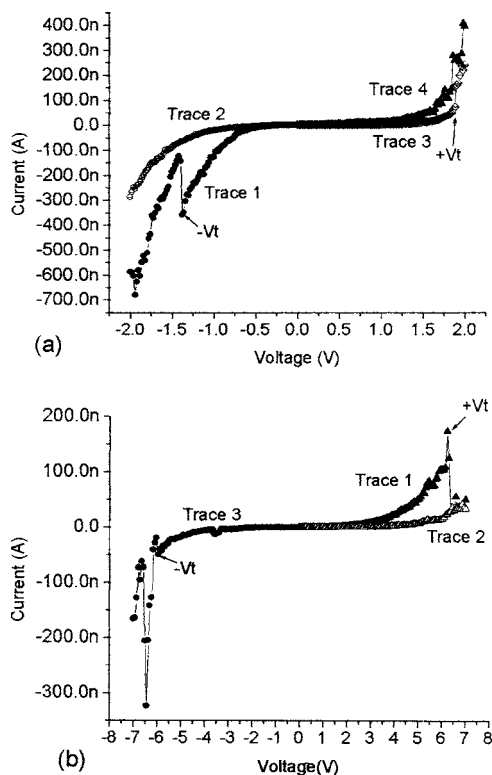
(a)

(b)

FIG. 5. (a) Plot of current vs voltage for Molecule 2: Trace 1 shows a trace from 0 to −2 V where the current switches from a high to a low conductivity state at −Vt. Trace 2 is from 0 to −2 V and holds the low conductivity state. Trace 3 shows a trace from 0 to +2 V where the current switches from low to high conductivity at +Vt and is followed by a repeat trace from 0 to +2 V (Trace 4) that holds the high conductivity state. (b) Additional *I-V* results for Molecule 2. Trace 1 shows voltage applied from 0 to +7 V where a switch from high to low conductivity can be observed at +Vt. This trace is followed by the repeat trace from 0 to +7 V (Trace 2) that holds the low conductivity state. Trace 3 shows a trace from 0 to −7 V where a change to the high conductivity state occurs at −Vt.

4(b) shows similar behavior as 4(a), but the on/off ratio on the negative side is larger in Fig. 4(b). Additionally, the −Vt value is smaller for Fig. 4(b) than for Fig. 4(a). Variations in threshold voltage and high/low ratios were seen between multiple experimental runs with the same type of molecule in the nanowell. Of the devices with Molecule 1 that showed switching/memory effects, 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 characteristics of the OPE with two nitro side groups (Molecule 2)

Figure 5(a) shows the electrical characteristics for an OPE molecule with two nitro side groups (Molecule 2). These characteristics look similar to those of Molecule 1. Of the devices with Molecule 2 that showed switching with memory, the average threshold voltage for the switch from high to low conductivity was $|2.5| \pm 0.58$ V and the average
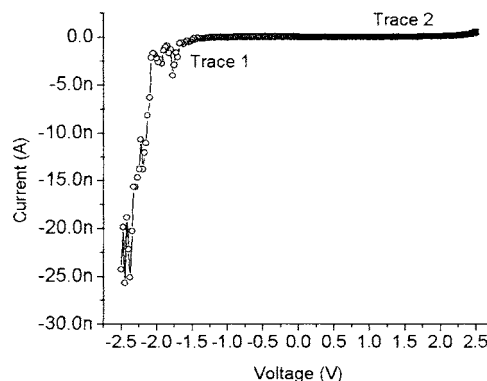

FIG. 6. Plot of current vs voltage for Molecule 3. Voltage is traced from 0 to −2.5 V where the current significantly increases in magnitude. Trace 2 shows voltage applied from 0 to +2.5 V. No switching or NDR peaks were observed. This rectifying behavior was reversible and the application of higher voltages resulted in irreversible electrical breakdown.

threshold voltage for the switch from low to high conductivity was $|2.5| \pm 0.52$ V. The current ratios for a switch from a high state to a low state ranged from 2:1 to 6:1, and the average current ratios for a switch from a low state to a high state ranged from 1:1 to 1:4.

Figure 5(b) shows additional results from testing Molecule 2 in the nanowell. In Fig. 5(b), the switch from a high conductivity state to a low conductivity state occurs on the positive voltage side and the switch from low to high occurs on the negative voltage side. Such *I-V* curves were occasionally observed for molecules with one as well as with two nitro side groups. There are additional noticeable differences between the graphs in Figs. 5(a) and 5(b) including that the +Vt and −Vt values are smaller in Fig. 5(a) than in Fig. 5(b) and that the high to low on/off ratio for Fig. 5(a) is larger than that for Fig. 5(b).

