Organic Materials and Thin-Film Structures for Cross-Point Memory Cells Based on Trapping in Metallic Nanoparticles

By Luisa D. Bozano, Bryan W. Kean, Matthias Beinhoff, Kenneth R. Carter, Philip M. Rice, and J. Campbell Scott

Non-volatile solid-state memory cells based on composites of metal nanoparticles and polymers are embedded in organic semiconducting host materials. This paper presents data from a wide range of materials and device structures and shows that the switching phenomenon is commonly observed.

1. Introduction

There is a growing interest in research on non-volatile solid-state memories, largely motivated by the perception that existing technologies are inadequate in one or more operating parameters. One of the most appealing device structures is an array of cross-point elements, where simple parallel linear electrodes, one set above and one below the storage medium, run in perpendicular directions. Each bit cell is then at a unique intersection of the electrode below (row or word line) and above (column or bit line). Most research activity focuses on the storage medium itself, ranging from amorphous to crystalline phase-change materials, ferroelectrics, and electrochemically reduced or oxidized materials. We and others have been exploring composite systems in which metal nanoparticles (NPs) are embedded in an organic semiconducting host.

In a previous publication, we described a mechanism, originally due to Simmons and Verderber (the SV mechanism), which appears to explain the major experimentally observed phenomena in this class of devices. The electrical conductance between the top and bottom electrodes depends on the amount of charge stored, or trapped, on the metallic NPs. A relatively high voltage pulse (~6 to 8 V in our samples) injects charge into the composite layer, leaving a large amount trapped on the NPs. When the state of the device is read at low voltage (~1 V), the space-charge field of the trapped charge inhibits charge injection from the electrodes, resulting in a low current, the OFF state. At an intermediate voltage (~2–3 V) the NPs discharge, removing the space-charge field and permitting charge injection. The reading voltage thus results in a high current passing between the electrodes, the ON state. This voltage-settable switch is therefore based on the trapping of charge in metallic NPs. For this reason, we will use the short name “nanotrap memory” to describe our devices throughout this paper.

Although the basic picture of the space-charge field due to trapped charge was given by Simmons and Verderber, many details remain to be examined: does the charge enter and leave the NPs? What is the nature of the conduction process in the ON state? How do the materials’ properties, device thickness, and NP size affect the device performance in terms of ON/OFF ratio, switching speed, retention time, etc.? In order to begin addressing these questions, we have undertaken a broad initial survey of several materials for use as the electrodes, the NPs, and the semiconducting host. Devices were made in various combinations. As will be seen, the switching phenomenon is remarkably universal—virtually all the devices that were fabricated show some evidence of bistable behavior—but no consistent dependencies are found on any of the materials’ properties.

Three architectures were considered for the fabrication of our bistable devices: spin-cast polymer–NP blends where the nanotrips are randomly distributed throughout the entire thickness of the host matrix; spin-cast blends layered with pure polymer; and evaporated structures where the nanotrips are located in the middle of organic layer. In addition, we examine single-layer devices without NPs.

2. Results and Discussion

The sketches in Figure 1 show the three different device architectures and the reference structure used in these studies. The simplest bistable device structure consists of a single layer of polymer semiconductor into which the NPs are blended, re-

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* Dr. L. D. Bozano, Dr. P. M. Rice, Dr. J. C. Scott
IBM Almaden Research Center
650 Harry Rd.
San Jose, CA 95120 (USA)
E-mail: lbozano@almaden.ibm.com

B. W. Kean
Department of Electrical Engineering, University of Santa Barbara
Santa Barbara, CA 93106 (USA)

Dr. M. Beinhoff
Max-Planck-Institute of Colloids and Interfaces
Wissenschaftspark Golm, D-14424 Potsdam (Germany)

Prof. K. R. Carter
University of Massachusetts
Department of Polymer Science and Engineering
120 Governors Drive, Amherst, MA 01003-4530 (USA)

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sulting in a random distribution of nanotraps (Fig. 1a). Because of the crosslinkable properties of the polymers used here, a second layer can be spun on the top without washing off the bottom layer. This property allows fabrication of structures in which one layer contains NPs and the other does not, as shown in Figure 1b. Clearly, this approach can be generalized to additional layers, but we do not report them here.

In Figure 1c, the evaporated structure with a granular layer is represented. Important in this case is the nominal thickness of the middle layer, as will be explained. The traps are deposited in a single plane, preferably near the middle of the semiconducting material. In this structure, the semiconductor material comprises small organic molecules (or an evaporable inorganic material), and the metallic nanotraps are formed by island growth that is terminated before the islands coalesce to form a connected layer. As a reference, devices without metal NPs or a granular layer were also fabricated (Fig. 1d).

