Molecular Wires, Switches, and Memories

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ABSTRACT: Design and measurements of molecular wires, switches, and memories offer an increased device capability with reduced elements. We report: Measurements on through-bond electronic transport properties of nanoscale metal–1,4-phenylene diisocyanide–metal junctions are reported, where nonohmic thermionic emission is the dominant process, with isocyanide–Pd showing the lowest thermionic barrier of 0.22 eV; robust and large reversible switching behavior in an electronic device that utilizes molecules containing redox centers as the active component, exhibiting negative differential resistance (NDR) and large on-off peak-to-valley ratio (PVR) are realized; erasable storage of higher conductivity states in these redox-center-containing molecular devices are observed; and a two-terminal electronically programmable and erasable molecular memory cell with long bit retention time is demonstrated.

KEYWORDS: molecular electronics; molecular devices; molecular wires; molecular switches; molecular memories; negative differential resistance; metal–molecule–metal junctions; erasable and programmable molecular memory cell

1. INTRODUCTION

The ability to utilize single molecules that function as self-contained electronic devices has motivated researchers around the world for years. It allows chemical engineering of organic molecules with their physical and electronic properties tailored by synthetic methods, bringing a new dimension in design flexibility that does not exist in typical inorganic electronic materials. It is possible that electronically functional...
molecular components can not only address the ultimate limits of possible miniaturization, but also provide promising new methodologies for novel architectures, as well as nonlinear devices and memories. Up until now, most of the work on molecular electronics has been focused on the study of electronic transport properties of molecules. Investigations of the electronic conduction through conjugated molecules that are end-bound onto the surface have been demonstrated using an STM, micromachined silicon nanopores, and between proximal probes. Although a lot of information about the structural properties of various functional terminal moieties on both aliphatic and aromatic molecules has been obtained, very little is known about the electronic properties of through-bond novel transport. In this paper, we discuss the metal–SAM contact barrier, demonstrate non-FET switching devices, and a prototype of memory cell using single SAMs as the active component.

2. METAL–SAM CONTACTS

In charge transport across a metal–SAM–metal system, both the electronic structure of the SAM and the metal–SAM coupling play important roles. The most well-known and studied SAM–metal system is thiolate on gold surfaces. Reed et al. have measured transport properties through a gold–thiolate SAM–gold junction. They proposed that the current is largely limited by Au–S contacts, later confirmed by theoretical calculations of Di Ventra et al. Recently, Zhu et al. reported that the interfacial electronic structure of thiolate SAM on metal surfaces is dominated by $\sigma^*$ orbitals localized to the C–S–metal anchor, is strongly coupled to the metal substrate, and is independent of the nature of the backbone, further emphasizing the importance of the metal–SAM interface contact. We will discuss a second type of SAM–metal junction, specifically 1,4-phenylene diisocyanide with metal (Au or Pd) contacts. This system has significant electronic advantages over the thiol and other Group VI systems (e.g., Se, Te).

To understand the electrical conduction of a metal–molecule system, the energy-level matching (or mismatching) of the available electrons in the metal (the Fermi level) and the available molecular orbital in the terminal molecule must be considered. In general, the Fermi level of the metallic contact does not energetically line up with either the HOMO or LUMO levels in the molecule. This mismatch gives rise to a contact barrier, analogous to a Schottky contact. Electron (or hole) transport through such a contact will exhibit a range of phenomena, depending on the height of the barrier, the effective barrier thickness, and the presence of defects; the most prevalent are thermionic emission, direct tunneling, and defect-mediated transport, such as hopping.

Previous work on self-assembled monothiol-terminated (but asymmetric) oligomers illustrated that one can deduce the basic transport mechanisms by measuring the $I(V,T)$ characteristics. In previous work, it has been found that the physisorbed aryl–Ti interface gave a thermionic emission barrier of approximately 0.25 eV, whereas the Au–thiol (and other Group VI termini, such as Se and Te) bond exhibited a hopping barrier of roughly 0.2 eV. This is consistent with other transport measurements on a single molecule that measured an apparent gap of 0.7 eV, and the interpretation of the observed gap as the mismatch between the contact Fermi level and the LUMO of the molecule was supported by theoretical calculations.
That is, because the contribution from the 0.2-eV defect-mediated hopping barrier (not present in the single-molecule experiment) is significantly larger than that from the 0.7-eV barrier symmetric structures.

In this work, we investigate two new aspects of through-bond electronic conduction in the nanopore configuration, namely: (1) the transport through the self-assembled functional termini of isocyanides, and its effective electron transport barrier; and (2) a symmetric termini–metal contact structure.

To reliably measure transport through metal–molecule–metal systems, we employ a fabrication technique to directly measure the conduction through a small number of self-assembled molecules sandwiched between top and bottom metallic contacts. This technique guarantees good control over the device area and intrinsic contact stability, and produces a large number of devices with acceptable yield so that statistically significant results can be produced. Two features are essential to the process, the first of which is the employment of a nanoscale device area. The area is made to be smaller than the domain size of the SAM, and thus the adsorbed organic layer is highly ordered and (mostly) defect free. The second feature is that during the deposition (evaporation) of the contact onto the SAM, several measures are taken to ensure that the deposited metal atoms accumulate at the SAM surface and do not penetrate into the organic layer. These methods also provide minimized damage to the SAM during the deposition.

Unlike the extensive research on thiol SAMs, very little has been reported on isocyanide SAMs. Angelici et al. reported the binding of aryl isocyanides to gold powder, whose infrared spectroscopy measurements on 1,4-phenylene diisocyanide–gold show there exists two CN bands: an unbound CN, and a CN bound perpendicular to gold. Henderson et al. studied surface structure properties of aryl diisocyanides on gold film deposited on silicon substrate and reached the same conclusion. Isocyanides have a high affinity for transition metals, for example, W, Pd, Pt. When they bind to metal surfaces, the metal’s (e.g., Pd) d orbital overlaps with the π* orbital of the ligand. In this way, delocalization of the electron density occurs via the overlap of d orbitals on the metal with orbitals of the ligand. The electron density is shifted via the π bond from the metal atom to the ligand. The metal–1,4 phenylene–diisocyanide–metal thus form a delocalized dπ–pπ–dπ system, whereas Au–1,4 dithiol benzene–Au forms a σ–pπ–σ system. For symmetry reasons, the delocalized π states within the conjugated molecule cannot couple strongly to the localized σ states at the interface. These σ states do not serve as efficient “bridging states” between the molecule and the metal. Therefore we expect a smaller contact barrier in a CN–metal (e.g., CN–Pd) system with dπ–pπ–dπ orbital overlap than that in the S–Au system with σ–pπ–σ orbital overlap.