E. Electrical characteristics of the simple OPE molecule (Molecule 3)

Figure 6 shows electrical behavior of an OPE lacking nitro side groups (Molecule 3). Trace 1 shows voltage applied from 0 to −2.5 V. Trace 2 shows voltage applied from 0 to +2.5 V. As one can see, there is no NDR nor switching observed over the applied voltage range. When voltages beyond this range were applied, irreversible electrical breakdown was observed. Current rectification is obvious, as the negative current increases exponentially at around −1.9 V. This rectification is similar to what has been observed for other similar conjugated molecules.[7,16] Of the devices tested with non-nitro OPE molecules, 53% showed classical open or short results. Of the 15 devices that were not open or shorts, 33% showed rectification. The only structural difference between the OPE molecule without nitro groups (Molecule 3) and the nitro molecules (Molecule 1 and Molecule 2) is the lack of nitro groups. Thus, one can conclude that the presence of nitro groups results in the switching and molecular memory.

F. Comparison between the electrical results from the nitro molecule tested in the nanowell and results from other groups

Qualitatively, our switching results matched those reported by others. Both our nanowell device, as well as the nanopore device of Reed *et al.*,[2] started in a high conductivity state, switched to a low state when the threshold voltage was applied, and then held the state until the threshold voltage with the opposite magnitude was applied. Reed *et al.*[2] and Zhou *et al.*[3] saw switching from a mononitro molecule with an additional amino side group, but the conductivity for this molecule started in the low state. Neither group reported how switching behaviors varied with changing the initial trace direction. For our nanowell device, switching behavior appeared to be independent of the initial trace direction.

Although our switching results matched others' qualitatively,[2,3] there were quantitative differences in switching thresholds. The average thresholds for the high to low switch of the nanowell were $|2.3| \pm 1.27$ V for the mononitro molecule and $|2.5| \pm 0.58$ V for the dinitro molecule. These values are in the range of those reported by Reed *et al.*[2] of 1.5 V and by Zhou *et al.*[3] of 3 V. Reed *et al.*[2] reported a high/low ratio of about 5:1 for the mononitro molecule, which compares well to our mean high/low ratio of 7:1 for the mononitro molecule. However, there is a large spread of high/low ratios among groups. Zhou *et al.*[3] reported a high/low ratio of 370:1 for the mononitro molecule with the amino side group.

Additionally, there were quantitative differences in current densities. Reed *et al.*[2] reported a high state current of 325 pA at 1 V for the mononitro molecules tested in the nanopore (30–50 nm device diameter). These values result in a current density ranging from 0.46 to 0.17 pA/nm^2. Zhou *et al.*[3] reported a high state current of 5 nA at 1 V and did not report an estimated device area, but devices have 150-nm-long bottom electrodes and a maximum top contact length of 10–15 nm (diameter of the nanowire top contact). Thus, the minimum current density should be 3.3–2.2 pA/nm^2. Allara *et al.*[17] (who did not report switching with memory behavior) reported approximately 325 nA of current from the mononitro molecule at 10 K and 1 V for an inwire device. This would result in a room temperature current of approximately 439 nA (according to their reported current-temperature dependence).[17] Since their device area diameter is 35–45 nm, the resulting current density would range from 456 to 276 pA/nm^2. Our mean high state current density at 1 V ranges from 1 pA/nm^2 (assuming a well diameter of 50 nm) to 25 pA/nm^2 (assuming a well diameter of 10 nm) for the nanowell with mononitro molecules, and 0.2–5.6 pA/nm^2 for the nanowell with dinitro molecules. Thus, different groups testing similar molecules in different test devices have reported vastly different current densities.

Simarily, although the mean current density for nitro molecules in the nanowell device was in the range of the current densities from the other two groups that observed switching with memory,[2,3] the current densities for the nanowell devices ranged from pAs to uAs of current. 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.[17] 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.[15] It is interesting to note that Allara *et al.*[17] (who did not observe electrical switching with memory from nitro molecules) observed a current density that was about 100 times that of the groups that did report electrical switching wth memory. Thus, if device variations, such as differences in monolayer defects, inhibited or aided switching or charging, there may be a correlation between electrical switching and the current density. Additionally, the degree of the switching inhibitor or enhancement may affect the observed current density.

One qualitative difference between our results and those of other groups is that the only NDR we observed was non-reversible and occurred during the switching from high to low state. Zhou *et al.*[3] (who observed switching with memory) did not report observing any reversible NDR. However, other groups reported reversible NDR from the mononitro molecule.[2,4,5] Reversible NDR and electrical switching with memory may be two separate phenomen a that could be observed either independently or jointly.

In summary, our nanowell device showed a general switching trend that is similar to that of other groups.[2,3] Although the switching threshold, on to off ratio, and current density of the nanowell device were in the range of reported results, the range was extremely large. The explanation for such group variances is unclear, especially since groups do not generally report statistical averages of yields, standard deviations, etc. Hopefully, with more information, uniform results between groups can be established.

IV. CONCLUSION

We have presented data that show bi-stable states with memory that is similar to the behavior that has been reported by other groups.[2,3] Additionally, we supply the full statistics of what we have observed from all devices tested including the yield of devices that show switching with memory, as well as the statistics on the variations observed between our devices. Unlike the reversible NDR reported by other groups,[2,4,5] the NDR observed from the nitro molecules in the nanowell device was not reversible. Because the switching with memory behavior was not observed from the OPE molecule lacking the nitro groups and the behavior did not match that expected for filament growth, we attribute the electrical switching with memory observed to the nitro molecule.

ACKNOWLEDGMENT

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