Figure 2 shows the chemical structures of the polymeric and small-molecule organic semiconductors used as hosts in the memory cell, together with the literature values of their HOMO (highest occupied molecular orbital) and LUMO (lowest occupied molecular orbital) energies, and bandgaps. For some of the materials the HOMO and LUMO levels are not known, and only the optical bandgap is given. All the polymers used in this study possess thermally crosslinkable 4-phenylethynyl end groups (indicated by an “-” in front of their names).

For device operation, the granular nature of the metallic films plays a critical role. Therefore, the structures were analyzed, at various stages of processing, by atomic force microscopy (AFM), transmission electron microscopy (TEM), focused-ion-beam cross-section scanning electron microscopy (FIB-SEM), secondary-ion mass spectroscopy (SIMS), and X-ray photoemission spectroscopy (XPS). In particular, we rely on FIB-SEM, performed after electrical testing, to examine the granularity of the metal layer in complete and functional evaporated devices.

More detailed information about intermediate structures and their morphology was obtained via top-view AFM and TEM. An AFM image of a nominally 5 nm thick Al layer grown on Alq3 is shown in Figure 3a.

Higher resolution is given by dark-field TEM, but because of issues of sample preparation the Al was deposited on a 20 nm layer of SiO2 on a carbon grid (Fig. 3b). Although the surfaces are different, the AFM and TEM images show that there is island growth in both cases. The islands exhibit a large variation in shape and size (from 20 to 200 nm), and they cover a large fraction of the surface but are clearly disconnected. The gaps between islands are of the order of 5–20 nm in the TEM image and are similar, but are not fully resolved in the AFM image. AFM images on several other partially completed device structures (not shown) provide convincing evidence that island growth is a common feature of this method of deposition.

XPS studies of a 5 nm film of Al on SiO2, prepared side-by-side with that for TEM, reveal the relative fractions of oxidized and metallic Al. Even though the sample was exposed to air between deposition and XPS measurement, approximately half of the Al remained metallic, as shown in Figure 4. The angle dependence shows that there is some additional surface oxidation. One may therefore expect that in the devices, which are

![Figure 1](image1.png)  
**Figure 1.** Fabricated device structures. The organic material (gray) is sandwiched between metal contacts (black). Single-layer polymer–NP blends (a), bilayer polymer–NP blends (b), all-evaporated (small molecules) organic structure with metal-NP middle layer (c), and reference organic layer with no added metal particles (d).

![Figure 2](image2.png)  
**Figure 2.** Chemical structure of the materials used. a) Aluminum tris(8-hydroxyquinoline) (Alq3); b) N,N'-Dinaphthalene-1,4,1'-biphenyl,4,4'-di-amine (according to IUPAC) or N,N'-bis-(naphthalene-1-yl)-N,N'-bis(phenyl)benzidine (NPB); c) crosslinkable poly(9,9-di-hexylfluorene) (xDHF); d) crosslinkable poly(4-hexyltriphénylamine) (xHTPA); e) crosslinkable poly([1,1'-biphenyl][4,4'-di-yl]-[2,2,2-trifluoro-1-[(trifluoromethyl)ethylidene]]) (xBPFF); and f) crosslinkable poly([1,1'-biphenyl][4,4'-diyl]-9H-fluoren-9-ylidene) (xBPFF). Values represent the optical bandgap derived from the Einstein equation; the values could differ from the electrical bandgap.
Electrical direct-current (DC), alternating-current (AC), and pulse measurements were performed on the fabricated devices. In this paper we focus on the DC results, since they reveal the most basic features of the switching behavior, while in further publications, we will discuss the AC results.\textsuperscript{[10]}

The operational characteristics of nanotrap memory devices are described with reference to the generic behavior, as represented in Figure 6.\textsuperscript{[5]} This shows the typical semilogarithmic curve of current density versus applied voltage ($I-V$) for a switchable element at room temperature, specifically an ITO/ xBP9F:Al-NP/Al device. We parameterize the behavior in terms of the forward-bias (i.e., with ITO positive) response. A very similar set of parameters would apply to the reverse-bias case, since the response is nearly symmetric. The device parameters that identify the switching properties are the threshold voltage ($V_{th}$), which indicates the voltage at which a device initially in the OFF state increases its conductance, turning on, and the voltages at the local maximum and local minimum of its current density, indicated as $V_{ON}$ and $V_{OFF}$, respectively, since the states of the device can be activated by applying pulses at $V_{ON}$ and $V_{OFF}$. The state can be read at, for example, 1 V ($V_{read}$) without disturbance. Another important parameter is the ratio between the currents in the ON and OFF states at $V_{read}$, the ON/OFF ratio. It is noteworthy that the ON and OFF states of the device can be set by pulses of either polarity and read in either polarity.

