

Electron Transport in Single Molecules: From Benzene to Graphene

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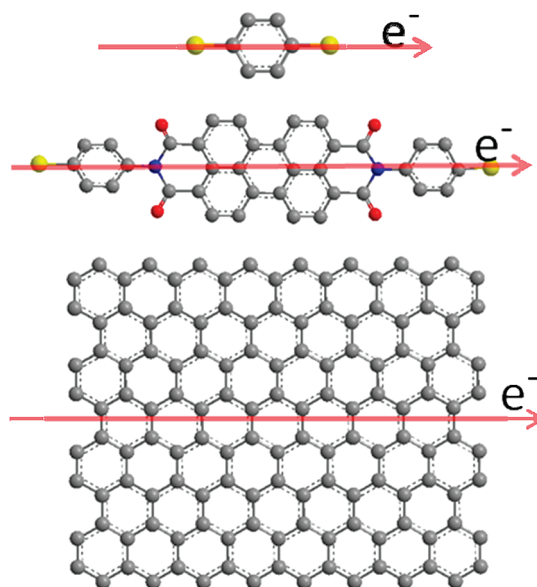
Electron movement within and between molecules—that is, electron transfer—is important in many chemical, electrochemical, and biological processes. Recent advances, particularly in scanning electrochemical microscopy (SECM), scanning-tunneling microscopy (STM), and atomic force microscopy (AFM), permit the study of electron movement within single molecules. In this Account, we describe electron transport at the single-molecule level. We begin by examining the distinction between electron transport (from semiconductor physics) and electron transfer (a more general term referring to electron movement between donor and acceptor). The relation between these phenomena allows us to apply our understanding of single-molecule electron transport between electrodes to a broad range of other electron transfer processes.

Electron transport is most efficient when the electron transmission probability via a molecule reaches 100%; the corresponding conductance is then $2e^2/h$ (e is the charge of the electron and h is the Planck constant). This ideal conduction has been observed in a single metal atom and a string of metal atoms connected between two electrodes. However, the conductance of a molecule connected to two electrodes is often orders of magnitude less than the ideal and strongly depends on both the intrinsic properties of the molecule and its local environment. Molecular length, means of coupling to the electrodes, the presence of conjugated double bonds, and the inclusion of possible redox centers (for example, ferrocene) within the molecular wire have a pronounced effect on the conductance. This complex behavior is responsible for diverse chemical and biological phenomena and is potentially useful for device applications.

Polycyclic aromatic hydrocarbons (PAHs) afford unique insight into electron transport in single molecules. The simplest one, benzene, has a conductance much less than $2e^2/h$ due to its large LUMO–HOMO gap. At the other end of the spectrum, graphene sheets and carbon nanotubes—consisting of infinite numbers of aromatic rings—have small or even zero energy gaps between the conduction and valence bands. Between these two limits are intermediate molecules with rich properties, such as perylene derivatives made of seven aromatic rings; the properties of these types of molecules have yet to be fully explored. Studying PAHs is important not only in answering fundamental questions about electron transport but also in the ongoing quest for molecular-scale electronic devices. This line of research also helps bridge the gap between electron transfer phenomena in small redox molecules and electron transport properties in nanostructures.

Introduction

An electron can transfer from one part of a molecule to another, between two molecules or between a molecule and an electrode. This is



known as electron transfer phenomenon, which has been extensively studied due to its critical role in many chemical, electrochemical, and biological processes.¹ Most of the studies to date

are based on measurements averaged over many molecules, but probing electron transfer at the level of single molecules has become possible. For example, individual electrochemical luminescent reactions have been observed optically,² and multiple electron transfer reactions of a single molecule trapped between two closely placed electrodes have been studied using a scanning electrochemical microscope.³ In this Account, we focus on an approach in which a molecule is bridged between two electrodes and the electrical current (I) through the molecule is directly measured by applying a voltage (V) between the electrodes (Figure 1a). This is exciting because it provides us with a fresh approach to study electron transfer in molecules, and it is also directly relevant to the ongoing quest for molecular scale electronic devices.⁴

