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Abstract:

Ferrocene-based molecular components for nanoelectronics offer a number of distinct advantages relative to all carbon frameworks due to metal-centered molecular states that should be closer in energy to the Fermi levels of the metal electrodes in metal / molecule / metal heterojunctions. Given this, the overall goal of the project was to investigate the conduction physics of a variety of proposed ferrocene diode / transistor designs in order to address the fundamental question; can electron transport within nm-length scale structures be modulated in a controlled fashion? During the funded period, substantial progress towards achieving this goal was made by surmounting a number of scientific and technical obstacles. More specifically, a concise and general synthetic route to several mono- and diferrocene dithiols and monothiols was achieved that now allows for the directed and controlled assembly of a variety of metal / molecule /metal test structures for the single molecule conductance measurements and the fabrication of self-assembled monolayers (SAMs) on Au(111) that are amenable to quantitative electrochemical characterization of electron-transfer rates. Most importantly, by using an electromigrated test structure, reproducible I/V data for one of the ferrocene dithiol molecules have been collected which exhibit surprisingly high conductance. Exceptional agreement of this result with theory serves to substantiate the original hypothesis that metal-centered states within a molecular bridge can indeed serve to establish higher conductance relative to all-organic molecular bridges. Overall, the successful demonstration of the ability of ferrocene-molecular frameworks to serve as exceptional molecular conductors will play an important role in the continued evolution in design of molecular components for nanoelectronic devices, which in turn, will have a positive impact on the science and potential technologies associated with these systems.

Summary of Findings

Significance. Experimental and theoretical interest in the conduction physics of metal lead / molecule / metal lead (LML) heterojunctions remains unabated - and for good reason. After electron transfer theory, which describes the coupling of electronic and nuclear motions as the basis for electronic transfer rates, a thorough understanding of the dependence of transport through LML heterojunctions as a function of molecular structure is the next logical step by which to further build the foundations of modern chemistry as conductance directly measures the connection of wave functions between elements of a molecular framework and the response of these connections to an applied electron flux. Further, just as the successful experimental validation of electron transfer theory found a wide range of applications, a unified molecular conductance theory will be critical to a large number of emerging, and as-of-yet-unforeseen, technologies, such as those involving conduction through (ultra) thin organic films, nanosensors for chemical sensing and bioanalytics, and 'molecular electronics' in which single molecules are envisioned as serving as components within nanoscale electronic devices, to name just a few.

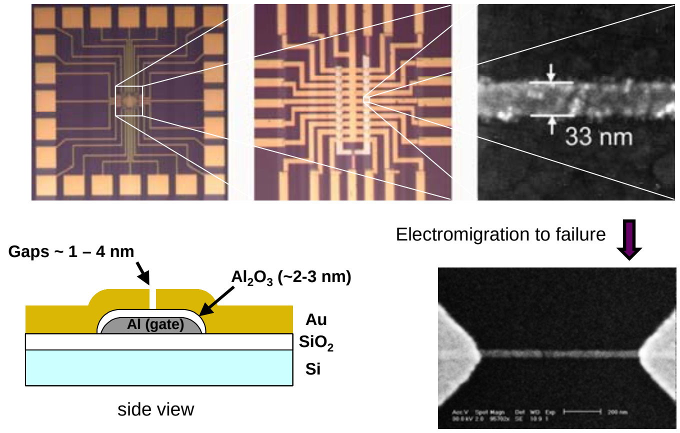
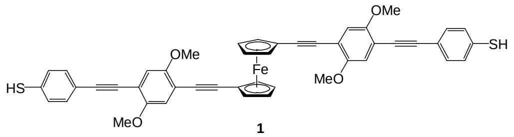


Figure 1. Experimental nanogap test structures for making single molecule conductance measurements.