In Figure 6, the device current switches between states of low and high conduction at the threshold, reaches the maximum, and then goes through a negative-resistance region to a minimum, after which it increases again almost exponentially. Therefore, three different regions can be identified. The low-voltage region below $V_{th}$ is the region of bistability (or multistability),\textsuperscript{[5]} in which the state of the device can be read. Typical values of the OFF- and ON-state currents at $V_{read} = 1$ V are from $10^{-7}$ A cm$^{-2}$ and $10^{-2}$ A cm$^{-2}$, respectively.

The region between $V_{ON}$ and $V_{OFF}$ exhibits negative differential resistance (NDR). Any pulse at a voltage in this region sets an intermediate state between ON and OFF. The ON/OFF

Figure 4. XPS results on a 5 nm thick Al layer on top of a SiO$_2$ layer. The two spectra were obtained relative to the bulk (dashed line) or the surface (solid line), as indicated.

prepared entirely in inert atmospheres, a larger fraction of metal remains, most likely as a metallic core surrounded by an oxide shell.

For the case of gold NPs dispersed in a semiconducting polymer matrix, Figure 5a shows a cross-section dark-field TEM image of a bilayer structure in which two crosslinkable polymer films are sandwiched between two metal contacts: the bottom layer is the polymer–Au-NP blend and the top one is plain polymer. Overall, the NPs are well distributed throughout only the lower layer and there is no evidence of clustering. The particle size distribution ranges from <1 nm to about 5 nm. Some of the larger NPs are arranged on the bottom at the interface with the metal, an interesting phenomenon for which we have no explanation. Higher-resolution TEM studies (Fig. 5b) reveal more clearly the large number of 1 nm diameter NPs while, in this sample, fewer of larger size are seen. The size distribution peaks at small sizes, but we do not present a quantitative analysis because the contrast in the images is insufficient to distinguish the smallest particles.

Figure 5. a) Dark-field TEM image of a bilayer structure of polymer (xHTPA)–NP blend device. The two polymer layers are distinct, and the NPs are confined in the bottom layer as desired. ITO: indium tin oxide. b) High-resolution dark-field TEM image of polymer (xBP9F)–NP blend film showing the smaller size distribution of the NPs (<1 nm).
ratio is directly related to the currents at $V_{\text{ON}}$ and $V_{\text{OFF}}$, and so also would be the number of levels useful for multibit operation. In the high-voltage region ($V > V_{\text{OFF}}$), the current increases again monotonically with voltage.

Similar $I-V$ characteristics were previously observed by Simmons and Verderber\cite{8} for a SiO layer sandwiched between Al and Au contacts. The authors showed that the processes of conduction and bistability were initiated by electroforming, i.e., by applying a high positive voltage (5 V for a 40 nm SiO layer). Attempting to interpret this phenomenon, Simmons and Verderber attributed the increase in conduction subsequent to the forming process to the introduction of Au atoms and clusters into the SiO matrix. According to their assumption, these atoms acted as donor sites for charge transport and as traps. In the case of our nanotrap devices, we previously showed that NPs are required for observing switching and bistability.\cite{9} No electroforming is necessary.

Comparison of devices with and without NPs shows that the NPs increase the conduction of the device. As with the SV mechanism, the NPs appear to have the dual role of traps (in their case, the gold clusters) and conduction sites (gold atoms in the SiO matrix) for the injected charges. For example, see Figure 7a, in which the $I-V$ characteristics of a plain HTPA layer (open symbols) sandwiched between ITO and Ca/Al contacts are compared to those of a device in which the polymer is blended with NPs (closed symbols). Both devices have a polymer-layer thickness of about 50 nm. With this choice of electrodes, hole injection dominates and the polymer is a hole transporter, but electron injection and transport are poor. The device with NPs displays the typical properties of switching devices described above: it has a voltage threshold just below 3 V, and an ON/OFF ratio of about 100. At low voltages, the characteristics of the layer without NPs are comparable in magnitude to the OFF-state branch of the NP device, but differ in

