Electronic Properties of Molecular Memory Circuits on a Nanoscale Scaffold

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***Abstract*—Significant challenges exist in assembling and interconnecting the building blocks of a nanoscale device and being able to electronically address or measure responses at the molecular level. Here we demonstrate the usefulness of engineered proteins as scaffolds for bottom-up self-assembly for building nanoscale devices out of multiple components. Using genetically engineered cowpea mosaic virus, modified to express cysteine residues on the capsid exterior, gold nanoparticles were attached to the viral scaffold in a specific predetermined pattern to produce specific interparticle distances. The nanoparticles were then interconnected using thiol-terminated conjugated organic molecules, resulting in a three-dimensional network. Network properties were engineered by using molecular components with different *I–V* characteristics. Networks consisting of molecular wires alone were compared with networks containing voltage controlled molecular switches with two stable conductance states. Using such bistable molecules enabled the formation of switchable molecular networks that could be used in nanoscale memory circuits.**

***Index Terms*—Biomaterials, molecular electronics, nanotechnology.**

I. Introduction

In RECENT years, molecular electronics has been proposed as a pathway for high-density nanoelectronic devices. Such devices are of great interest for their potential to enable lightweight, low-cost, and low-power technologies. However, for molecular electronics to deliver on such promises, it is necessary to produce molecules that exhibit reproducible nonlinear electronic properties such as reversible switching between two conducting states, rectification, or gating. Even after such molecules have been developed, significant challenges exist in assembling and interconnecting them to create nanoscale devices and in electronically addressing or measuring responses at the molecular level. Here, we discuss the characterization of a molecular switch and a technique for self-assembly of such molecules into circuits on the nanoscale.

In order for a molecular electronics circuit to provide computational or memory function, it is necessary to utilize a molecule which exhibits nonlinear *I–V* characteristics [1]–[4].

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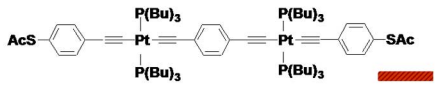
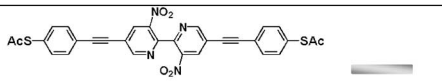
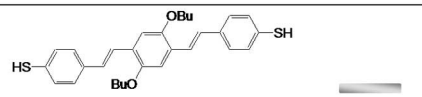
TABLE I
THE MOLECULAR STRUCTURE OF THE MOLECULES USED

Molecule	Molecular Structure	Length (nm)
di-Pt		3.04
BPDN		2.41
OPV		2.07

Previous observations indicate two types of switching behaviors in molecular electronic systems—switching due to an applied external voltage [5]–[7] and stochastic switching attributed to statistical fluctuations in the state of the molecule [8]–[10]. Because the fabrication of a molecular memory device requires control of the electronic state of the molecule, voltage controlled switches provide a more direct path towards molecule-based electronics [6]. While a wide range of molecules have been investigated for use as potential molecular switches, nitro containing molecules have received an enormous amount of attention due to early reports of nonlinear *I–V* characteristics [1], [5], [6]. Here we focus on results from junctions formed from bipyridyl-dinitro oligophenylene ethynylene dithiol (BPDN) whose molecular structure is shown in Table I [11].

Once molecules of interest have been identified, a key issue for use in devices is assembling and interconnecting the molecules to create molecular circuits of interest. Self-assembly is one of the few practical strategies for making ensembles of nanostructures and will therefore be an essential part of nanotechnology [12]. One promising area of self-assembly involves using biological molecules such as DNA as a template for organization [13]–[15]. Although several groups have demonstrated the usefulness of this approach, building ordered three-dimensional structures with this technique is difficult due to the one-dimensional nature of the scaffold [13], [16]. In order to generate more complex structures, it is possible to use a three-dimensional scaffold, such as a viral capsid [17], [18]. Viral capsids are monodisperse and chemically identical, allowing for excellent control in the positioning of nanocomponents for assembly. Such a scaffold can either interface with lithographically defined structures, or undergo

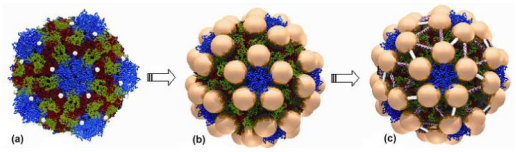


Fig 1. (a) EF CPMV mutant, cysteine sites in white. (b) EF CPMV + 5 nm gold nanoparticles. (c) EF-CPMV + 5 nm gold nanoparticles + molecular electronics components.

further self-assembly into extended structures [19], [20]. Here, we demonstrate the usefulness of this approach by designing, building, and measuring three-dimensional switchable nanoscale molecular networks on a 30 nm diameter cowpea mosaic virus (CPMV) particle.