Specific Aims. The primary objective of the proposed work is simple, but substantial in scope and impact. Namely, we seek to explore new paradigms for molecular conduction physics that can arise through the incorporation of metal atoms within the molecular bridge of LML heterojunctions. The aim is to design and study molecules which are (a) likely to be understood within simple models motivated by chemistry and mesoscopic physics, and (b) likely to have unique observable signatures upon oxidation/reduction, or application of electrical bias or magnetic field. While the long-term objective of the combined experimental / computational approach taken in this project is to ultimately contribute to the development of a unified theory for molecular conductance, the most immediate goals are: (1) to greatly expand the number and types of metal-containing molecular frameworks whose conduction properties have been extensively studied, (2) to carefully investigate, both experimentally and theoretically, all these molecular frameworks to understand their systematics with regard to conduction, and (3) to distill out from this new amount of data, some rules of thumb or simple models for how to think about conduction within metal-containing molecular frameworks. It is the coordinated tackling of all three of these goals that could have the greatest potential intellectual benefit - namely the laying of a basic understanding of molecular conduction that extends over a broad range of molecular framework types. Without these simple, yet predictive, chemistry-based models that can apply to large classes of molecules, little progress toward the application of molecular conduction is likely.

Results

Figure 1 shows images of test structures for making single molecule conductance measurements that were mass produced at the Cornell Nanoscale Facility. A key feature of these test structures is the inclusion of an aluminum gate electrode that provides for the ability to probe molecular conductance as a function of a perturbing gate voltage. Figure 2 presents separately recorded current / voltage (*I* / *V*) (red line) and conductance spectra (*G* / *V*) (blue line) of LML heterojunctions that are reproducibly prepared from the ferrocene adsorbate **1** following the published procedure. Importantly, contrary to other single-molecule conductance measurements that reveal Coulomb blockade to be in effect, examination of the conductance spectra for LML heterojunctions based on **1** reveals a finite conductance at zero source-drain bias and broad resonance peaks occurring at low bias voltage (< 100 mV). These symmetrically disposed conductance resonances, which are absent in single molecule conductance measurements of corresponding-in-length all-organic phenylethynyl systems, are believed to originate with a low-lying molecular state of the system that can be brought into resonance by applying either a forward or reverse bias. Remarkably, the peak conductances associated with these resonances can be upwards of 70% of the conductance quantum, G_0. It can further be noted that the Lorentzian lineshape of these conductance resonances are as predicted by the Landauer theory for conduction through a molecular level, and lineshape analysis (green line in Figure 2) was used to establish that this high on-resonance conductance is associated with strong, symmetric molecule-electrode coupling. Of equal importance to the experimental results are the theoretical calculations for this system shown in Figure 3. DFT is used for electronic structure calculations and this methodology is combined with Green function techniques (NEGF) to calculate the transmission at zero bias. To model the LML heterojunction, the atomic structure of the molecule and the molecule-lead separation are fully optimized and each lead presents a (001) surface that is $4\sqrt{2}$ by $4\sqrt{2}$ in size to the molecule which is adsorbed at the hollow site. The PBE



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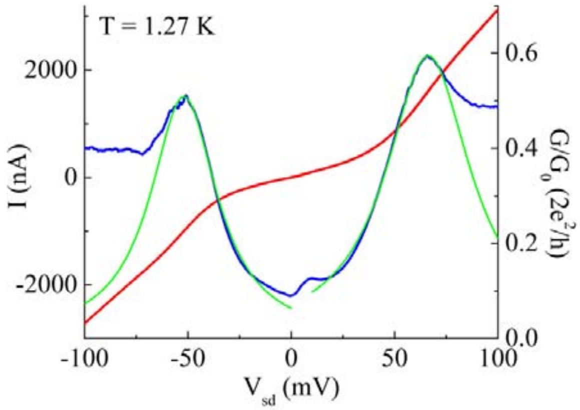

Figure 2. Single molecule conductance measurements for metal / molecule / metal heterojunctions derived from adsorbate **1**. Legend: (—) I / V, (—) G / V, (—) Lorentzian fit.