Electronic measurements were performed in a nanostructure (Fig. 1) that has a metal top contact, a self-assembled monolayer (SAM) active region, and a metal bottom contact. This nanostructure is similar to that reported previously [Ref. 20; note that the process employed here was slightly modified (the bowl is inverted) over that employed in Ref. 3], and its fabrication process is described in Ref. 4. To deposit the SAM layer onto the first metallic contact, the sample is transferred immediately into 1-mM 1,4-phenylene diisocyanide in toluene (Aldrich) under an inert atmosphere of Ar. After 48 hours, the sample is taken out, rinsed with fresh toluene, and gently blown dry with N2 gas. It is then loaded into a high vacuum chamber right away for the top-layer metallization and characterized as discussed previously.
Although the Au–isocyanide SAM–Au system appears to be symmetric, there is a subtle difference in the two SAM–metal interfaces formed during the fabrication process (FIG. 1). The first interface is formed when isocyanide chemisorbs onto a gold surface; the second interface is formed when gold is evaporated onto isocyanide, as pointed out in FIGURE 1. We refer to them as the chemisorbed contact, and the evaporated contact, respectively.

To determine the effective transport characteristics, $I(V, T)$ measurements are performed from 300 K to 20 K, with the voltage swept between $-1$ and $+1$ V. Positive bias corresponds to electron injection from the evaporated metal–SAM contact. Current changes five orders of magnitude over 300 K and freezes out at low temperature. This dramatic change of current with temperature suggests an activated type of behavior. FIGURE 2a illustrates reduced $I(T)$ characteristics at various voltages; one sees that the dependence of $\ln(I/T^2)$ vs. $1/T$ (0.1 V to 1 V) has a clear linear dependence at biases less than 0.7 V. This dependence is characteristic of thermionic emission,14–16 where

\[ I = e^\frac{qV}{kT} \]

At low temperatures (~40 K), biases higher than 1 V are applied.

**FIGURE 1.** Schematics of nanopore fabrication process.
where $A^*$ is the effective Richardson constant multiplied by the current injection area, $\Phi$ is the thermal emission barrier height, $k$ is Boltzmann’s constant, $q$ is the electron charge, $\varepsilon_0$ is the vacuum dielectric constant, $\varepsilon$ is the relative dielectric constant.

\begin{equation}
I = A^* T^2 \exp\left(\frac{q\Phi - \alpha \sqrt{V}}{kT}\right), \quad \alpha = q \frac{q}{\sqrt{4\pi \varepsilon_0 \varepsilon d}}
\end{equation}
constant of the isocyanide SAM, and \(d\) is the thickness of the film.\(^8\) For \(V > 0.7\) (\(E \sim 7\) MV/cm), deviation from a linear dependence is observed; the origin is not known, but it is probably due to high field breakdown effects. One possible scenario is that at high field, impact ionization generates electron–hole pairs, and the resulting hole current cancels the electron injection.

Below 0.1 V, the dependence does not have the voltage dependence characteristic of thermionic emission, and instead one finds a linear dependence of \(\ln(I/V)\) vs. \(1/T\). This dependence is characteristic of hopping conduction,

\[
\ln(I/V) = f(N) - \Delta E/(kT)
\]

where \(\Delta E\) is the activation energy to hop from one site to another and \(f(N)\) is a function of the trap concentration.\(^16\) Figure 2b shows this dependence in the regime of bias less than 0.1V. Whereas the physical interpretation of the thermionic transport barrier is clearly the molecule–metal contact potential, the physical sites giving rise to hopping transport is less well defined. Structural defects in the nanopore, or edge defects are potential candidates for the low-bias defect-mediated transport.

To determine the energetic barriers, we plot the slope of \((\ln(I/V^2) vs. 1/T) vs. V^{0.5}\) in Figure 3. For the isocyanide–Au contact, we obtain for \(0.1 \text{ V} < V < 1 \text{ V}\), the intercept of the line fit gives \(-q\Phi/k\), with a thermionic barrier of \(\Phi = 0.38 \text{ (±0.01) eV}\); the slope of the line fit gives \(a/k\), where \(a = q(q\Phi/(4\pi\varepsilon_0\varepsilon d))^{0.5}\), with the dielectric constant of the isocyanide film \(\varepsilon\) of 3.5. The effective Richardson constant can be obtained from Figure 2a. With a device area of \(300 \times 300 \text{ Å}^2\), the effective Richardson constant was found to be around 120 A/cm\(^2\) at low electrical field, and 40 A/cm\(^2\) at high fields (\(E > 7\) MV/cm). This could be caused by the reduced effective area at high current density/high electrical fields around nonuniform metal–SAM interfacial regions. For \(0 \text{ V} < V < 0.1 \text{ V}\), the slope does not depend on bias voltage. A hop-
When the junction is biased in the reverse direction such that electrons are injected from the chemisorbed Au–isocyanide contact, similar activation behavior is observed from $-0.01$ V to $-1$ V (FIG. 4a). The current changes more than five orders of magnitude over 200 K at both the low- and high-bias regime. The barrier height is determined in FIGURE 4b, where the slope of $(\ln(I/T^2) vs. 1/T)$ vs. $V^{0.5}$ of a Au–SAM–Au junction shows a linear dependence. Thermal barrier height of the junction can be deduced from the interception of the straight line. The straight line is $\chi^2$ fits for the data set.

When the junction is biased in the reverse direction such that electrons are injected from the chemisorbed Au–isocyanide contact, similar activation behavior is observed from $-0.01$ V to $-1$ V (FIG. 4a). The current changes more than five orders of magnitude over 200 K at both the low- and high-bias regime. The barrier height is determined in FIGURE 4b, where the slope of $(\ln(I/T^2) vs. 1/T)$ was plotted against $V^{0.5}$. The intercept of the line fit gives a thermionic barrier of $\Phi = 0.35$ (±0.01) eV and an effective Richardson constant of 120 A/cm². The observation of the various mechanisms in a given junction will depend on both the magnitude of the various barriers and the defect density. If the thermionic emission barrier is too large, such as in the case of thiol-like termini onto Au, only the hopping barrier would be ob-
servable. As defect-mediated conduction is a complicated function of trap concentration and details, a significantly more extensive study would be necessary to elucidate the nature and effects of the process on the defects. The present study serves to identify the characteristic energy, although the origin and density (and thus the current magnitude) is not well controlled. From our experiment, under negative bias (chemisorbed metal–SAM contact), we only observe thermionic emission, with an unobservable defect component. Under positive bias (evaporated metal–SAM contact), the defect component is larger, and we observe both simultaneously. The preceding result suggests that defects are likely located at the evaporated metal–SAM interface, possibly introduced during metal evaporation onto organic-film surface.