CPMV is an icosahedral particle made of 60 copies of a protein subunit, with a spherically averaged diameter of 30 nm and provides a nanoscale template to generate complex three-dimensional patterns of gold nanoparticles [21]–[23]. CPMV is well-suited for use as a template due to its tolerance of organic solvents, and its stability in pH 3-10 at temperatures up to 70 °C. An infectious clone of the virus enables site-directed and insertional mutagenesis to be performed, allowing the production of mutants with specific predetermined patterns of fiunctional groups. For example, the crystal structure of wildtype CPMV demonstrates that there are no solvent accessible cysteine (cys) residues on the capsid surface, enabling the insertion of cys at desired locations on the capsid. Using mutagenesis, we have produced genetically engineered cys CPMV mutants that enable anchoring of gold nanoparticles at specific locations [21], [22] on the surface and subsequently interconnecting them by molecular wires to create a three-dimensional conducting network on the nanoscale [23].

In the current work, we utilized the previously reported EF-CPMV mutant [Fig. 1(a)], which was constructed by a five residue insertion (GGCGG) on the EF loop between positions 98 and 99 of the large subunit [24], [25]. We reported the interparticle distance of bound gold [Fig. 1(b)] to be 6.4 $\pm$ 0.5 nm (projection of 3-D crystallographic data indicates distances of 5.3 nm for neighbors around the same fivefold axis, and 6.5 nm for nearest neighbors on adjacent fivefold axes) [22]. These distances enable dithiol molecules of an appropriate length to bridge the gold nanoparticles, generating a conductive network on the nanoscale (Fig. 1c) [23]. Building on earlier work in this area, we used 1,4 -C $_6H_4$ [trans-(4-AcSC $_6H_4$C $\equiv$ CPt(PBu$_3$) $_2$C $\equiv$ C] $_2$ (di-Pt) along with oligophenylene-vinylene (OPV) or BPDN to generate two molecular networks. The network properties reflected the properties of the OPV or BPDN molecular building blocks. Using the CPMV viral capsid as a template, and the bistable switch molecule BPDN, we were able to engineer molecular networks that could potentially be used as nanoscale memory devices.

II. Materials and Methods

A. Molecular Network Formation

To form self-assembled molecular networks, 5 nm gold nanoparticles (Ted Pella) were bound to EF mutants as previously described [21]–[23]. Once the gold nanoparticles were bound to the viral scaffold, stock solution ($\sim$ 4.31 μM) of di-Pt, and BPDN in THF were prepared. To generate switchable networks, 75 μL of the BPDN solution and 75 μL of the di-Pt solution were added to 750 μL of EF virus-gold complex (0.04 mg mL $^{-1}$) in phosphate buffer (50 mM) at pH 7.3 and incubated for 12 h at room temperature. After reaction, the virus-gold-BPDN complexes (BPDN/diPt-CPMV) were washed twice with 1.5 mL 80 : 20 phosphate buffer (50 mM, pH 7.3) : THF solution and then twice with 1.5 mL phosphate buffer (50 mM, pH 7.3) using Microsep filters (MWCO 100 kDa, Pall Life Sciences). Control networks were generated, in a similar way using oligophenylene-vinylene (OPV) molecules that can act as molecular wires with linear *I–V* characteristics to create virus-gold-OPV complexes (OPV/diPt-CPMV). Di-Pt was used in both the networks to bridge the longer 3 nm interparticle distances. After purification, the virus-templated networks were characterized with UV/visible spectroscopy to determine the final concentration, and fluorescence spectroscopy to ensure that the viral capsids were intact [26] following exposure to organic solvents and molecules using an excitation wavelength of 290 nm.

B. STM Measurements

The *I–V* characteristics of individual OPV and BPDN molecules inserted into a tightly packed self-assembled matrix of undecanethiol (C11) were measured with a Digital Instruments Multimode (Veeco Instruments Inc., Woodbury, NY) scanning tunneling microscope (STM) [27]–[29]. For these experiments, self-assembled monolayers (SAMs) of C11 alkanethiols were deposited out of ethanol onto a Au (111) surface evaporated onto a mica substrate (SPI, West Chester, PA). The C11 monolayers were then exposed to OPV or BPDN for one hour, allowing the test molecule to insert into the alkane matrix at defect sites such as step edges and domain boundaries [30]. After insertion, the films were exposed to unfunctionalized 2 nm gold colloidal particles (SPI, West Chester, PA), used as received, for 30 minutes [Fig. 2(a)]. The gold nanoparticles bind to the inserted OPV or BPDN molecules, making visualization and measurement with the STM easier. Control experiments on C11 SAMs without inserted molecules show no nanoparticle attachment. STM measurements were performed under ambient conditions.