**Figure 6.** DC current-density–voltage ($I-V$) characteristics at room temperature for an ITO/polymer:Au-NP/Al device. The organic film thickness was 50 nm. In forward bias, the device was ramped from 0 to 7 V and back to 0 V. The $I-V$ curve can be divided into three operating regions that are associated with different working regimes of the device: the bistable region $0 < V < V_{\text{ON}}$; the negative-resistance region $V_{\text{ON}} < V < V_{\text{OFF}}$; and the monotonic region $V > V_{\text{OFF}}$. Similar behavior can be found in the reverse-bias region, sweeping the voltage from 0 to ~8 V and then back to 0 V. The device starts in the OFF state (low current density) for both forward- and reverse-bias curves.

**Figure 7.** a) $I-V$ characteristics comparing the ITO/xHTPA/Ca/Al device with (closed symbols) and without (open symbols) Au NPs. In both cases the film thickness is 50 nm. b) $I-V$ characteristics comparing the evaporated Al/Alq$_3$(100 nm)/Al structure (open symbols) with the embedded 5 nm Al granular layer (closed symbols) structure.

shape. The characteristics of the two devices are again similar at high voltage.

Similar behavior is observed for the Al/Alq$_3$(50 nm)/Al(5 nm)/Alq$_3$(50 nm) structure (Fig. 7b): the device doesn’t display bistable properties unless NPs are added to the organic matrix. For the device with no NPs, because of the mismatch of the metal work functions to the HOMO and LUMO levels of the Alq$_3$, there is poor charge injection (injection limited) and the $I-V$ characteristics of the device exhibit low current density (between $10^{-8}$ and $10^{-6}$ A cm$^{-2}$). Hence we conclude that not only do the NPs induce bistability, but they also contribute to the conduction process.

Next, we consider the effect of the nominal thickness of the middle granular layer in the evaporated device structure (Fig. 1c). Thin Al layers are evaporated at the center of a set of Alq$_3$ organic films of fixed thickness: 100 nm. The electrodes are also Al. The evaporation rate is important during the fabrication process and is controlled by a quartz rate monitor. A rate less than 1 Å s$^{-1}$ was used since a higher rate (>5 Å s$^{-1}$) produced continuous films and, therefore, non-switching devices. The results are summarized in Table 1. In the absence of metal NPs (i.e., zero thickness) the device does not switch. The results consistently show that to obtain switching properties it
is necessary to introduce metal NPs. The thicker the layer, the greater are both the ON and OFF currents of the device, but the ratio of the two quantities diminishes for thicknesses greater than 10 nm. We also note that the most reliable and reproducible devices were obtained for the device with Al thicknesses of 5 and 10 nm.

It is important to understand the role of the barrier height between the metal Fermi energy and the HOMO or LUMO levels of the organic material. To study this dependence, devices with electrodes that had different work functions in combination with various NPs were fabricated. Figure 8 shows a scheme of the energy levels of the materials that were used for the device fabrication, each with a fixed 100 nm total thickness of Alq3. In this case, the top electrode and nanotrap were Al. The results are summarized in Table 2. Although the work function of the bottom electrode varies by 1 eV, surprisingly there is relatively little variation in the basic operating parameters, and the reported differences show no systematic behavior. Indeed, there is as much variation between different devices with the same composition as between those with different electrode materials.

With the same intent, different NPs were adopted for Al/Alq3/Al sandwich devices (Fig. 9). Again (Table 3), there is no systematic dependence between the variation in the work function of the nanotrap material and the parameters summarizing device performance. Only Au proved not to be a good choice, because all devices with evaporated Au were shorted. Notably, the organic semiconducting material copper phthalocyanine (CuPc) also produced switching devices.

Lastly, the semiconducting host in these experiments, designed to investigate the role of the material components, must be considered as well. Therefore, the I–V characteristics of evaporated devices based on the small molecules, NPB and Alq3, are compared in Figure 10. Al was used for both the traps and the electrodes. The two organic materials have different energy levels, but the resulting I–V curves are very similar. The results of the last three paragraphs all suggest that the specific materials used play at most a secondary role in the determination of device properties. We will return to this issue in the discussion.

The effect of temperature was studied between −25 and 50 °C. The results are summarized in Table 4 for devices based on Al/Alq3/Al/Alq3/Al and ITO/xHTPA:Au NP/xHTPA/Al.

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Table 1. Study of the current density at the reading voltage (V_read = 1 V) for the evaporated structure Al/Alq3(50 nm)/Al/Alq3(50 nm)/Al. Results for different nominal thicknesses of the outer Al layer are compared.

