Atomistic Modeling of Electron Transport in Self-Assembled Arene-Based Molecular Wires

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Abstract – **Genetically engineered, repetitive polypeptide sequences that can fold into β-sheets have been proposed as templates to form molecular wires built from molecules with selectable functional groups. This paper focuses on modeling of electron transport in such molecular wires. π-Stacked benzene wires with Au(111) electrodes are discussed first, followed by a discussion of the influence of benzene substituents on the electronic properties. In particular, the Peierls distortion, I-V characteristics, transmission spectra, and electrostatic potential distributions of short wires made from alternating pairs of phenolate and benzenediazonium ions and Au(111) electrodes are discussed. Wires made from this pair of molecular ions are much more thermally stable than those made from benzene, and conduct more current at a given voltage. A Peierls distortion significantly decreases the current.**

I. INTRODUCTION

As the dimensions of devices in integrated circuits continue to shrink, their performance is approaching limits imposed by fundamental laws of physics. Nanostructures, such as molecular wires, can be packed very densely and carry high current densities [1]. They have potential to increase functional density, minimize chip size, and enhance performance [2]. Investigation of nanoscale wires, including carbon nanotubes and inorganic and organic nanowires, need to be studied in more application-relevant detail to realize such potential. Recently, approaches to creating molecular wires using genetically engineered polypeptide structures and controlled self-assembly have been actively explored [3-8]. Genetically engineered, repetitive polypeptide sequences can fold into a β-sheet [6-8] that forms a template for molecular wires built from molecules with selectable functional groups. In addition to the promise of self-assembly, the synthesis protocol employs aqueous synthetic methods that are compatible with large-scale wafer processing. Thus, these methods facilitate industrial-scale production of genetically engineered polypeptides [3]. This paper focuses on modeling of electron transport in molecular wires that consist of π-stacked aromatic rings attached to the β-sheet scaffold that results from the folding of such a custom-designed polypeptide (Fig. 1a).

II. METHODS

We use self-consistent local orbital basis density functional theory (DFT) and nonequilibrium Green's functions (NEGF) formalism for finite bias problems [9] to determine the electronic structure and transport properties of π-stacked molecular wires. In this approach, physical quantities such as band energies are calculated by partition of the density matrix. Assuming coherent transport (ignore lattice phonon effects), the electron current is determined from the Landauer-Büttiker formalism,

$$I(V) = 2e/h \int T(E,V)[f(E-\mu_L) - f(E-\mu_R)] \, dE \qquad (1)$$

where f is the Fermi function and $T(E,V)$ is the transmission probability for electrons at a given energy E at applied bias voltage V, μ_L and μ_R are the chemical potentials of the left and right electrodes. The transmission probability is given by, $T(E,V) = \text{Tr}[\Gamma_L G^\dagger \Gamma_R G]$, where Γ_L and Γ_R are the broadening functions due to the left and right electrodes, and G is the retarded Green's function of the system.

Fig. 1b illustrates the simulation model. The system contains a 'device' region that consists of molecules
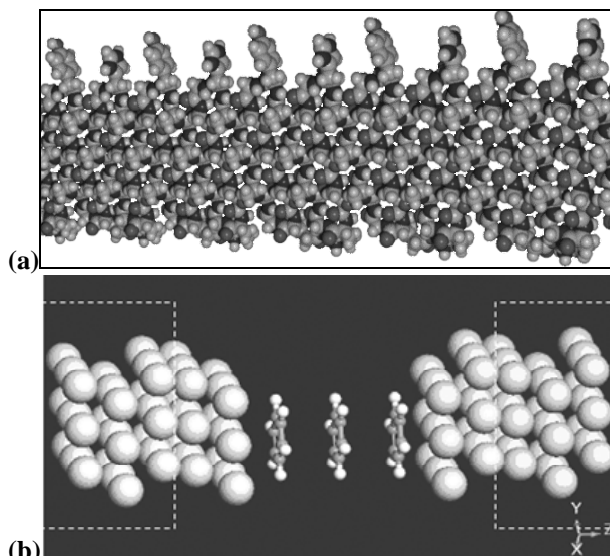