The conductance of molecular networks self-assembled on a single virus was also measured using STM. To generate isolated molecular networks, the dithiol-functionalized conducting molecule OPV (structure shown in Table I) was inserted into defect sites in the C11 film, as described previously. The prepared substrate was then exposed to dilute solutions of viral-templated networks (0.01 to 0.03 mg mL $^{-1}$) for 12 h to allow viral-templated networks to bind to inserted OPV molecules in the alkanethiol SAM. After 12 h, the substrates were washed with phosphate buffer three times and blown dry with N_2, resulting in isolated viruses bound to the underlying gold substrate via the inserted conducting molecules, as shown schematically in Fig. 3(a).

III. Results and Discussion

I–V measurements were made on isolated OPV [29], [30] and BPDN molecules [31] prior to use in molecular networks

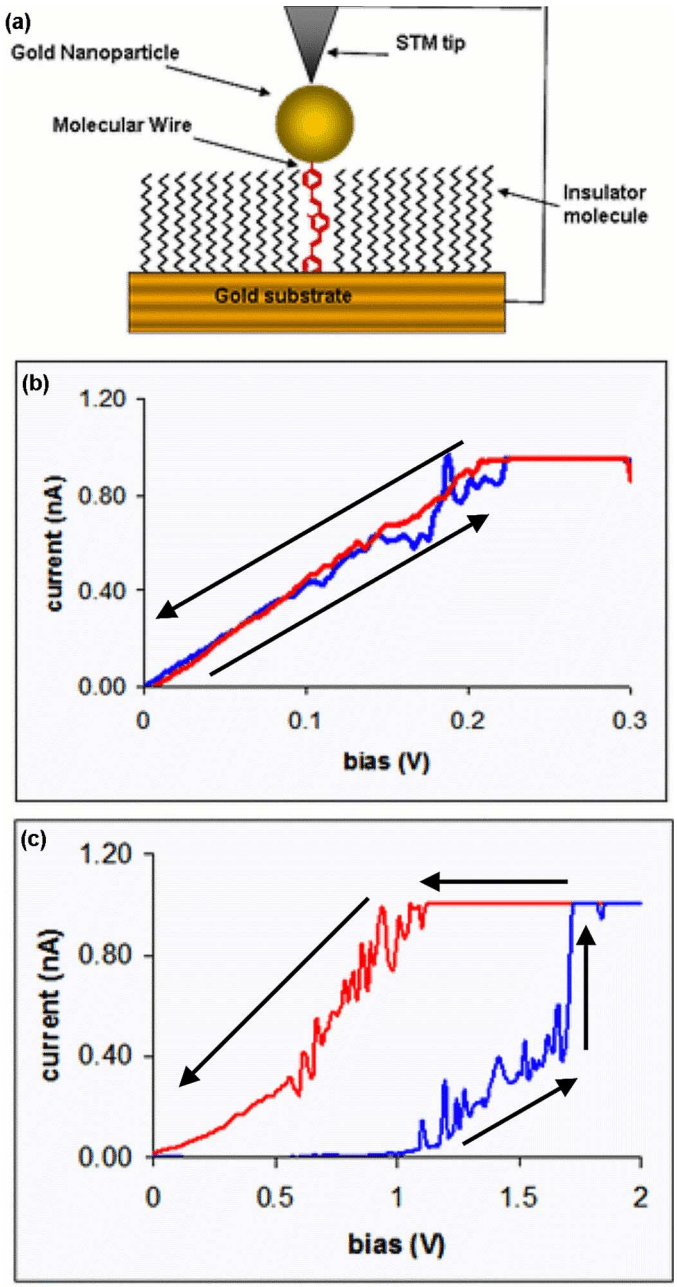


Fig 2. (a) Schematic of STM measurement configuration for isolated single molecules. (b) *I–V* measurement for an isolated OPV molecule. (c) *I–V* measurement for an isolated BPDN molecule showing voltage-triggered hysteretic behavior.