The voltage-driven electron migration between two electrodes is referred to as electron transport in semiconductor and device physics.⁵ Here we discuss some of the basic questions in the electron transport of single molecules: How is the electron transport related to the electron transfer processes? What is the most efficient electron transport through a single molecule? What are the factors that limit us from achieving the most efficient electron transport in a single molecule? How can we control electron transport through the molecule? In the case of redox molecules that can be reversibly oxidized or reduced, a particularly interesting question is: Can we control the transport by changing the redox states? It should be noted that this Account is written for a general chemist audience, so the technical details are minimized. Readers who are interested in more details are encouraged to read several recent reviews.^{5–11}

Relationship between Electron Transport and Transfer Properties

The electron transport process described above involves a molecule bridged between two electrodes (Figure 1a), which is analogous to electron transfer via a molecular bridge between a donor and acceptor (Figure 1b). The two phenomena are closely related as shown by Niztan et al.^{12,13} An important quantity that describes the efficiency of electron transport is conductance, G , defined as $G = I/V$, which is proportional to the transmission probability of electrons from one electrode (L) to another (R) according to the Landauer formula,¹⁴

$$G = \frac{2e^2}{h} T \quad (1)$$

where e is the electron charge, h is the Planck constant, and T is the total transmission probability (sum over all possible transmission channels). T is related to the coupling strengths (Γ_1^L and Γ_N^R) of the molecule to the two electrodes as well as to the transmission probability through the molecule ($|G_{1N}|^2$), where G_{1N} is the Green function^{12,13} given by

$$T = \Gamma_1^L \Gamma_N^R |G_{1N}|^2 \quad (2)$$

On the other hand, electron transfer rate, k_{D-A} , between a donor and acceptor is

$$k_{D-A} = \frac{1}{h} |V_{D1} V_{NA}|^2 F |G_{1N}|^2 \quad (3)$$

where V_{D1} and V_{NA} describe the couplings of the molecule to the donor and acceptor, respectively, and F represents the coupling of the donor (acceptor) to the nuclear coordinates, including structural changes in the molecule and polarization of solvent molecules surrounding the molecule. Combining the above equations, we obtain

$$G = \frac{2e^2}{h} \frac{\Gamma_1^L \Gamma_N^R}{|V_{D1} V_{NA}|^2 F} h k_{D-A} \quad (4)$$

Equation 4 states that the conductance is proportional to the electron transfer rate. Calculating the precise value of conductance from ET rate using the above equation requires the coupling strengths of the molecule to the two electrodes and to the donor and acceptor, as well as the coupling of the donor (acceptor) to the nuclear coordinates.¹⁵

In the case where the molecular bridge is a redox molecule or has HOMO/LUMO close to the Fermi energy level of the metal electrodes, the bridge itself can also be an electron donor or acceptor. This is interesting because it points to the possibility of controlling the conductance of the molecule via controlling its redox states.

Electron Transport through a Single Metal Atom

Before discussing the conductance of a single molecule, let us consider a simpler system: a single metal atom. Bulk metals are generally good electrical conductors, but it is meaningless to discuss the conductance of a single atom unless we define the contact of the atom to two electrodes. If the atom is connected to the electrodes via a metallic bond (Figure 1c), then the question becomes well-defined, and the predicted conductance is $2e^2/h \approx 77.4 \mu S$ (per conduction channel).