<table>
<thead>
<tr>
<th>Sandwiched Al film thickness [nm]</th>
<th>/ [A cm⁻²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>OFF</td>
<td>10⁻⁶–10⁻⁶</td>
</tr>
<tr>
<td>ON</td>
<td>10⁻⁵–10⁻⁵</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bottom electrode</th>
<th>Semiconductor</th>
<th>Top electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>LUMO 3 eV</td>
<td>Al</td>
</tr>
<tr>
<td>Cr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au, Ni</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 8. Energy-level representation for different choices of bottom electrode for a bottom-electrode/Alq3(50 nm)/Al(5 nm)/Alq3(50 nm)/Al structure. The values of the metal work functions were taken from literature.

Figure 9. Energy-level representation for different choices of metal NPs for a Al/Alq3(50 nm)/NP/Alq3(50 nm)/Al structure.

Table 2. Summary of I–V values for different bottom electrodes.

<table>
<thead>
<tr>
<th>Bottom electrode</th>
<th>Work function [eV]</th>
<th>V_on [V]</th>
<th>V_off [V]</th>
<th>V_IN [V]</th>
<th>ON/OFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>4.28</td>
<td>3–3.5</td>
<td>6–8</td>
<td>2.6–3</td>
<td>10⁻³–10³</td>
</tr>
<tr>
<td>Cr</td>
<td>4.5</td>
<td>3.5</td>
<td>7</td>
<td>2.5</td>
<td>10⁻⁶</td>
</tr>
<tr>
<td>Cu</td>
<td>4.65</td>
<td>3–4</td>
<td>6–8</td>
<td>2.7–3</td>
<td>10⁻²</td>
</tr>
<tr>
<td>ITO</td>
<td>4.9–5.0</td>
<td>3.7</td>
<td>8</td>
<td>3.5</td>
<td>100</td>
</tr>
<tr>
<td>Au</td>
<td>5.1</td>
<td>3.5</td>
<td>6</td>
<td>2.6</td>
<td>10⁻¹⁰</td>
</tr>
<tr>
<td>Ni</td>
<td>5.15</td>
<td>3.5</td>
<td>7</td>
<td>2.5–3</td>
<td>10⁻¹⁰</td>
</tr>
</tbody>
</table>

Table 3. Summary of I–V values for different NPs. In the case of Au, the devices were shorted.

<table>
<thead>
<tr>
<th>Trap</th>
<th>Work function [eV]</th>
<th>V_IN [V]</th>
<th>V_ON [V]</th>
<th>V_OFF [V]</th>
<th>ON/OFF ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>3.66</td>
<td>2.6–3</td>
<td>6–7</td>
<td>2.6–3</td>
<td>10⁻¹–10³</td>
</tr>
<tr>
<td>Ag</td>
<td>4.26</td>
<td>2.3–2.7</td>
<td>3.3</td>
<td>2.3</td>
<td>20</td>
</tr>
<tr>
<td>Al</td>
<td>4.28</td>
<td>2.6–3</td>
<td>3–3.5</td>
<td>6–8</td>
<td>10⁻¹⁰–10⁴</td>
</tr>
<tr>
<td>Cr</td>
<td>4.5</td>
<td>2.4–2.8</td>
<td>3.5–5.6</td>
<td>6–8</td>
<td>10⁻³</td>
</tr>
<tr>
<td>Au</td>
<td>5.0</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>CuPc</td>
<td>3.1–5.29</td>
<td>3</td>
<td>4–8</td>
<td>3</td>
<td>10⁻³</td>
</tr>
</tbody>
</table>
The range of materials and structures that demonstrate switching and bistability is quite remarkable. The data presented above show that the phenomena occur in evaporated organic semiconductors with a layer of granular metal or semiconducting islands, in semiconducting polymers with metallic NPs distributed throughout the layer, or in only part of it, and in wide-bandgap inorganic semiconductors with metal clusters. There are relatively few exceptions, for example xDHF:Au NP with ITO and Ca/Al electrodes. In addition, the operating parameters of the switching devices are, in the structures studied to date, surprisingly insensitive to the specific materials.