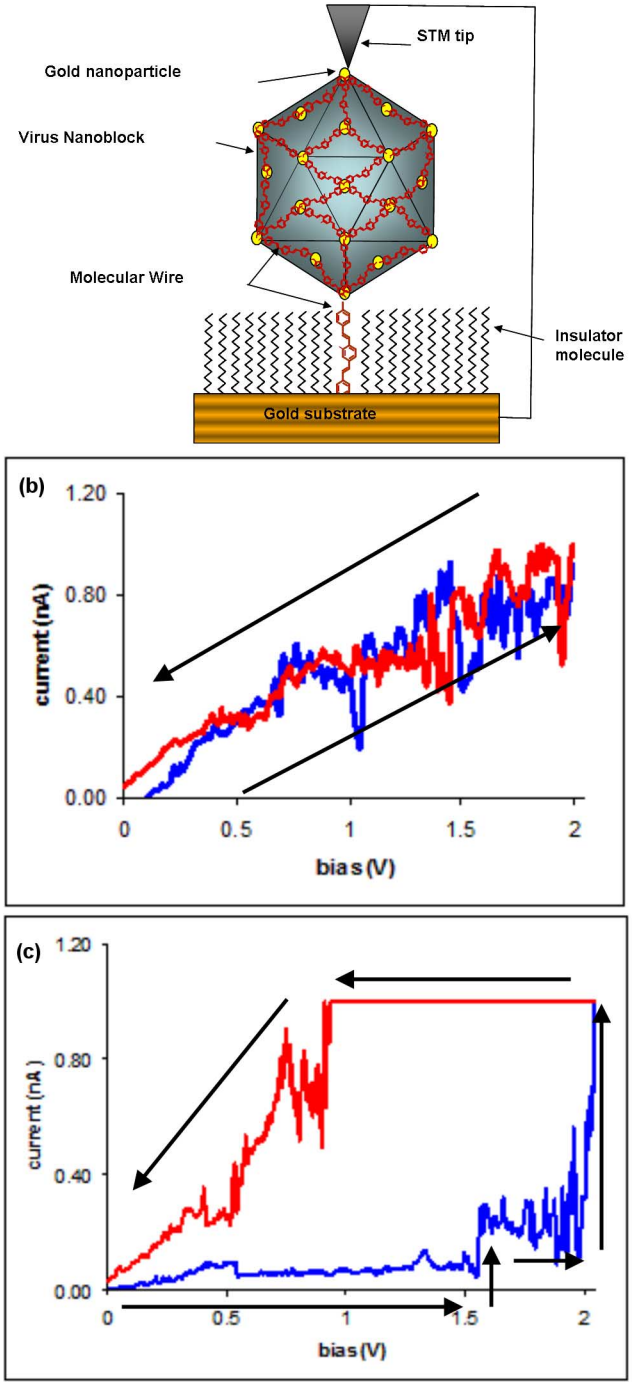


Fig 3. (a) Schematic of STM measurement configuration for an isolated virus templated network. (b) *I–V* for an isolated OPV/diPt-CPMV network. This control network does not display nonlinear behaviors. (c) *I–V* measurement for isolated BPDN/diPt-CPMV network showing steps in conductance and multistate behavior.

[Fig. 2(a)]. Viral-templated networks were then assembled using di-Pt and either OPV or BPDN, and network electronic properties were measured and compared. All measurements were done using STM, in which tunneling current is measured while the bias voltage is swept from 0 to 2 V, and then back to 0 V, with the feedback turned off. Fig. 2(b) shows a representative *I–V* measurement on an isolated OPV molecule. This measurement shows a linear current–voltage relationship until reaching the saturation current of 1 nA. This is typical for molecular conductance in the low bias limit [32].

Fig 2(c) shows a representative measurement on an isolated BPDN molecule. In this measurement, BPDN demonstrates voltage dependent nonlinear behavior. Specifically, the molecule starts off in a low conductance state (blue) and at a threshold voltage of 1.7 ± 0.5 V, the molecule "switches" to a higher conductance state where the tunneling current suddenly jumps to greater than 1 nA. The observed hysteresis in the measured *I–V* characteristics at 0.5 V corresponds to a 30-fold increase in the conductance of the molecule. The molecule remains in this higher conductance state (red) until the applied bias approaches 0 V. At that point the molecule switches back

into the low conductance state. If the voltage is scanned again from 0 to 2 V, the molecule exhibits the low conductance state until it is switched. The change in conductance state does not reflect an irreversible molecular process [31]—individual junctions could be repeatedly switched between the two conductance states, displaying hysteretic behavior for at least 40 cycles. In order to demonstrate that the observed *I–V* characteristics are a molecular phenomenon, and not an artifact of the experimental test-structure, [33], [34] we measured the *I–V* response for BPDN in three experimental geometries. For STM, a crossed-wire tunnel junction, [35]–[37] and a magnetic bead tunnel junction, [38] the *I–V* characteristics obtained for BPDN are qualitatively similar [31]. Since similar conductance-switching was never observed for junctions composed of alkyl or unsubstituted aryl systems, and a consistent signature is observed for the three testbeds, we conclude that the observed conductance-switching is attributable to the BPDN molecule. Further evidence for bistable conductance switching in BPDN comes from different testbeds in other research groups [39]–[41].