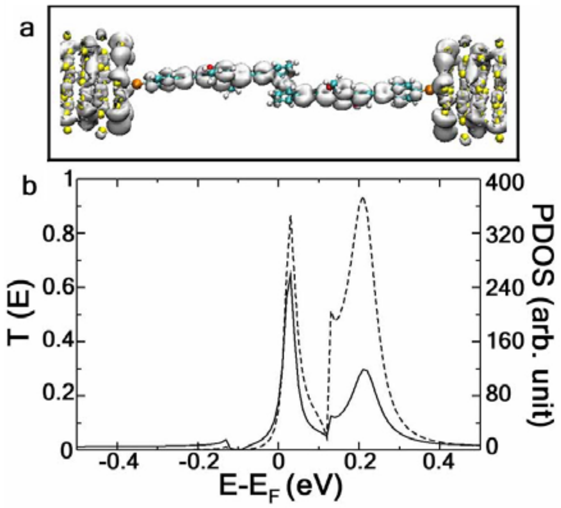

Figure 3. (a) Surface of constant local density of states (LDOS) at the energy of peak transmission. (b) Transmission between the Au leads (dashed) and the density of states projected onto the molecule (solid) at zero bias.

version of the generalized gradient approximation (GGA) is used for the electron exchange and correlation, and optimized Troullier-Martins pseudopotentials are used for the atomic cores. A high-level double-zeta plus polarization basis set (DZP) is additionally used in relaxing the molecules, while a single-zeta plus polarization basis set (SZP) is used for the transmission calculation. For the transport calculation, an infinite lead-molecule-lead system is divided into three parts: left lead, right lead, and device region. For a steady state situation in which the device region is under a bias V (zero or finite), its density matrix and Hamiltonian can be determined self-consistently by the DFT+NEGF method. The Kohn-Sham wave-functions are then used to construct a single-particle Green function from which the transmission coefficient at any energy, $T(E)$, is calculated. For LML heterojunctions based on **1**, Figure 3 shows the results of using this computational methodology; they clearly support the presence of a low-lying, high transmission molecular level. More specifically, $T(E)$ in Figure 3b shows a clear resonance that is 30 meV above the Fermi energy (which would appear at ±60 mV in I / V spectra, in excellent agreement with experiment), and which attains nearly perfect transmission on-resonance. Further, the local density of states at the energy of the peak (Figure 3a) shows a conjugated state traversing the entire molecular framework from lead to lead.

Future Plans Successful demonstration of this collaborative team's technical ability to reproducibly record molecular conduction for LML heterojunctions derived from the extended organometallic framework of **1**, as well as to provide a firm foundation upon which to rationalize the observed near perfect conduction through application of state-of-art computational methods, provides strong motivation and justification for investigating the molecular conduction of more elaborately designed organometallic frameworks. Currently, a proposal has been invited for the full competition of the Collaborative Research in Chemistry (CRC) program of the NSF which may ensure continued support for this project.

Publications

(1) Getty, S. A.; Engtrakul, L.; Wang, L.; Liu, R.; Ke, S.-H.; Baranger, H. U.; Yang, W.; Fuhrer, M. S.; Sita, L. R. "Near-Perfect Conduction Through a Ferrocene-Based Molecular Wire," *Phys. Rev. B (Rapid Commun.)*. **2005**, *71*, 241401/1-241401/4.

(2) Engtrakul, C.; Sita, L. R. "Ferrocene-Based Nanoelectronics: 2,5-Diethynylpyridine as a Reversible Switching Element," *NanoLetters* **2001**, *1*, 541-549.

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Near-perfect conduction through a ferrocene-based molecular wire

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Here we describe the design, single-molecule transport measurements, and theoretical modeling of a ferrocene-based organometallic molecular wire, whose bias-dependent conductance shows a clear Lorentzian form with magnitude exceeding 70% of the conductance quantum G_0. We attribute this unprecedented level of single-molecule conductance to a manifestation of the low-lying molecular resonance and extended orbital network long predicted for a conjugated organic system. A similar-in-length, all-organic conjugated phenyl-ethynyl oligomer molecular framework shows much lower conductance.