Because the fabrication technique is generalizable to different termini and metals, it is easy to compare the effects of different contacts. Utilizing the same fabrication technique, but instead substituting the metal Au with Pd, Pd–1,4-phenylene diisocyanide, Pd junctions were fabricated and measured as before. **Figure 5** shows plots of: (a) \( \ln(I/V) \) vs. \( 1/T \) (low bias), illustrating hopping conduction; and (b) \( \ln(I/T^2) \) vs.

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**Figure 5.** Pd–SAM–Pd junction: (a) \( \ln(I/V) \) vs. \( 1/T \) at biases larger than \(-0.1 \) V; (b) series of plots of \( \ln(I/T^2) \) vs. \( 1/T \) at biases from \(-0.1 \) V to \(-1.0 \) V at \(-0.1 \) V increment. All the straight lines are \( \chi^2 \) fits for the respective data sets.
In Figure 6, the slope of $(\ln(I/T^2) vs. 1/T)$ vs. $V^{0.5}$ illustrates thermionic emission and hopping conduction. The barrier heights are obtained as follows: (a) for $-0.1 \, V < V < 0$, a hopping barrier of $\Delta E = 0.19$ (±0.02) eV; (b) for $V < -0.1 \, V$, a thermionic emission barrier of $\Phi = 0.22$ (±0.02) eV, with fitted Richardson constants of 130 A/cm² at low field and 30 A/cm² at high electrical field ($E > 5$ MV/cm). The larger fitted Richardson constant could be caused by deviation in device area, while the smaller fitted Richardson constant could be due to reduced effective area at high current density/high electrical fields around nonuniform metal–SAM interfacial regions. In this case, the unidentified defect component was large enough such that both thermionic and hopping are observed. When electrons are injected from the evaporated Pd–CN contact, the defect component is so large that only hopping is observed, with a barrier height of 0.21 (±0.02) eV.

As seen from the preceding results, the contact barrier between Au–isocyanide SAM is larger than that of Pd–isocyanide SAM. The difference is most likely caused by different electronic configuration between the two metals. In the noble metal Au, the $d$-shell is completely occupied and there is a single valence $s$ electron on the outer shell. The Fermi level of Au lies far enough above the $d$-band for the $s$-band to intersect $\epsilon_F$ (Fermi surface) at points where it is still quite similar to the free electron band. Consequently, the Fermi surface of Au is a slightly distorted free electron sphere. In the transition metal Pd, electrons are regarded as occupying overlapping a wide, low density of states $s$- and a narrow, high density of states $d$-bands. Unlike noble metals, the $d$-band in transition metals extends through the Fermi energy. In a word, the $d$-band plays a dominant part in the electronic properties of a transition metal such as Pd. When Pd is brought into contact with isocyanide ligand, its $d$ orbital overlaps with the $\pi^*$ orbital of ligand and forms a $d\pi/p\pi$ bond. However, when Au comes into contact with isocyanide, since its $d$-bands lie far below the Fermi surface, it cannot “backbond” to isocyanide effectively. The delocalization between Au and isocyanide is therefore not as efficient as that between Pd and isocyanide. This
could be responsible for the larger barrier height measured in Au–isocyanide SAM junctions.

Table 1 summarizes the results of the transport barriers of through-bond transport of isocyanide on the metals measured in this study. It is observed that thermal emission is the dominant conduction mechanism in chemisorbed metal–isocyanide junctions, while in the evaporated metal–isocyanide contact, both hopping and thermal emission can play an important role, depending on the defect level introduced during the fabrication process. The barriers of both the chemisorbed and the evaporated contact are approximately the same, which is expected given the symmetry of the structure. It appears that the hopping component in the chemisorbed metal–molecule junction is less significant than that in the evaporated metal–molecule junction, which suggests that there are fewer defects in the chemisorbed metal–molecular interface. Overall, the Pd–CN contact barrier is smaller than that of a Au–CN junction. The technique reported here elucidates the relevant electronic transport barriers and conduction mechanisms of through-bond metal–molecule contacts, which have been possible through the implementation of microfabricated electronic devices utilizing SAMs. The technique should be applicable to a large range of inorganic and biomolecular transport measurements, to quantitatively measure the dominant electron transport mechanisms.

3. NEGATIVE DIFFERENTIAL RESISTANCE MOLECULAR JUNCTIONS

The discovery of negative differential resistance (NDR) in semiconductor diodes has opened a new chapter in semiconductor device physics and device development. Through the use of NDR devices, circuits with complicated functions can be implemented with significantly fewer components. There are various NDR devices, such as the Esaki tunnel diode, Gunn-effect diode, and resonant-tunneling diode, caused by various physical mechanisms. There are also some organic switching devices that exhibit NDR behavior, whereas their NDR behavior has been attributed to the formation of highly conducting filaments. These filaments are formed by local joule heating, which produces material rearrangement or even melting. This type of organic switching device is insensitive to the polarity of the applied field, but suffers from some material rearrangement or damage. Besides, they also need high switching power consumption, and the type of metal that was used for contacts also plays an important role. The NDR they observed is not repeatable.

In the next section, we discuss the realization of large NDR behavior and room temperature operation in an electronic device that utilizes special molecules as the

<table>
<thead>
<tr>
<th>Metal</th>
<th>Chemisorbed contact 0.35 (\pm) 0.01 eV, thermionic</th>
<th>Evaporated contact 0.38 (\pm) 0.01 eV, thermionic</th>
</tr>
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<tbody>
<tr>
<td>Au</td>
<td>0.22 (\pm) 0.02 eV, thermionic (0.19 \pm 0.02) eV hopping at low bias</td>
<td>0.21 (\pm) 0.02 eV hopping (0.3 \pm 0.01) eV hopping at low bias</td>
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<tr>
<td>Pd</td>
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active component. Unlike in the Esaki diode or in RTD, the monolayer thickness is determined by the SAM thickness, which inherently/ultimately solves the monolayer fluctuation problem at the interfaces. Being different from bulk organic switching devices, our nanoscale NDR devices are both reproducible and reversible. 5

A molecule containing a nitroamine redox center (2′-amino-4,4′-di(ethynylphenyl)-5′-nitro-1-benzenethiolate) is used in the active SAM in the nanopore configuration discussed in Section 2. Its structure is illustrated in Figure 7a. Apart from the ethynylphenyl-based backbone, there is a redox center introduced in the middle benzene ring: the electron-withdrawing nitro (–NO2) group and the electron-rich amino (–NH2) group.