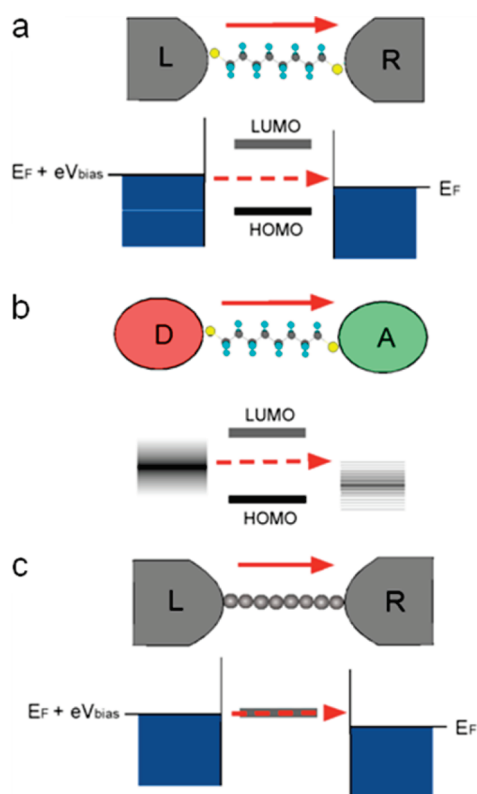


FIGURE 1. (a) Electron transport through a molecule connected to two electrodes, (b) electron transfer from a donor to an acceptor via a molecular bridge, and (c) electron transport through an atomic metal wire connected two electrodes.

The simple result is expected from the Landauer formula (eq 1), which predicts that the conductance is determined by the transmission probability, T . When $T = 100\%$, the conductance is $2e^2/h$, which is the most efficient electron transport via a single conduction channel. This result is surprisingly accurate for monovalent metals, such as Na, Au, Cu, and Ag, which have only one conduction channel,¹⁶ and it applies also to a linear chain of atoms (or atomic wire) as long as the wire is shorter than the mean free path, the average distance an electron can travel without collision with defects or impurities. For metals such as Cu, the mean free path is a few tens of nanometers at room temperature. The theoretical result is simple, but one may wonder why if the transmission probability is 100%, the conductance of a perfect conductor is not infinitely large. The answer is that conductance measurement always involves contacts between the wire and the electrodes, which gives rise to a finite conductance. In other words, $2e^2/h$ may be regarded as the contact conductance. In fact, the conductance of the atomic wire itself should be $G = (2e^2/h)(T/(1 - T))$, which indeed becomes infinite when $T = 100\%$.

The conductance of a single metal atom or atomic wire is also surprisingly easy to measure experimentally. Two methods have been developed so far: one is mechanical

method^{17–19} and the second one is electrochemical etching or deposition.^{20–22} Direct evidence of a single atom or atomic wire has been observed by electron microscopy.²³

Electron Transport through a Molecular Wire

The conductance of a perfect single metal atom is $\sim 2e^2/h$, as shown both theoretically and experimentally. What is the conductance of a single molecule? This is a much harder question. To determine the conductance of a molecule, one must first bring it into contact with at least two external electrodes (Figure 1a). The electrode–molecule contacts must be reproducible and provide efficient electronic coupling between the molecule and the electrodes. This has been a difficult experimental challenge.⁵ One approach is to functionalize the molecule with two linker groups that can chemically bind to the electrodes. The most popular choice of the linker groups is $-SH$ although other groups, such as amines,²⁴ pyridines,²⁵ $C-C$,²⁶ carboxylic acids,²⁷ isocyanide,²⁸ and Se ^{29,30} have also been used. These linker groups can bind to many noble metals, such as Au, Pt, and Pd, but one has little control over the exact binding site of a molecule on the electrodes. This fact, together with the sensitive dependence of the conductance on the bind site, makes it difficult to compare results between two experiments and between experiments and theories. To overcome this difficulty, a statistical approach has been developed to extract the conductance of a single molecule with the most probable molecule–electrode contact geometry.²⁵ STM,²⁵ AFM,^{31,32} and other mechanical break junction^{33,34} approaches can quickly create thousands of molecular junctions, which are particularly suitable for the statistical analysis.