Figure 1: (a) Schematic of β-sheet peptide with molecular wire components along the 'top' (at the turns). (b) Simulation model for molecular wire containing π-stacked benzene molecules (n=3) between Au(111) surfaces.

and two layers of Au contact with (111) surface orientation at each end. Three layers of Au atoms, calculated separately, provide the Green's function of a semi-infinite (bulk) Au electrode. The 'device' Hamiltonian is solved self-consistently via DFT with a voltage applied on the electrodes. We have studied band structures, transmission spectra, I-V characteristics, and electrostatic potential distributions in order to evaluate the influence of functional substituent groups on the performance of the proposed molecular wire; i.e., the functional groups on the molecules in a wire. In an iterative manner, this information guides the experimental construction of candidate molecular building blocks for wires.

III. RESULTS

Since the β-sheets are non-conducting, we model the I-V characteristics of the pendant aromatic groups located on the sheets as chains of aromatic molecules located between electrodes; *i.e.*, we treat the β-sheets as perfect dielectrics. We first simulated π-stacked benzene molecules ($C_6H_6(n)$, where n is the number of molecules considered) with Au(111) junctions for its simplicity and prototyping. Fig. 2a shows the I-V characteristics of the above system with n=3. The circles are the self-consistent NEGF result at the applied bias. The solid curve is the estimation assuming the zero bias transmission coefficients only. The difference between the results from the two approaches starts from about 1 V in applied bias, where the transition from tunneling to resonant conduction occurs. In Fig. 2b, the local density of states on the molecules are plotted for two cases, 0 V and 1.4 V. Notice that the energy of the highest occupied molecular orbital (HOMO) increases about 0.4 eV at the higher applied voltage.

With a simple aromatic such as benzene, a lack of thermal stability is apparent on consideration of the binding energy for a π-stacked molecular wire. Fig. 3 shows the binding energy curve for a π-stacked molecular wire consisting of benzene rings, calculated using Abinit [10]. The computational unit cell is subject to periodic boundary conditions effectively giving rise to an infinite collection of parallel infinitely-long wires. The unit cell sizes in the directions transverse to the wire axis were chosen to be sufficiently large so that the wires were essentially non-interacting. The total energy vs. the inter-molecular distance, plotted in Fig. 3, confirms that the rings are weakly interacting and that the potential well depth is about 0.04 eV, comparable to the average thermal energy at room temperature. Clearly thermal effects will be important for this system.

The influence of benzene functionalization by substituent groups was investigated to determine if there is any correlation with the electrical and thermal performance of molecular wire candidates. In particular, the electrical and thermal performance of various arene compounds is
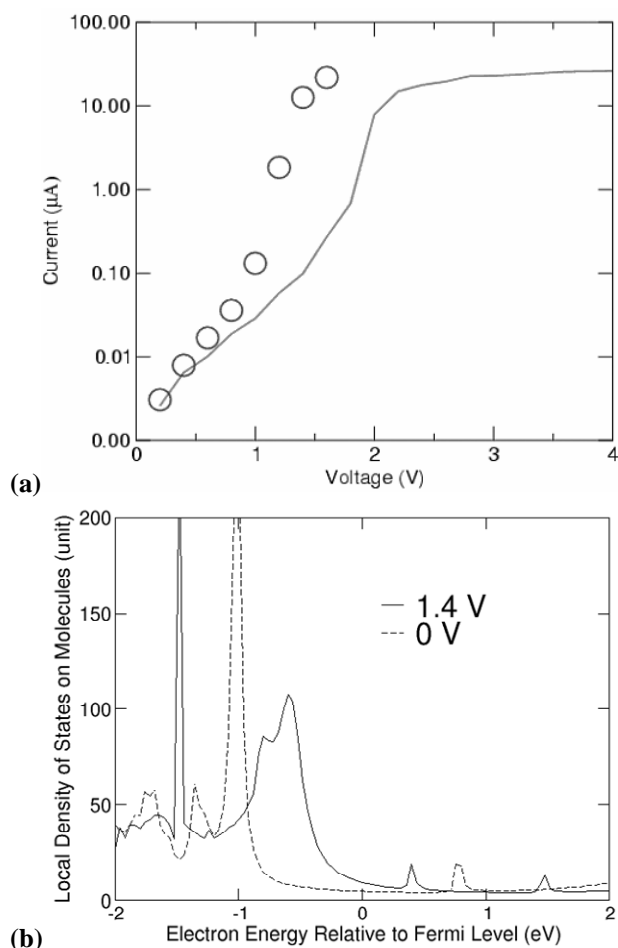
(a)