To deposit the SAM layer onto the gold electrode, we transfer the prefabricated nanopores into a 0.5 mM 2′-amino-4,4′-di(ethynylphenyl)-5′-nitro-1-(thioacetyl)benzene (1a) [the starting compound (1a) was prepared by sequential Pd/Cu-catalyzed coupling of 2,5-dibromo-4-nitroacetanilide with phenylacetylene and 4-ethynyl(thioacetyl)benzene] in tetrahydrofuran (THF) solution. The thioacetyl groups are then selectively hydrolyzed with ammonium hydroxide (concentrated aqueous 14.8 M NH3OH, 5 µL per mg of 1a) in tetrahydrofuran (THF) to yield the free thiol, 2′-amino-4,4′-di(ethynylphenyl)-5′-nitro-1-benzenethiol (1b), which then forms the

FIGURE 7. (a) The structures of active molecular compound 1, and its precursors, the free thiol 1b, and the thiol-protected system 1a; (b) I(V) characteristics of a Au–1–Au device at 60 K. The peak current density is ~50 A/cm², the NDR is ~−400 µΩ-cm², and the PVR is 1030:1.
thiolate, 2′-amino-4,4′-(diethynylphenyl)-5′-nitro-1-benzenethiolate (1) upon exposure to Au after 48,31 under an inert atmosphere of Ar. The sample was then prepared and characterized as discussed in Section 2.

A device containing a SAM of conjugated molecules similar to 1, but not bearing the nitroamine functionalities, was fabricated and measured in nearly identical conditions12 and did not exhibit any NDR behavior. Therefore, the nitroamine redox center is responsible for the NDR behavior.

Typical $I(V)$ characteristics of a Au–(1)–Au device at 60 K are shown in Figure 7b. Positive bias corresponds to hole injection from the chemisorbed thiol–Au contact and electron injection from the evaporated contact. The peak current density for this device was greater than 53 A/cm$^2$, the NDR is less than $-380 \mu\Omega$-cm$^2$, and the PVR is 1030:1. Unlike previous devices that also used molecules to form the active region (Ref. 33; weak room temperature NDR has been previously reported), this device exhibits a robust and large NDR. Some device-to-device variations of peak voltage position ($-x_2$) and peak current ($-x_3$) were observed. Device-to-device current fluctuations can be attributed to fluctuations in the pore diameter size. As total voltage applied to the molecular junction can be divided into the voltage drop on the molecules and the voltage drop on the metal–molecule contacts, device-to-device peak voltage fluctuations can be caused by different voltage drops on the metal–molecule contacts. As shown by Di Ventra et al.,10 the detailed metal–molecule contact configuration plays an important part in the conductance of the metal–molecular junction. Different contact geometry caused by differences in fabrication processes, such as in etching and metallization, could result in different contact potentials. Fur-
ther fine-tuning of the fabrication processes should improve uniformity and reduce device-to-device fluctuation.

The \( I(V) \) curve is fully reversible upon change in the bias sweep direction (from negative bias to positive bias), as shown in Figure 8; for a given device, small fluctuations (~1% in voltage peak position and ~6% in peak current) are observed with consecutive positive and negative sweeps, but could be attributed to temperature fluctuations of ~2 K (within the experimental thermal stability). The performance exceeds that observed in typical solid-state quantum-well resonant-tunneling heterostructures.\textsuperscript{34-37} In addition to the obvious size advantages for scaling, the intrinsic device characteristics (that is, the valley current shutoff) may be superior to that of solid-state devices. The intrinsic PVR of the molecule may be considerably greater than that reported here, because the valley currents observed (on the order of picoamperes) are comparable to typical leakage currents in the silicon nitride film. At negative bias, when electrons were injected from the chemisorbed contact, the current level was approximately one order of magnitude smaller than that of positive bias. Negative bias corresponds to electron injection from the chemisorbed thiol–Au contact. As mentioned previously, its contact barrier is around 0.7 eV, larger than the evaporated contact. The rectifying behavior (\( I_+ : I_- = 30:1 \)) is most likely caused by the asymmetric metal–molecular contacts.

Cyclic voltammetry (CV) measurements of compound 1c are performed at room temperature on a BAS CV 50-W voltammetric analyzer using a Ag/AgNO\(_3\) reference electrode, and using a solution of 1.0 M \( n \)-tetrabutylammonium tetrafluoroborate in dimethylformamide (DMF) with a scan rate of 100 mV/s. Figure 9a shows the CV reduction curve where the first and second reduction potentials for compound 1c are \(-1.70 \) V and \(-2.33 \) V, respectively. There is no interesting feature in the positive scan (oxidation reaction). CV measurements on the thiomethyl (SCH\(_3\)) derivative of 1c (structure and CV shown in Figure 9b) show that its reduction potential and that of 1c differ by less than 0.05 V, confirming that sulfur-containing functionality does not participate significantly in the electrochemical studies. Therefore, the sulfur-containing endgroups are omitted in further cyclic voltammetry studies. The free thiol (1b) is not used, since oxidative dimerization of the thiol could complicate the analysis, and the thioacetate (1a) could cleave in solution to the thiol, thereby confusing the studies. As a control experiment, under the same electrochemical conditions described earlier, CV measurements of a compound with very similar structure to 1, but without nitroamine redox center, was also examined. No distinctive reduction peaks were observed within the range of interest.