The common features required for a device to exhibit bistability seem to be a semiconducting host containing dispersed NPs. This work has focused primarily on metallic NPs, although we have also seen the effect with a semiconducting CuPc granular layer. The host materials used in this work can all be classified as wide-bandgap semiconductors, although other groups have employed insulating polymers such as polystyrene or molecularly doped polymers. Charge transport through these devices can thus occur either through the semiconducting medium itself or, as the data presented here suggests, by tunneling between the NPs. In both cases, the charge transport falls into the category of “hopping,” where the electronic states are highly localized. In the case of hopping between molecular sites in the amorphous semiconductor, it is well documented that phonon assistance overcomes the energetic disorder, leading to exponentially activated temperature dependence. In the case of hopping between the metallic NPs themselves, the mechanism is direct tunneling and is known to be temperature independent. Thus, the preliminary experiments support the idea that NP tunneling is dominant.

The common feature of these devices is that NPs are embedded in a host matrix, but the specific energy-level structure provided by the electrode and metal NP Fermi energies and the HOMO–LUMO of the host is relatively unimportant. One explanation for this may lie in the uncontrolled nature of the particle size distribution. For both the evaporated granular layers and the synthetic gold NPs, the range of particle sizes is comparable to their mean value. Since the capacitance of a particle is proportional to its size, so is the electrostatic-energy change associated with adding or removing an electron. Therefore, the range of particle sizes may be at least as important as the energy structure of the materials in the device. One expects, for example, that small particles, with higher charging energies, contribute primarily to the conduction process, while larger particles, which have longer retention times, are more effective as traps. This is a point that clearly requires further investigation.

3. Conclusions

Additional clues to the underlying mechanism(s) might be given by examining the way in which the ON and OFF currents scale with device area. Therefore, devices with sizes down to 40 μm × 110 μm were fabricated (using evaporated Alq3 and Al NPs). Both currents were found to scale proportionally with area, indicating that switching is, most likely, not related to filament formation within the organic film. Similar scaling results were found, down to 0.25 mm², for polymer-based devices.
ments for switching behavior appear to be rather minimal: discrete nanoscopic traps embedded in a wide-bandgap semiconducting host. The results indicate that transport occurs predominantly by tunneling between NPs. The results have been interpreted primarily within the context of the SV model, in which the space-charge field of trapped charges inhibits injection. However, some detailed aspects of the data remain to be explained: the insensitivity of the switching parameters to the work functions of the metals used; the magnitude of the ON-state current; and the observation that most pristine devices are in the OFF state.

4. Experimental

All the devices were prepared on 1 in. x 1 in. (25.4 mm x 25.4 mm) square quartz substrates that were first thoroughly cleaned, as previously described [5], and then moved inside the nitrogen environment of a glovebox for the processing steps. Polymer films were prepared by spin-casting using a Chemat Technology spin-coater, KW-4A. The sample was first spun at 600 rpm for 8 s, then its speed was automatically switched to 1000 rpm for 60 s. The film thickness was controlled by varying the spin speed and then measured by AFM, TEM, or profilometry. The crosslinkable polymers were heated at 150 °C for 1 h to form the polymer network and to allow the preparation of multiple layers of polymers. Crosslinking of the materials was tested by observing the optical absorption of the film before and after washing it with solvent. For uncrosslinked material the spectrum returned to the baseline, indicating that the process removed all the material from the substrate.

All small-molecule materials and metals were purchased: Alq3 was purchased from Kodak and all the metals from Aldrich. The polymers (xHTPA, xDHF, xBP9F, and xBP6F) were prepared in IBM according to procedures described elsewhere [11–13].

Metal electrodes and small-molecule organics were evaporated in a vacuum chamber at a pressure of 10−7 torr (1 torr = 133 Pa) using shadow masking and with the substrate at room temperature. Different evaporation rates were used for the different materials: for Alq3 and NPB, a rate of 11 Å/s was used; for the granular metal layer a rate of 1 Å/s was used; and for the top and bottom electrodes rates of 1 and 10 Å/s, respectively, were used. The layer thickness and its evaporation rate were controlled by a calibrated quartz monitor. Samples were moved between the glovebox and the vacuum chamber without exposure to air.

The Au NPs were prepared according to the literature [23]. Due to the synthetic procedure, they possess a triphenylphosphine surfactant layer. They were blended with the polymer at a nominal 30% concentration by weight by mixing in the polymer solution.

The electrical measurements were conducted in a nitrogen environment and by interfacing a computer with a Keithley 238 source measure unit. The temperature was varied between −25 and 50 °C using a McShane 5C7-361 thermoelectric controller.

For one defined structure, many (>12) devices were fabricated and tested. Sometimes small variations (−5%) from one device to the other were noticed. The reported current–voltage characteristics are representative of a particular device structure.