(b)

Figure 2: (a) The I-V results of π-stacked benzene molecules (n=3)/Au(111) wires (see text). (b) Projected density of states on molecules for the same wire at 0 and 1.4 V.

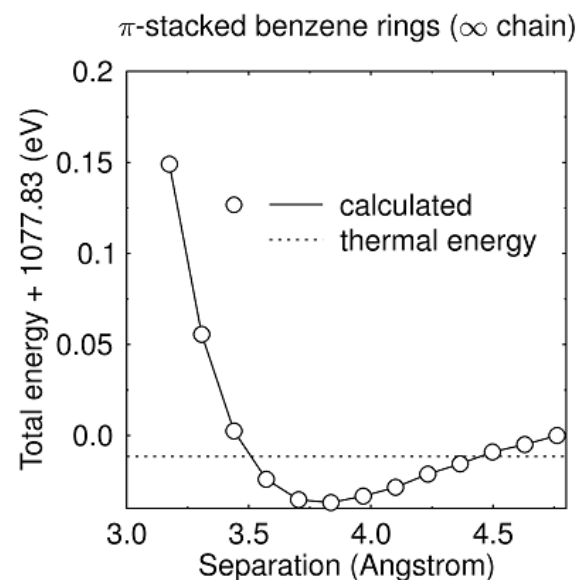Figure 3: Calculated binding energy curve for a π-stacked molecular chain consisting of benzene rings. Total energy is plotted vs. inter-ring separation. Also indicated is the (room temperature) thermal energy relative to the bottom of the potential well.

being determined for their potential use in molecular wires. Arenes are chosen based upon a Hammett parameter (σ_p) analysis [11] of the substituents and the potential of introducing such a substituent in a biologically derived system. The Hammett parameter is derived from a linear free energy relationship that characterizes the effects of substituting functional groups for hydrogen atoms on benzene. The σ_p values for a wide variety of functional groups are known and can be used to infer the influence of those substituents on arene electron density. The best candidate pair evaluated to date consists of phenolate and benzenediazonium ions (C_6H_5O, $C_6H_5N_2$) with the most negative and positive σ_p values, respectively. This pair of molecules has a high binding energy (~2 eV) when they are held parallel to each other in the computational geometries, and is very thermally stable. The band structure of such geometrically constrained pairs in periodic arrays also reveals states near the Fermi level.

A Peierls distortion causes large band splitting near the Fermi level on relaxation of the tilting constraints on the pair of rings (Fig. 4a). Fig. 4b compares the transmission spectra of phenolate and benzenediazonium ions in a periodic array (infinite), indicating a metallic to semiconductor transition after the Peierls distortion.