The concept of redox-reaction-induced conductivity change is not new. However, bistable switching but not NDR behavior was observed. In some of the early studies on charge-transfer complex, Potember \textit{et al.}\textsuperscript{38} postulated that a field-induced, solid-state, reversible electrochemical redox reaction results in mixed-valence species.\textsuperscript{39} It was believed that the mixed-valence species have higher conductivity than the original charge-transfer complexes.\textsuperscript{39} Integral charge species are semiconductors due to their filled HOMO orbitals, which usually show nonohmic behavior in the switching devices, consistent with cyclic voltammetry results on the integer oxidation-state metal complex. In contrast, in nonintegral charge (mix-valence) species, there are

\textsuperscript{39}The noninteger oxidation state species exist in a solid-state equilibrium with the integer oxidation species.
more anions than there are unpaired electrons, and electrostatic repulsion of charge carriers is kept at a minimum by allowing conduction electrons to occupy the empty molecular orbital; they display high conductivity and usually show ohmic behavior. A two-step electron reduction process was proposed to be a candidate mechanism for the NDR behavior observed in our experiments by Seminario et al.\textsuperscript{40}

Collier et al.\textsuperscript{41} have recently shown that a catenane-based L-B film is capable of reversibly switching from on to off under application of an oxidation voltage, but no NDR phenomenon was observed in their system.

All of the Au–1c–Au devices examined exhibit peak voltage position and current magnitude shifts with temperature, such as shown in Figure 10. We observe a decrease in peak intensity with increasing temperature. This could be caused by scat-

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**FIGURE 9.** Cyclic voltammagram of (a) compound 1c; (b) the thiomethyl (SCH\textsubscript{3}) derivative of 1c shows two distinct reduction peaks. The reduction potentials of (a) and (b) differ by 0.05 V.
tering in the junction. However, the fact that the peak intensity has a maximum at 60 K is not understood yet. It could be caused by thermally activated conformation change in the SAM layer. We also observe that the peak position shifts to smaller voltage with increasing temperature (Fig. 11). The shift can be fit by the following expression:

$$\Delta V_{\text{peak}} = \frac{C_1}{1 + e^{-\left(34 \text{ meV}/kT\right)}}$$  (3.1)

**FIGURE 10.** $I(V,T)$ characteristics of a Au–1c–Au device.

**FIGURE 11.** Peak voltage vs. temperature relationship of the same Au–1c–Au device.
This expression can be explained by a two-energy-level model using a Boltzmann distribution, where the $34 \pm 0.7$ meV corresponds to the activation barrier from the bound state, and $c_1$ is a proportionality constant. Another piece of supporting evidence for the preceding model comes from the temperature dependence of peak width (FIG. 10). This width remains constant (which corresponds to the difference in reduction potential in CV experiments) at low temperatures and widens at higher temperature. Further discussions of temperature dependencies and comparison with other compounds will be carried out later in the paper.

Similar NDR behavior is also observed in devices with nitro-only moiety (2).\textsuperscript{1} The PVR is smaller than that of 1, but NDR behavior persisted from low temperature to room temperature. $I(V)$ characteristics of a Au–(2)–Au device at 300 K is shown in FIGURE 12a. The device has 300 K characteristics of a peak current density greater than 16 A/cm$^2$, NDR smaller than $-144$ mW-cm$^2$, and a PVR of 1.5:1. At 190 K (FIG. 12b), the NDR peak is much sharper than that of 1, although its PVR is not as big as that of 1. The degradation in PVR (decreasing in peak current) can probably

\textsuperscript{1}Recent results show that similar NDR behavior also is observed in a biphenyl dinitro molecule.
be caused by increased inelastic scattering with increasing temperature. Figure 13 shows the cyclic voltammogram curve for compound 2c, where the reduction potentials peaked at $-1.39 \text{ V}$ and $-2.09 \text{ V}$, respectively. The reduction potential difference is in approximate agreement with the width of the $I(V)$ peak. The potentials are shifted about 0.3 V less than that of the nitroamino device. The fact that 2 is more readily reduced than 1 could be responsible for the observation of room temperature NDR
in 2 but not in 1. Since the presence of amine group in 1 undermines its reducibility compared to the nitro-only moiety 2, we can infer that the nitro group is most likely responsible for the presence of NDR behavior.

The next experiment that naturally follows is the electronic transport and electrochemistry experiments of an amino-only molecule (2'-amino-4,4'-di(ethynylphenyl)-1-benzenethiolate, compound 3). We observe no NDR behavior in 3 at both low temperature (60 K) and room temperature, as shown in Figure 14. To avoid a breakdown of the molecular junction, bias at room temperature was restricted to 1 V to limit current through the junction. There is no reduction peak in its CV curve in the range of interest. Concluding from the preceding experimental results, we suggest that the nitro group is responsible for the NDR behavior. Further understanding of the underlying mechanism and experimentation with various redox centers should allow us to engineer molecular compounds in the future to improve PVR at room temperature and above.

Shown in Figure 15 is the temperature dependence of peak positions of a Au–2–Au device. The peak voltage is observed to drop linearly with increasing temperature: \( DV_{\text{peak}} = -0.025 \Delta T \). It appears to be very different from that of Au–1c–Au device. To compare possible effects of different redox centers on temperature dependence, we show in Figure 16 a plot of voltage values at a constant current of 10 nA vs. temperature of a Au–3–Au device. Interestingly, it can also be fit to a two-level model:

\[
\Delta V_{@10nA} = \frac{C_3}{1 + e^{-(30 \text{ meV} / kT)}}
\]

where \( C_3 \) is a proportionality constant, and the binding energy for the trap state on 3 is around 30 (±0.2) meV. On the other hand, the transition region of \( V_{\text{peak}} \) vs. \( T \) of nitro-amine redox molecule can be fit in a piecewise to linear relationship, with \( DV = -0.014 \Delta T \) and \( DV = -0.034 \Delta T \), respectively; and the transition region of \( V@10 \text{ nA} \) vs. \( T \) of amine-only moiety can also be fit to the linear relationship, with \( DV = -0.005 \Delta T \). The fitting results and comparison between compound 1c, 2, and 3 of sweeping S1's are summarized in Table 2.
The preceding result suggests that the presence of the amine group gives rise to a bound state around 30 meV in the molecule, whereas the nitro group is responsible for NDR behavior. The exact mechanism of the linear shift of peak position with temperature is not yet understood at this stage. However, we provide a possible explanation as follows.