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Since its theoretical inception,[1] molecular electronics has been an area of significant interdisciplinary interest. The conduction occurring through single molecular states can be manipulated by electric field, light, conformational changes, etc., promising a range of useful devices. The ideal molecular electronic device[2] would allow ballistic conduction between metal reservoirs at the quantum of conductance $G_0 \approx 77\ \mu\mathrm{S}$, corresponding to interface conductivities of order $10^{10}\ \mathrm{S/cm^2}$. To date, delocalized orbital networks in conjugated organic molecules have been proposed as the ideal design for molecular wires. Unfortunately, such all-organic molecules show conductances (in individual molecules) (Refs. 3–6) and conductivities (in films) (Refs. 7 and 8) orders of magnitude lower than theoretically predicted.[9–13]

Our general strategy for the design of components for nanoscale electronic devices has been to incorporate the known favorable physical and electronic properties of ferrocene, $(\eta^5\text{-}C_5H_5)_2Fe$, into molecular frameworks.[14] Since recent results have shown that the rate of electron transfer through a conjugated backbone containing a ferrocene moiety can rival that through an all-organic conjugated system,[15] and given the proposed relationship between electron-transfer rates and conductance,[16] it is of interest to compare the electron transport properties of the two identical-length molecular wires, one containing a ferrocene center [Fc-oligophenylethynyl dithiol (Fc-OPE), Fig. 1(a)] and the other a ferrocene-absent phenylethynyl analog [OPE, Fig. 3(a)].

Synthesis of the molecular adsorbates was achieved in a straightforward manner, although it is important to note that methoxy (OMe) groups were incorporated on the phenyl rings to impart favorable solubility characteristics (rather than for any perceived electronic benefit).[15] A substrate with a lithographically defined array of (intact) Au wires is immersed in a methylene chloride solution of molecular adsorbates, with terminal thiol groups Figs. 1(b) and 1(d)] or with acetate thiol protecting groups [Figs. 1(e) and 1(f)], for approximately 12 h, whereupon chemisorption of the molecules to the Au occurs. Similar results have been obtained for both types of solutions. Upon removal from the solution and rinsing, the substrate is wire bonded and introduced into a sample-in-vapor ^{4}He cryostat. Once at base temperature ($T = 1.3$ K), a molecule is localized within a nanometer-sized gap formed via electromigration of a gold wire.[17] The resulting geometry is that of a field effect transistor, with source and drain electrodes bonded to the molecule by the Au–thiol bond. The third gate electrode in initial work was degenerately doped silicon capped with 500 nm of thermally grown SiO_2. More recently, we have employed an aluminum layer as a gate electrode and roughly 2 nm of native Al_2O_3 as the gate dielectric.[18] More than one device has been measured in each configuration with consistent results.

We first discuss electron transport characteristics at $T = 1.3$ K for five separate gold nanogap junctions formed in the presence of Fc-OPE [Figs. 1(b)–1(f)]. As discussed below, we believe each junction contains a single molecule or, in some cases [Figs. 1(c) and 1(e)], two molecules. Out of over 50 junctions fabricated, only these junctions showed significant conductance; the other junctions showed conductances consistent with tunneling gaps formed in the absence of molecules.[19] For each junction the conductance curves are highly stable and reproducible; this is illustrated in Fig. 1(b) by plotting five sequential sweeps of the bias voltage. Examination of the conductance spectra reveals several common features: (1) finite conductance at zero source-drain bias V, (2) broad resonance peaks at low bias voltage ($V < 100$ mV), and (3) a dip in the conductance near $V = 0$ (see insets, Fig. 1). The peak conductances can be a significant fraction of the conductance quantum G_0 [60% in Fig. 1(b) 70% in Fig. 1(d); conductance greater than G_0 in Fig. 1(e) is likely due to two molecules as discussed below]. The observation of these features only in junctions exposed to Fc-OPE and never in bare nanogaps or nanogaps exposed to OPE (see below) suggests that they are intrinsic to Fc-OPE.