Once *I–V* data on individual molecules were completed, OPV and BPDN were integrated into molecular networks, as previously described. Measurements were performed on OPV/diPt-CPMV networks isolated in C11 monolayers, as has been discussed in detail elsewhere [23]. Briefly, STM measurements demonstrated that it was possible to construct 30 nm molecular networks through hierarchical self-assembly. The measured network conductance is in good agreement with models based on the conductance of the individual molecular wires that the network is built from. Fig. 3(b) shows *I–V* behavior for an individual OPV/diPt-CPMV network. The current shows no discontinuities, hysteresis, or other nonlinear behaviors over a voltage range of 0 to 2 V.

In contrast, STM measurements of isolated BPDN/diPt-CPMV networks show pronounced hysteretic behavior. A representative *I–V* measurement, shown in Fig. 3(c), shows that in contrast to the linear *I–V* behavior measured for control OPV/diPt-CPMV networks [Fig. 2(c)], BPDN/diPt-CPMV networks show a similar discontinuity in the measured *I–V* behavior to that observed in individual BPDN molecules. 80% of the isolated BPDN/diPt-CPMV networks measured demonstrate this 2-state behavior. In addition, stepped features appear at $\sim$ 1.5 and 2 V, suggesting that there are multiple conductance states accessible to the molecular network. 75% of the isolated BPDN/diPt-CPMV networks that show nonlinear features display this multistate stepped behavior within the measurement window of 0 to 2 V and 0 to 1 nA. Since the measurement preamp saturates at 1 nA current, it is possible that more BPDN/diPt-CPMV networks have multiple accessible states above this current threshold. These steps may occur when different molecules in the network change conductance state.

To understand the measured characteristics of the BPDN/diPt-CPMV networks, we used a simple resistive model based on the observed two-conductance state behavior of BPDN molecules, and the measured conductance of BPDN, OPV, and di-Pt molecules, to calculate the expected *I–V* behavior. In this model, we assumed that all of the cysteine sites are occupied by gold nanoparticles, and that all of the nearest

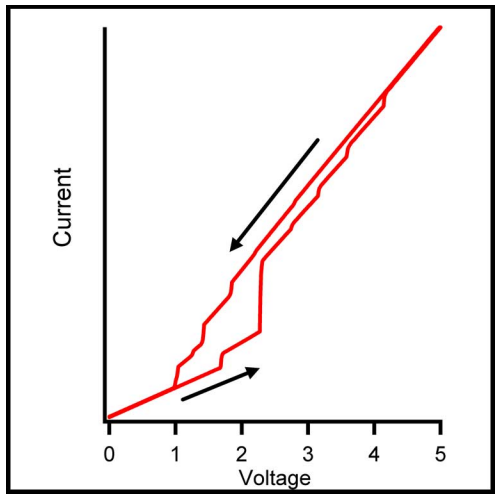


Fig 4. Model of BPDN/diPt-CPMV network based on measured characteristics of individual BPDN molecules.

neighbor nanoparticles are bridged by molecules. Distances of 5.3 nm for neighbors around the same fivefold axis, were bridged by BPDN, and distances of 6.5 nm for nearest neighbors on adjacent fivefold axes were bridged by di-Pt. The resulting calculation, shown in Fig. 4, suggests that BPDN/diPt-CPMV network should have multiple conductance states that are due to different molecules in the network changing from the low conductance state to the high conductance state. The initial jump in conductance comes at about 1.5 V, which is good agreement with the voltage triggered conductance transition in isolated BPDN molecules.

In summary, we have produced conductive networks on the nanoscale using CPMV as a template for self-assembly. We can engineer the behavior of the networks by selecting appropriate molecular components. Building such electronic circuits from molecular building blocks is an area of great interest. The CPMV scaffold uses the chemical specificity present in biological systems to organize inorganic components with great precision in three dimensions. Building on previous work to replace the conductive OPV molecule with molecules that can act as bistable molecular switches enabled us to build switchable molecular networks with a 28 nm footprint. Such CPMV-based bit storage devices have a theoretical density of 1 petabit/cm ^{2}, with the potential for increased storage density due to the availability of more than two conductance states on each virus.

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Authors' photographs and biographies not available at the time of publication.