The peak position shift with temperature could be caused by different vibrational modes excited at different temperatures. These vibrational modes can cause instantaneous dipole changes in the molecule, which in turn interacts with electrons passing through the molecule, changing the transmission coefficient. The nitro-amine substituents in 1 have nonzero dipole moments. For instance, in nitromethane, the nitrogen atom has four bonds rather than the usual three and must be represented as having a formal positive charge. The singly bonded oxygen atom, by contrast, has one bond rather than the usual two and must be represented as having a formal negative charge. The dipole moment of nitromethane resulting from the polar bonds just

**TABLE 2. Comparison between compound 1c, 2, and 3 on temperature dependence**

<table>
<thead>
<tr>
<th>Redox</th>
<th>NDR</th>
<th>Best fit</th>
<th>Piecewise linear fit</th>
<th>$E_{binding}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitro-only (2)</td>
<td>√</td>
<td>$\Delta V_{\text{peak}} = -0.005 \Delta T$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\Delta V_{\text{peak}} = -0.010 \Delta T$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitro-amine (1c)</td>
<td>√</td>
<td>$\Delta V_{\text{peak}} = \frac{c_1}{1 + e^{(32 \text{ meV})/kT}}$</td>
<td>$\Delta V = -0.02 \Delta T$</td>
<td>32 meV</td>
</tr>
<tr>
<td>Amine-only (3)</td>
<td>×</td>
<td>$\Delta V_{10nA} = \frac{c_3}{1 + e^{(30 \text{ meV})/kT}}$</td>
<td>$\Delta V = -0.005 \Delta T$</td>
<td>30 meV</td>
</tr>
</tbody>
</table>

**FIGURE 16.** Voltage values at a constant current of 10 nA vs. temperature of an Au–3–Au device.

The preceding result suggests that the presence of the amine group gives rise to a bound state around 30 meV in the molecule, whereas the nitro group is responsible for NDR behavior. The exact mechanism of the linear shift of peak position with temperature is not yet understood at this stage. However, we provide a possible explanation as follows.

The peak position shift with temperature could be caused by different vibrational modes excited at different temperatures. These vibrational modes can cause instantaneous dipole changes in the molecule, which in turn interacts with electrons passing through the molecule, changing the transmission coefficient. The nitro-amine substituents in 1 have nonzero dipole moments. For instance, in nitromethane, the nitrogen atom has four bonds rather than the usual three and must be represented as having a formal positive charge. The singly bonded oxygen atom, by contrast, has one bond rather than the usual two and must be represented as having a formal negative charge. The dipole moment of nitromethane resulting from the polar bonds just
mentioned is $3.46D$, where $D = 3.336 \times 10^{-30}$ C·m.$^{42}$ On the other hand, the lone pair in the amine group can also lead to a dipole moment. The dipole moment of ammonia (NH$_3$) is $1.47D$. The nitro substituent on the benzene ring withdraws electrons from the aromatic ring by resonance (overlap of a $p$ orbital on the substituent with a $p$ orbital on the aromatic ring). Conversely, the amine substituent donates electrons (through the lone pair) to the aromatic ring by resonance. With a dipole moment of $3.8D$ between the nitro-amine group (private communication with A.G. Zacarias), the energy of the dipole on 1 under an electrical field of 10 MV/cm is approximately 40 meV, comparable to the energy scale observed in our experiment. Rotation is therefore possible. Similar rotation of the benzene ring caused by the nitro-amine dipole interaction has been observed by others.$^{44}$ Further IR spectroscopy experiments on 1 should help to elucidate this point.

It has been known that different rotational conformations of a molecule with the same chemical composition leads to a different HOMO-LUMO gap. For instance, in ethane (CH$_3$-CH$_3$), the lowest-energy, most stable conformation is a staggered configuration where all six carbon–hydrogen bonds are as far away from each other as possible; whereas the highest-energy, least stable conformation is an eclipsed one where the six carbon–hydrogen bonds are as close as possible. Between these two limiting conformations are an infinite number of other possibilities. Experiments show that the energy barrier to rotation is 12 kJ/mol.$^{45}$ The 12 kJ/mol of extra energy present in the eclipsed conformation of ethane is also called torsional strain, which is believed to be due to the slight repulsion between electron clouds in the carbon–hydrogen bonds as they pass by each other at close quarters in the eclipsed conformer. As a result of this, the HOMO-LUMO gap energy of these two configurations is different, with the 10.99-eV gap of staggered ethane and 10.94 eV of the eclipsed conformer. A much bigger effect is observed in nitramide, $^{45}$ where the rotational barrier is about 48 kJ/mol, causing a change in the HOMO-LUMO gap of about 0.99 eV.

We propose that at different temperatures, the dipole induced by the excited vibrational modes rotates the molecule, or part of it, under the electric field, thereby changing the position of the NDR peak. In fact, a recent theoretical simulation by DiVentra et al.$^{46}$ substantiates this point, which is not seen in semiconductor nanostructures.

We have realized two-terminal NDR devices with large PVR at low temperature and NDR devices at room temperature. The NDR behavior is caused by the reduction nature of substituents on ethynylphenyl molecules. Based on our experiments, the electron-withdrawing nitro group is responsible for NDR behavior, whereas the electron-donating amine group gives rise to a bound state in the molecule of approximately 30 meV. We have learned that conformational change (rotation) and/or charging can change the conjugation of molecular orbitals. Further exploration of the design and engineering of molecules with various redox substituents should help to realize nonlinear electronic devices with multiple functionalities.

4. MOLECULAR MEMORY EFFECTS

The programmable storage of digital information as packets of charge is beginning to reach not only technological but fundamental limits. Electronic memories
that operate at the charge limit (e.g., by single-electron effects) have been
demonstrated\(^4\) (a single-electron memory operating at 4 K was demonstrated in
Ref. 48), but have not yet addressed the dimensional limit; that is, a single molecule.
Although memory phenomena have been studied in bulk organic materials (such as
organometallic charge-transfer complex salts\(^4\)), we will demonstrate nanoscale
electronically programmable and erasable memory devices utilizing molecular
SAM; and a memory cell applicable to a random-access memory (RAM).

**FIGURE 17** lists the molecules used in this study. (They were introduced in the pre-
ceding section, but we list them again for convenience.) The four systems studied are:

1. Au—(1)—Au (1: 2′-amino-4,4′-di(ethylnylphenyl)-5′-nitro-1-benzenethiolate);
2. Au—(2)—Au (2: 4,4′-di(ethylnylphenyl)-2′-nitro-1-benzenethiolate);
3. Au—(3)—Au (3: 2′-amino-4,4′-di(ethylnylphenyl)-1-benzenethiolate); as well as
4. Au—(4)—Au (4: 4,4′-di(ethylnylphenyl)-1-benzenethiolate) that had neither the nitro nor amine functionalities.