The most studied molecular system is n -alkanes consisting of saturated $C-C$ bonds terminated with linkers that can bind to electrodes.^{24,25,35–39} The conductance (G) of even a short alkane ($n = 4$) is found to be several orders of magnitude smaller than $2e^2/h$, the conductance of a single atomic metal wire. Another sharp contrast between n -alkanes and the atomic wire is the length dependence of the conductance. For the atomic wire, the conductance is independent of the wire length as long as it is shorter than the mean free path, while the conductance of alkanes decreases exponentially with the molecular length (L), which is described by $G = A \exp(-\beta L)$, where A is a constant, β is a decay constant varying between 0.6 and 0.9 \AA^{-1} (Figure 2). The exponential decay, together with temperature independence,^{37,40} indicates electron tunneling as the conduction mechanism in these molecules (also for peptide chains).⁴¹ The tunneling probabilities are small because

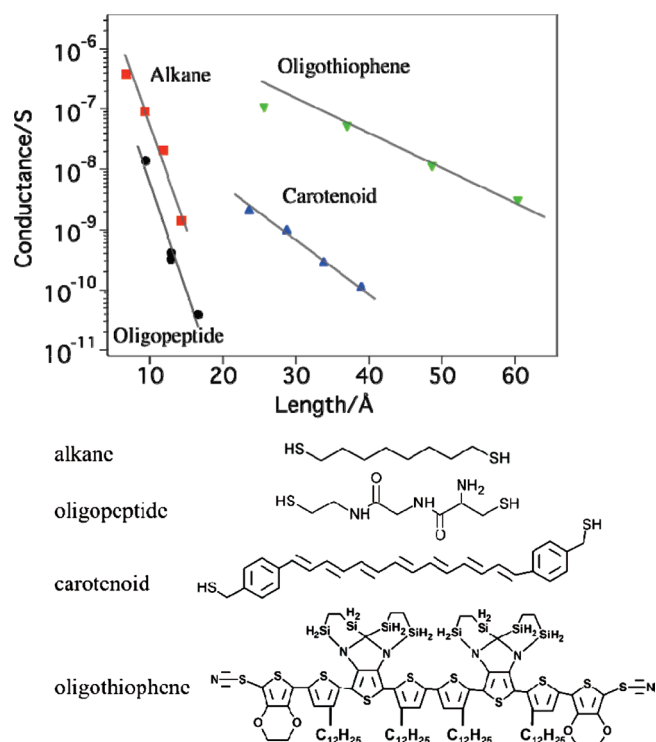


FIGURE 2. Length dependence of conductance for saturated chains and conjugated molecules. The conductance in each system decreases exponentially with the length but with a different slope (decay constant).

of the large HOMO–LUMO gaps of these molecules. In contrast, conjugated molecules with alternating double and single bonds have much smaller HOMO–LUMO gaps and are expected to transport electrons more efficiently.^{42,43} One such example is oligothiophenes with measured β of 0.1 \AA^{-1} , the smallest decay value in molecular wires reported so far;⁴⁴ nevertheless, the conductance is still much smaller than the theoretical limit, $2e^2/h$.

Controlling Electron Transport through a Redox Molecule

The conductance of molecules is small ($\ll 2e^2/h$) because the HOMO and LUMO are typically not aligned with the Fermi energy level of the electrodes and electrons must tunnel through the molecule with a small probability given by^{45,46}

$$T \propto e^{-\beta L} \quad (5)$$

Since β decreases with the energy gap between the LUMO (or HOMO) and the Fermi energy level, one expects that the probability increase if one brings the LUMO closer to the Fermi levels of the electrodes. For a simple double potential barrier model, the transmission probability is