Applied gate voltage, V_g, has a variable effect from junction to junction. V_g dependence is shown for the three junctions that exhibit the most pronounced effect [Figs. 1(c), 1(e), and 1(f)]. The energy of the lowest-lying molecular level relative to E_F of the electrodes (above or below E_F, as determined from the direction of peak motion as a function

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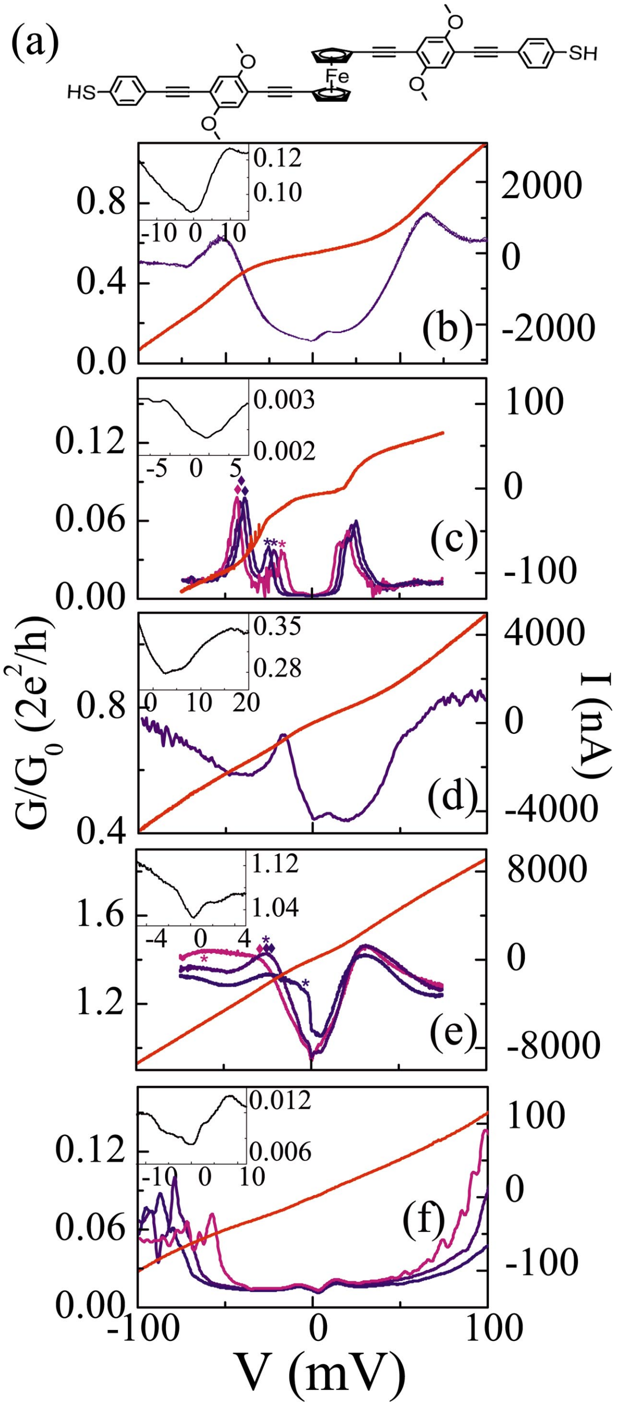

FIG. 1. (Color) (a) Fc-OPE, 3.5 nm long, with methoxy side groups.[14] (b–f) Current I (red) and conductance G (blue, in units of G_0) vs source-drain voltage V in Fc-OPE $T<1.5$ K. Insets: low-energy structure. Five sweeps ($V=-100$ to 100 mV) are shown in (b); the curves are nearly indistinguishable. (b–d) used a doped Si gate with thiol-terminated adsorbates. (e, f) used an Al gate with thioacetate-protected adsorbates. Gate voltage V_g-dependence is shown: (c) $-5\ \text{V} \leqslant V_g \leqslant 5$ V; (e) $-1\ \text{V} \leqslant V_g \leqslant 1$ V; (f) $1.1\ \text{V} \leqslant V_g \leqslant 1.7$ V, with navy most negative and magenta most positive, evenly spaced in V_g. (c, e) show two pairs of peaks that respond independently to V_g. Diamond and star shapes, colored to denote varying V_g, illustrate peak motion.