The memory device operates by the storage of a high- or low-conductivity state.
The write, read, and erase sequences for (1) are described as follows: an initially
low-conductivity state (low \(\sigma\)) is changed (written) into a high-conductivity state
(high \(\sigma\)) upon application of a voltage pulse. The direction of current that flows dur-
ing this “write” pulse is diagrammed. The high \(\sigma\) state persists as a stored “bit,”
which is unaffected by successive read pulses. Molecules with the nitro moieties (1
and 2) are observed to change the conductivity state, whereas the amine-only (3)
and the unfunctionalized molecule (4) do not exhibit storage. In the following, we first
describe the characteristics obtained by linear voltage sweeps (so as to generate \(I(V)\)
characteristics). Second we demonstrate the same effects and a circuit using voltage
pulses.

**FIGURE 18a** shows the \(I(V)\) characteristics of a Au—(1)—Au device at 200 K initially
(defined as “0”) and after (defined as “1”) a write pulse, as well as the difference
between the two states (defined as “1”-“0”). Positive bias corresponds to hole injec-
tion from the chemisorbed thiol–Au contact. The device initially probed with a pos-
tive voltage sweep from 0 to 2 V in one minute exhibits a low-conductivity state.
Subsequent positive sweeps show a high-conductivity state with \(I(V)\) characteristics.
Device bias swept in the reverse-bias direction from 0 to $-2 \text{ V}$ in one minute causes the $I(V)$ to be identically reset to the initial, $I(0)$ characteristic. The characteristics are repeatable to high accuracy, and device degradation is not observed. This ability to program, read, and refresh the state of the molecular device accomplishes the functionality of a RAM. Figure 18b shows the difference characteristic ($I_1 - I_0$) of an Au–(1)–Au device as a function of temperature.

A characteristic bit-retention time was obtained by measuring the stored high-conductivity state at various time intervals after programming the Au–(1)–Au device. After an initial positive write sweep from 0 to 2 V in one minute, a second sweep was measured at different time intervals, and the difference between the first and the second sweeps at peak current position was taken and plotted against time in Figure 19a. Notice that after each second sweep during the experiment, the junction had to be reset to the initial state by a negative bias sweep from 0 to $-2 \text{ V}$ in one minute. It is found that the difference “1”-“0” exhibits an exponential decay with a time constant ($\tau$) of approximately 800 s at 260 K. Similar measurements were per-
formed from 260 K to 190 K.\(^1\) The stored state was found to decay exponentially with increasing time constants at lower temperatures. Shown in Figure 19b is a plot of the decay time constant (retention time) at different temperatures, exhibiting an exponential dependence with \(\frac{1}{T}\). It indicates an activation behavior: \(\tau = \tau_0 \exp\left(\frac{E_a}{kT}\right)\), suggesting activation over a single trap state. The activation energy \(E_a\) for this molecule over this bias regime was found to be approximately 80 meV.

So far we have only discussed the memory effects when the molecular junction is under positive bias (other than the negative sweep used to refresh the written state). Figure 20a shows the first ("0") and second ("1") traces when the same junction is biased negatively (0, −5 V) at 100 K. The window over which the "0" and "1" differ by a constant amount of ~120 pA is nearly 4 V, providing well-separated thresholds. The third trace and so on overlap with the second one. Contrary to the positive bias, initially, the molecular junction is in a higher conductivity state, whereas it is changed to a lower conductivity. After applying a positive sweep, we

\(^1\)Below 190 K, the \(I(V)\) characteristic changes considerably, with the NDR peak shifting greatly toward higher voltage. No appreciable decay of current was observed.
observe that the junction is set back to the initial negative trace (overlaps with “0”).

Shown in Figure 20b is the difference between the first and second $I(V)$ traces ("0"-"1") at various temperatures. Notice that the width of the plateau decreases with increasing temperature. The decay of the stored state under negative bias is very slow. The decay constant is estimated to be larger than hours.$^5$

Memory effects are also observed in devices with the molecules having only the nitro moiety (2), although in this case the storage was of a low conductivity state$^6$

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$^5$Dynamic experiments on stored states under negative bias have not yet been performed.

$^6$Not including the NDR region, where current level is higher than the initial state.
after an initial positive sweep from 0 to 1.75 V in one minute, opposite to that of molecule (1). Figure 21 demonstrates the storage of this state in molecule (2) at 300 K. NDR was observed in the stored state “1.” As described previously, subsequent reads and resets identically recovered the $I(V)$ characteristics. At 300 K, thermal activation does contribute some nonzero “0” current, although the thresholds are still well separated (approximately 250 pA).

A characteristic bit retention time is obtained by measuring the stored low-conductivity state at various time intervals after programming the Au–(2)–Au device. After an initial write bias sweep, current ($I_1$) at 1.5 V of the stored state, “1” increases gradually until it recovers the initial “0” high-conductivity state ($I_0$). Their difference ($I_0 - I_1$) exhibits an exponential decay with a time constant ($\tau$) of approximately 900 seconds at 300 K (FIG. 22).
Memory effects are not observed in molecule (3) with the amine-only group. The first and second traces at a constant temperature overlap with each other. The current level is higher than that of both Au–(1)–Au and Au–(2)–Au devices, suggesting that the presence of the nitro group impedes charge transport, causing a high-conductivity state in (1) (with the nitro-amine group) and a low-conductivity state in (2) (with the nitro-only group). Consequently, the 80-meV energy level observed in (1) is most likely associated with the nitro group.

In addition to the nanopore configuration, planar devices with promising batch-fabrication capability are fabricated. Molecular junctions of Au/Ti–2′-nitro-4-ethynylphenyl-4′-ethynylphenyl-5′-nitro-1-benzenethiolate–Au (FIG. 23) with 150- × 150-nm active area demonstrate prominent NDR, and memory effect is observed at room temperature. Figure 24a shows consecutive I–V measurements from 0 to 1 V. The first trace shows the SAM initially in a high-conductivity state ($R \sim 800 \Omega$) followed by NDR at about 0.7 V with a peak-to-valley ratio of 230. The NDR occurs as the SAM is switched from a high-conductivity state to a low-conductivity state. The second trace shows the SAM in the low-conductivity state ($R \sim 1.6 \text{ M} \Omega$). Figure 24b shows a magnified view of the second trace. A third measurement in the negative bias (0 to –1 V) will return the device to the high-conductivity state. More than twenty devices showing these characteristics have been fabricated and repeatedly cycled between high- and low-conductivity states. However, the devices degrade quickly and become Ohmic shorts after roughly ten cycles. The preceding results further substantiate the important role of the NO$_2^-$ group in both NDR and memory phenomena.