Fig. 5a shows the I-V characteristics of phenolate and benzenediazonium ions ($C_6H_5N_2$-C_6H_5O-$C_6H_5N_2$) between Au(111) electrodes when the inter-ring tilt is constrained to be parallel or is relaxed. The metallic states of the parallel structure demonstrate a dramatic improvement in the electrical performance when compared to that of

benzene rings. However, the tilted ring structure reduces the enhancement. Nonetheless, the low voltage currents are still quite large compared with those of benzene based wires. To understand this phenomenon, consider the transmission spectrum of electrons (at zero bias) shown in Fig. 5b. We find that there is a shift of Fermi level of ~0.8 eV in the Au junction case for the tilted rings, thereby the transmission peak is near the Fermi level of the system. To further study this, we carried out a study in the same system with longer molecular chains (n=5), this feature in the transmission spectrum is essentially unchanged, as seen in Fig. 5b. The Fermi level shift could be due to the Fermi level alignment change between the Au(111) surface and the molecular rings during the Peierls distortion. The validity of this explanation is unclear and the phenomenon needs further investigation.

In Fig. 6, the electrostatic potential distribution at 0.6 V for both tilted pair rings (Fig. 6a) and parallel π
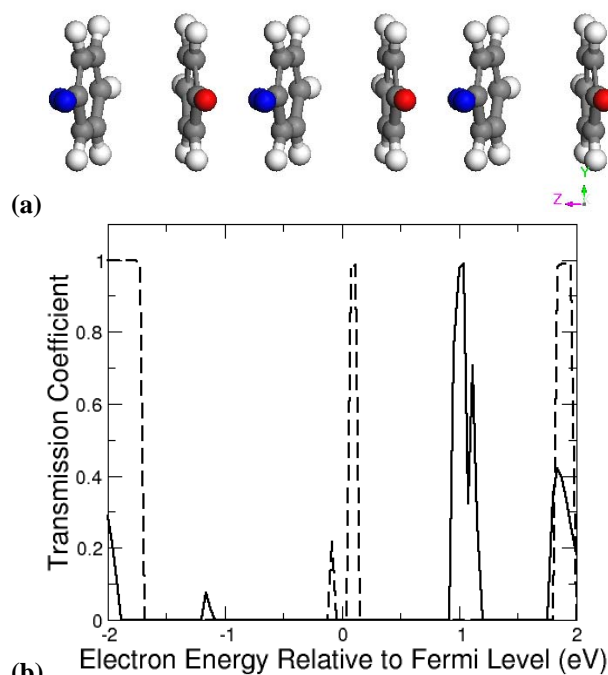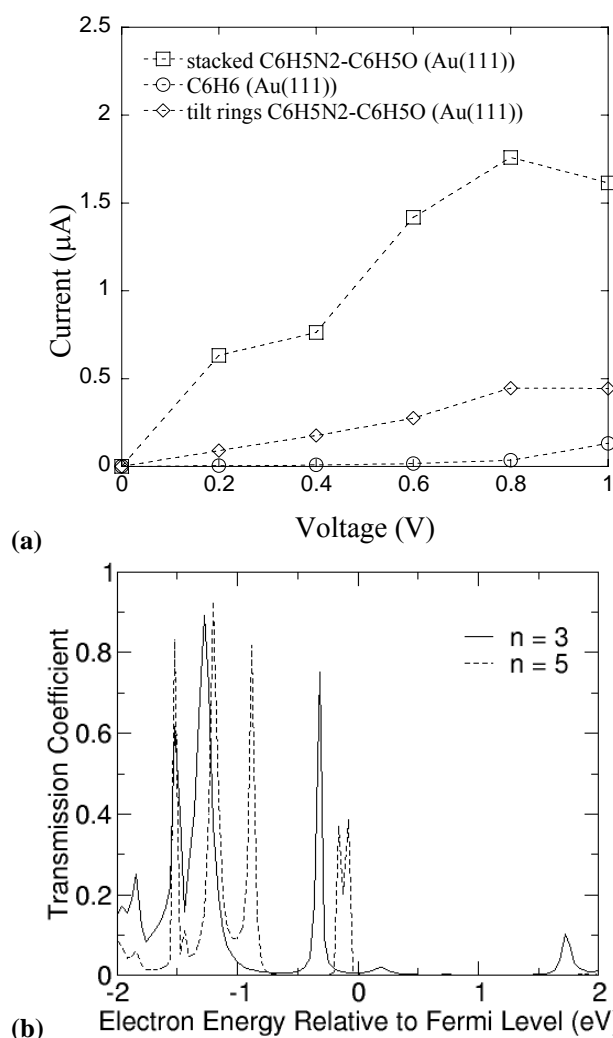
(a)

(a)

(b)

Figure 4: (a) The tilted ring structure of phenolate-benzenediazonium pairs. (b) The transmission spectrum of the tilted rings shown in (a) (solid) and parallel π stacked rings (dash) in periodic arrays at zero bias.