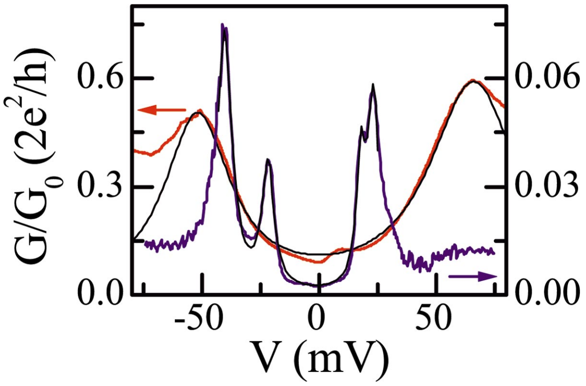

FIG. 2. (Color) G in units of G_0 vs V (mV) for two separately formed Fc-OPE molecular junctions. The red curve represents a highly conducting single molecule from Fig. 1(b); the blue curve a moderately conducting junction consisting of two molecules from Fig. 1(c). We interpret each pair of resonances in the blue curve to represent a single molecule. The thin black curves are Lorentzian fits of the data, using two peaks and four peaks for fitting the red curve and blue curve, respectively.

of V_g) also exhibits interjunction variations. This energy distribution is probably due to local electrostatic variations in the presence of an insulating substrate and is not surprising given the closeness of the molecular level to E_F, as substantiated by the theoretical calculations discussed below.

Conduction through the ferrocene molecule—or any extended molecular state—should be understood within the theory of resonant conduction through a localized state. The total conductance of a one-dimensional wire is given by the Landauer formula[2]

$$G = \frac{2e^2}{h}\sum_i T_i, \tag{1}$$

where the prefactor is the quantum of conductance, G_0, the upper theoretical limit for transmission through a spin-degenerate one-dimensional system, and T_i is the transmission probability for each conducting channel. In the resonant level case, the transmission coefficient is

$$T = \frac{\Gamma_1\Gamma_2}{\Gamma}\frac{\Gamma}{(E-E_m)^2+\Gamma^2}, \tag{2}$$

in terms of coupling parameters Γ_1, Γ_2, and $\Gamma=\Gamma_1+\Gamma_2$, which can be modified to include additional lifetime effects, and E_m, energy of the mth resonance. We neglect the specific components of Γ in our analysis and assume that interjunction differences in coupling are dominated by variations in molecule-electrode coupling. We also ignore thermal broadening, negligible compared to the experimental peak widths. Ideally, in a symmetric molecule, a single molecular level should result in a pair of Lorentzian peaks in $G(V)$ with half-width $2\Gamma/e$ centered at $\pm 2E_m/e$, since forward or reverse bias can bring the resonance into the bias window.

We have performed Lorentzian fits of the observed conductance resonances for two junctions (Fig. 2). We find that the conductance resonances as well as the zero-bias conductance level are well described by Lorentzian fits (with the