The preceding observation leads us to the following preliminary model for the memory effect. We have identified from the earlier experimental results that the nitro group is responsible for the memory effect, while the presence of the amine group...
changes the initial conductivity states of the molecule (most likely caused by the different dipole distribution it introduces to the molecule). Here we use molecule 1 as an example. Depending on its history, 1 can be in one of the two states, \( L \) (low-conductivity state) or \( H \) (high-conductivity state). We propose that the different conductivity states are caused by different trap levels occupied by electrons in the molecule. Different trap levels occupied by electrons in a molecule could mean either different electronic states with different charge distribution (such as different dipole distribution), or different conformation states in a molecule (such as rotational conformation and possible rotational conformation), or both. These trap levels can cause different electronic distribution, leading to various conductivity states of the molecule. From Figure 18a, 1 is initially in a low-conductivity state \( L \). As the junction

FIGURE 24. (a) \( I(V) \) characteristics of planar device at room temperature. First trace shows high conductivity state \( (R \sim 800 \Omega) \) and NDR with peak-to-valley ratio of 230. Second trace shows low conductivity state \( (R \sim 1.6 \text{M}\Omega) \). (b) Magnification of second trace.
When the bias is removed the electron remains undisturbed in the same localized state $H$ they occupied under bias for a period of time equal to $(\nu P)^{-1}$, where $\nu$ is attempting frequency to escape and $P$ is the probability of escaping the localized state $H$. In general, $P$ is proportional to the Boltzmann factor $\exp(-E/kT)$, where $E$ denotes the energy barrier of the localized state $H$. It corresponds to the measured 80 meV, as shown in FIGURE 19b. For subsequent positive biases at times $t < (\nu P)^{-1}$, the electron is trapped in state $H$. Only with negative bias can the electron be “liberated” and go back to state $L$. At times $t > (\nu P)^{-1}$, the electron leaks through the barrier and finally returns to state $L$. The electron will be trapped in state $L$ with the following negative sweeps, and it can only be refreshed to the $H$ state by positive bias. This explains well that the first negative sweep on the junction shows a high-conductivity state (Fig. 20a), that is, the initial $H$ state after positive sweeps; the following negative traces show low-conductivity states; and a positive trace resets the state.

A sense circuit was built to demonstrate the storage of a conductivity state. A TTL-level signal (5 V) from a function generator is first converted to the operating point of the memory cell (set at the points diagrammed in Fig. 21, 1.5 V) and applied to the molecular junction. The current through the molecular junction is measured via a feedback resistor and amplified ten times using low-noise operational amplifiers. Then the signal is fed into a comparator and compared with the “1” setpoint (low-conductivity state) as measured in FIGURE 21. To demonstrate the storage of a low-conductivity state, the signal is inverted and gated with the input pulse from the function generator. A measured logic diagram utilizing the preceding sensing circuit and a Au–2–Au device is shown in FIGURE 23, demonstrating a molecular RAM cell at ambient temperature.

The upper trace shown in FIGURE 25 is an input waveform applied to the device, and the lower is the RAM cell output. The first positive pulse configures the state of the cell by writing a bit, and the second and third positive pulses read the cell. The
third pulse (and subsequent read pulses, not shown here for simplicity) demonstrates that the cell is robust and continues to hold the state (up to the limit of the bit-retention time; this demonstration highlights the dramatically long bit-retention time). The negative pulse erases the bit, resetting the cell. The second set of four pulses repeats this pattern, and many hours of continuous operation have been observed with no degradation in performance.

The present devices utilize nanoscale structures that limit the number of molecules in the active region to ~1000, which is determined by lithographic limitations in defining the contacts. We have seen no evidence in the device characteristics indicating that limitations exist for scaling the number of molecules in the active region to one, assuming that an appropriate fabrication scheme can be identified.

5. CONCLUSIONS

We have investigated the contact barrier between isocyanide SAM and metal systems. Nonohmic behavior—thermionic and hopping conduction—is observed to be the dominate conduction mechanism. We have shown that thermal emission is the dominant conduction mechanism in chemisorbed metal–isocyanide junctions, while in the evaporated metal–isocyanide contact, both hopping and thermal emission can play an important role, depending on the defect level introduced during the fabrication process, suggesting that there are fewer defects in the chemisorbed metal–molecular interface. Overall, the Pd–CN contact barrier is smaller than that of a Au–CN junction, in agreement with the more efficient $\pi$ backbond formed between Pd–CN. Our results also show that the contact barrier between $\pi$-bonded isocyanide SAM–metal is less than that of the more extensively studied $\sigma$-bonded thiol SAM–metal systems. The technique reported here elucidates the relevant electronic transport barriers and conduction mechanisms of through-bond metal–molecule contacts, which have been possible through the implementation of microfabricated electronic devices utilizing SAMs. The technique should be applicable to a wide range of inorganic and biomolecular transport measurements, to quantitatively measure the dominant electron transport mechanisms.

We demonstrated novel non-FET switching devices and a prototype of memory cell using single SAMs as the active component. We learned that conformational change like rotation of molecular bonds can change the conjugation of molecular orbitals, leading to the observed conductor–insulator type of transition that can be thermally controlled. We have realized two-terminal NDR devices with large PVR at low temperature and NDR devices at room temperature. The NDR behavior is caused by the reduction nature of substituents on ethynylphenyl molecules. Based on our experiments, the electron-withdrawing nitro group is responsible for NDR behavior, whereas the electron-donating amine group gives rise to a bound state in the molecule of approximately 30 meV. Through the design of the molecular switches we learned that incorporation of different redox centers can change charge distribution and/or conformation in a molecule, leading to different conjugation of molecular orbitals. Further exploration of the design and engineering of molecules with various redox substituents should help one to realize nonlinear electronic devices with multiple functionalities. We also discovered erasable storage effects in redox-center-containing ethynylphenyl molecules. The storage behavior can be discreetly added.
on a molecule by engineering electron-withdrawing or/and electron-donating side-groups onto its backbone. We have concluded from our experiments that the electron-withdrawing nitro group is responsible for the observed memory effects, while the presence of the electron-donating amine group changes the storage of different conductivity states. Our results show that the storage behavior is controlled by a single thermal activation process, associated with the nitro group. Finally, we successfully demonstrated an erasable molecular memory cell that can store a high-conductivity state with a bit-retention time orders of magnitudes longer than that of a DRAM. Further engineering of different molecules shall permit potential applications, such as nonvolatile memories on flexible substrates.

REFERENCES