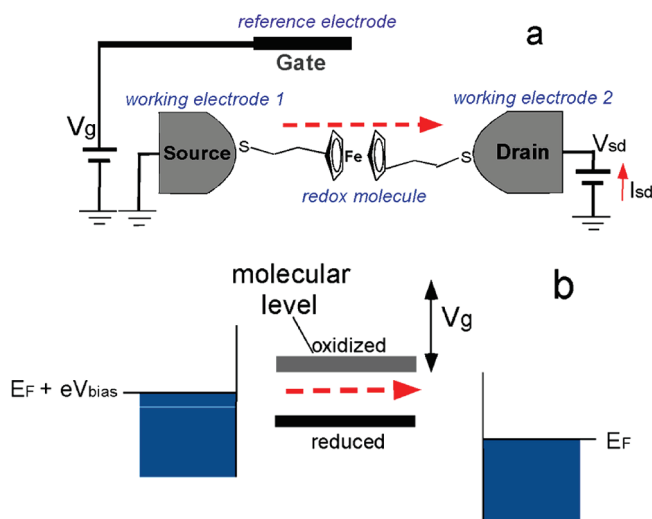


FIGURE 3. (a) Controlling electron transport in a ferrocene derivative by switching its redox state with an electrochemical gate. (b) The electrochemical gate voltage (V_g) shifts the molecular energy levels up and down relative to the Fermi energy levels of the electrodes, which controls the redox state and the electron transport via the molecule.

$$T = \Gamma_1^L \Gamma_N^R \frac{4}{(\Delta E)^2 + (\Gamma_1^L + \Gamma_N^R)^2} \quad (6)$$

where ΔE is the separation between the LUMO and Fermi energy.⁴⁷ When the LUMO is aligned to the Fermi level, $\Delta E = 0$ and T reaches 100% if the molecule couples symmetrically to the two electrodes ($\Gamma_1^L = \Gamma_N^R$). This is the so-called resonant tunneling, and the corresponding conductance is $2e^2/h$, just like an atomic wire. A recent study shows that the conductance of a ferrocene-based organometallic molecular wire exceeds 70% of the conductance quantum, $2e^2/h$.⁴⁸ This level of single-molecule conductance appears to be rare due to the misalignment of the Fermi level to the molecular energy levels in most cases. Di Ventra et al.⁴⁹ proposed a resonant tunneling field effect transistor in which the conductance of a molecule is tunable by moving the LUMO to the Fermi levels with a gate electrode. Their calculation shows that the conductance can reach $\sim 2e^2/h$ at resonance in the case of benzenedithiol.

To apply the gate field effectively, the gate electrode must be placed close to the molecule within a distance on the order of the molecular size. This is difficult to achieve experimentally using the conventional fabrication techniques. An alternative way to achieve this goal is to use an electrochemical gate, in which a reference electrode placed in the electrolyte serves as the gate electrode (Figure 3a). This electrochemical gate approach was used to demonstrate transistor-like behavior of conducting polymer materials in electrolytes⁵⁰ and also

to study redox molecules in electrochemical STM^{51–53} and carbon nanotube field transistors.^{54,55}

In terms of the energy diagram, the electrochemical gate shifts the energy levels of the molecule up and down relative to the Fermi energy levels of the electrodes (Figure 3b). Schmickler et al.^{56,57} considered resonant tunneling through a redox molecule adsorbed on an electrode in electrochemical STM. Experimental evidence of resonance tunneling was reported in porphyrins adsorbed on a substrate.⁵¹ However, since there was no well-defined contact between the STM tip and the molecule, the conductance of the system was not determined. More recently the redox molecules bound to two electrodes have been studied by several groups.^{43,58–60} Although the conductance can be controlled by the electrochemical gate, the maximum conductance value achieved so far is still several orders of magnitude smaller than $2e^2/h$, the value predicted by the simple resonant tunneling model.

One example of such studies is ferrocene compounds terminated with two cysteamine groups (Figure 3).⁶¹ Ferrocene, one of the most well-studied redox molecules, is a good model system for studying electron transport phenomena because it exhibits fast and reversible one-electron transfer. Cyclic voltammetry shows well-defined redox peaks near 0.6 V (vs Ag/AgCl) for the molecules adsorbed on gold electrodes (Figure 4a). When the electrochemical gate potential is held near 0 V, the conductance is ~ 23 nS. The conductance increases by nearly 1 order of magnitude when the gate voltage is larger than 0.6 V. This conductance increase is pronounced, but it is far less than $2e^2/h$. The simple resonant tunneling theory also fails to explain the following observations: (1) lack of a peak in the conductance vs gate voltage plots, (2) large fluctuations in the conductance, and (3) hysteresis between forward and backward sweeping of the gate voltage (Figure 4b).