(b)

Figure 5: (a) I-V curves of benzene based wires, and phenolate – benzenediazonium based wires (see text), both tilted pair rings and parallel π stacked pair rings (all n=3) with Au(111) electrodes. (b) Transmission spectra for phenolate – benzenediazonium based wires with tilted rings (n=3, and n=5) with Au(111) electrodes at zero bias.

stacked pair rings (Fig. 6b) with Au(111) electrodes are shown. For the tilted rings with Au(111) electrodes, the electrostatic potential drop across the wire is realized in several approximately equal steps. This is similar to the electrostatic potential distribution pattern in the benzene based wires [12]. For the parallel π stacked pair rings with Au(111) electrodes, the electrostatic potential drop across the wire is very different. The voltage drop starts approximately in the middle of the molecular rings and shows strong localization around the molecules, reflecting an inhomogeneous pattern. We consider that this is mainly determined by the conducting nature of the molecular rings, and not much related to the electrode junctions. Other species in aromatic groups investigated include nitrobenzene and nitrobenzene/n-methylaniline pairs and arrays. On-going work includes studying new proposed species, solvent effects, and evaluating the role of polaronic conduction effects through electron-phonon interactions.

IV. CONCLUSIONS

In summary, we have performed first-principles based simulations to study the electron transport properties in self-assembled arene-based molecular wires in the context of aromatic rings attached to β-sheet scaffold. We find a substantial difference in I-V characteristics at high voltages but minimal difference for low voltages for the benzene based wires, between the self-consistent NEGF results and the non-self-consistent results. We model replacements for benzene by introducing selected functional groups, to improve the electrical and thermal stability performance of the π stacked molecular wires. We studied the Peierls distortion, I-V characteristics, transmission spectra, and the electrostatic potential distributions in the phenolate-benzenediazonium pair arrays with Au(111) electrodes. We find substantial increases in the currents at low voltages, relative to benzene molecules, in parallel π stacked rings. We find that the Peierls distortion tilts these rings, and this greatly reduces such enhancement in the currents.

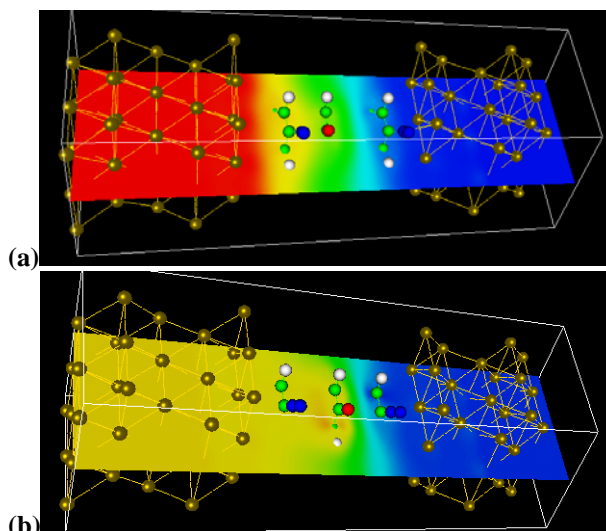## ACKNOWLEDGMENTS

(a)

(b)

Figure 6: The electrostatic potential distribution for pehnolate – benzenediazonium wires at 0.6 V: (a) tilted pair rings with Au(111) electrodes, (b) parallel π stacked pair rings with Au(111) junction.

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