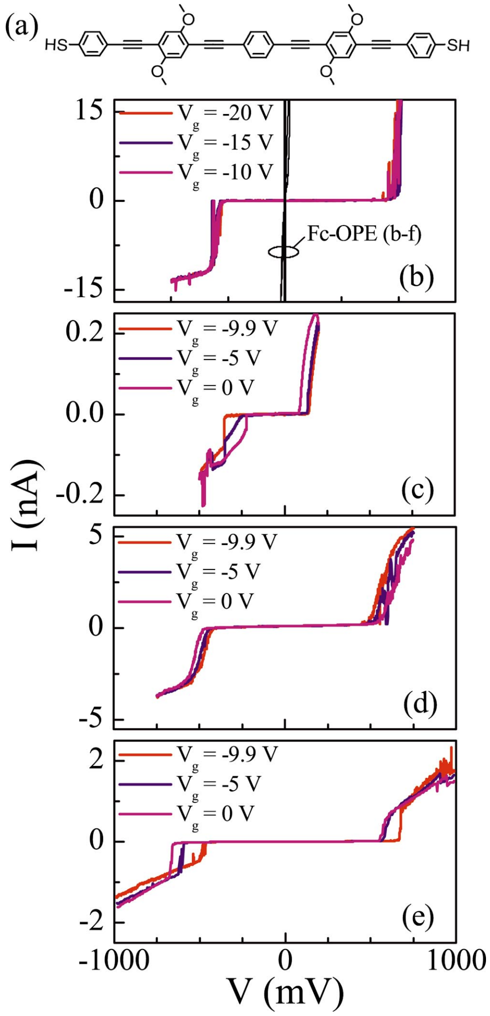

FIG. 3. (Color) (a) Poorly conducting ferrocene-absent phenylethynyl dithiol (OPE), featuring methoxy side groups for solubility purposes. (b–e) I (nA) vs V (mV) in the ferroceneless control species at $T < 1.5$ K. For comparison, the I-V curves for the five Fc-OPE junctions, Figures 1(b–f), are reproduced in (b) (black lines). The four OPE curves demonstrate the relative suppression of current levels and the development of a zero-conductance gap in the absence of the ferrocene moiety. As in the Fc-OPE, the effectiveness of the gate is seen to vary between junctions. All devices were measured in the Si/SiO$_2$ global gate geometry; variations in V_g are denoted in the figure legends.

exception of the anomalous dip around zero bias). At biases higher than the resonance, enhanced conduction is observed, possibly due to inelastic channels available for conduction. These fits demonstrate a correlation between high on-resonance conductance and strong molecule-electrode coupling. From the Lorentzian fits of all five devices, we extracted values of Γ that vary from 1.2 to 12 meV ($\Gamma \gg k_B T$ for all Fc-OPE molecules measured). We note that this Lorentzian resonance is different in nature from the Kondo resonance observed in single-molecule organometallic[18,20] and fullerene[21] transistors; the Kondo resonance is a collective-electron effect that appears exactly at E_F ($V=0$) and is inherently a low-temperature phenomenon. We also observe conductance structure near zero-bias in all five ferrocene-based devices that may be due to many-body effects; further studies of this low-bias region are underway.

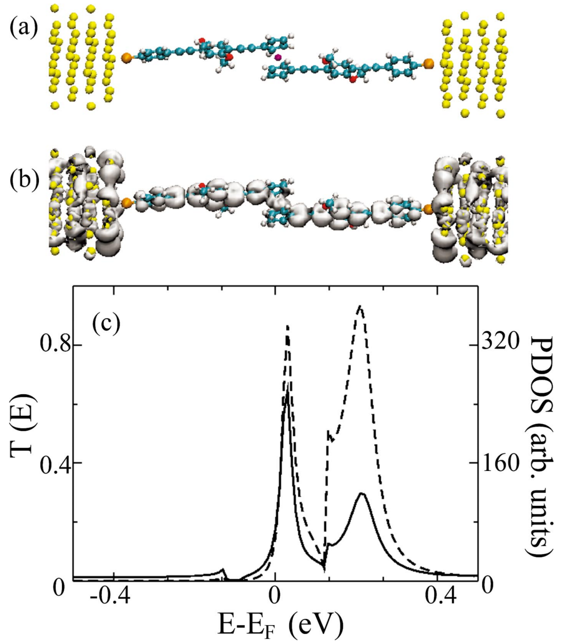

FIG. 4. (Color) (a) Relaxed configuration of Fc-OPE between two gold (001) leads. All the phenyl rings are coplanar. (b) The surface of constant local density of states (LDOS) at the energy of peak transmission. (c) Transmission between the gold leads (dashed) and the density of states projected onto the molecule (solid) at zero bias. Note the resonance 30 meV above the Fermi energy in both curves. The molecular level causing the large transmission is imaged through the LDOS in panel (b).

We now discuss evidence that the observed effects are due to *single* molecules. It is clear that no multiplicative normalization procedure would scale the two curves in Fig. 2 to coincide. Such an analysis has been proposed to “count” the number of molecules contacted in monolayers,[8,22] however significant differences in bonding and electrostatic environment in few-molecule junctions are likely to cause the observed differences between junctions found in our data and in the literature:[3–6] bonding differences are likely to produce changes in the magnitude and width of the resonances,[10–12] while electrostatic effects will shift the position of the resonances.[23] In this light, we argue that the observation of a single pair of Lorentzian resonances is the strongest evidence for transport through a single molecule. It is unlikely that a small ensemble of molecules with resonances of different width, height, and position could make up the single resonances observed in our data and more unlikely that each observed resonance would shift uniformly with application of gate voltage, since gate coupling should vary significantly from molecule to molecule.

In some cases two pairs of resonances are resolved in the devices [Figs. 1(c) and 1(e)]. An applied gate voltage has a separable effect on each pair of resonances; the effect is particularly striking in Fig. 1(e), where one molecular resonance can actually be seen to move through the other. The independent behavior of the two pairs of resonances indicates that they are not from two levels of the same molecule but rather each arises from a different molecule. The separable effect suggests that the two molecules are sufficiently spaced from each other within the nanogap to be differently coupled to the gate electrode. The presence of two molecules is likely responsible for conductance that exceeds G_0 in Fig. 1(e).

To investigate the influence of the ferrocene center on the molecular transport, we have also measured the electron transport through the all-organic molecule OPE [Fig. 3(a)]. Following identical sample preparation as for Fc-OPE, very different behavior was observed for this conjugated species. Current-voltage measurements are shown [Figs. 3(b)–3(e)] for four molecular junctions out of approximately 50 nanogaps measured. The on-resonance conductance, obtained by numerical differentiation, is in the nS range, at least two orders of magnitude lower than in the ferrocene-based species. A zero-conductance gap is observed over several hundred mV, similar to what has been seen by other groups in single conjugated organic molecule junctions.[4,5] The Fc-OPE data are replotted in Fig. 3(b) to emphasize the differences between these two molecules.

Theoretical calculations support the presence of a low-lying, high-transmission molecular level in the Fc-OPE molecule. We use density functional theory (DFT) for the electronic structure combined with Green function techniques to calculate the transmission at zero bias.[2,9–13,19,24] For the optimized planar Fc-OPE [Fig. 4(a)], $T(E)$ shows a clear resonance 30 meV above the Fermi energy [Fig. 4(c)], attaining nearly perfect transmission. The local density of states at the energy of the peak [Fig. 4(b)] shows a conjugated level traversing the entire molecule from lead to lead: this is the molecular level causing the high conductance seen experimentally. Turning to the OPE control molecule, we find that for the configuration in which all five rings are coplanar, the conductance is high, in sharp disagreement with the experiments. This is an example of the well-known discrepancy between DFT (Refs. 9–13) and experiment[3–8] for all-organic conjugated molecules. While our work does not solve this long-standing problem, we emphasize that our measurements of the Fc-OPE molecule constitute the first instance where the simple theoretical scenario of resonant conduction through a single molecular level has been realized.

The precise role of the ferrocene in this regard is, however, not clear. One possibility is that it enhances the coplanarity of the rings; certainly, the conductance of an OPE molecule in a noncoplanar configuration is very low because of the broken conjugation. Another possibility is that the scissor mode made possible by the ferrocene moiety (i.e., rotation of the two five-member rings with respect to each other) allows a high conductance state to be realized—our calculations show that a bent Fc-OPE has a conductance lower than the linear one but within the experimental variation. Experimentally, the low conductance arrangement for OPE may be favored by steric repulsion or hydrogen bond formation caused by the methoxy side groups.

We have demonstrated the chemical modification of a simple conjugated molecular system to create an excellent molecular wire out of an otherwise poor (all-organic) conductor through incorporation of a central ferrocene unit. We believe that the ferrocene moiety is an attractive basis for a device "toolbox," in which a spectrum of device properties could be achieved by varying the ferrocene number, symmetry, and functionality of the linker segments. The molecule presently under study is a simple precursor to more complex chemically engineered species.

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