Several other small redox molecules are found to behave similarly,^{43,59} which all indicate that the electrochemical gate-controlled conductance in these redox molecules is not simple resonant tunneling. We believe that the gate effect is due to the oxidation and reduction of the molecules. In the case of ferrocene, when its HOMO is raised to the Fermi energy level of the electrodes, an electron transfers from a ferrocene molecule to one of the two electrodes and the molecule becomes oxidized. The electronic states of the molecule in its oxidized state are different from those in the reduced states, which is responsible for the change in the conductance. In other words, the electrochemical gate-induced conductance increase is due to the switching of the molecule from the low-conductance reduced state to the high-conductance oxidized

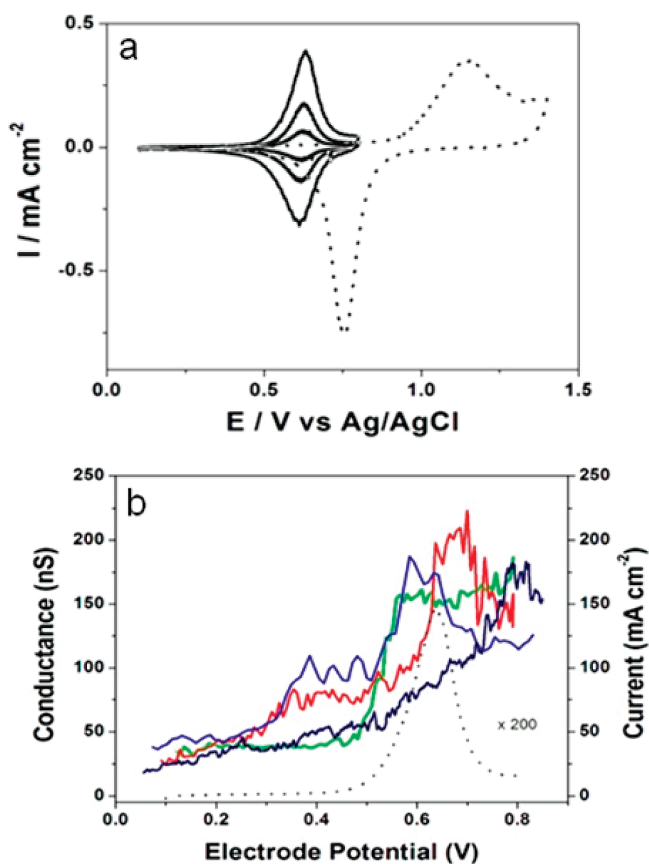


FIGURE 4. (a) Cyclic voltammograms of the ferrocene derivative adsorbed on Au electrodes at different sweep rates showing a pair of redox peaks near 0.6 V. The dashed line is a cyclic voltammogram of the bare Au electrode. (b) Conductance of the ferrocene derivative vs gate voltage.

state. This model is supported by the fact that the oxidation of the molecule is accompanied by a decrease in the HOMO–LUMO gap (change in the color).

This model also explains naturally the observed large fluctuations in the conductance near the redox potential. A well-studied case of stochastic conductance fluctuations is single conducting polymer strands, such as polyaniline and polypyrrole.^{62,63} It is well-known that bulk polyaniline and polypyrrole are insulating materials in the reduced states but become highly conductive in the oxidized states. The conductance of bulk polyaniline (or polypyrrole) increases smoothly by many orders of magnitude upon oxidation with electrochemical gate control. Like the bulk polymer materials, the conductance of the single polymer strands also increases with the electrochemical gate voltage, but large fluctuations are observed in the conductance of a single or a few polymer strands. The conductance fluctuations can be controlled via an electrochemical gate (Figures 5a,b). When the gate electrode is held at a potential far more negative than the redox potential, the molecule is in the reduced state and insulated (Fig-

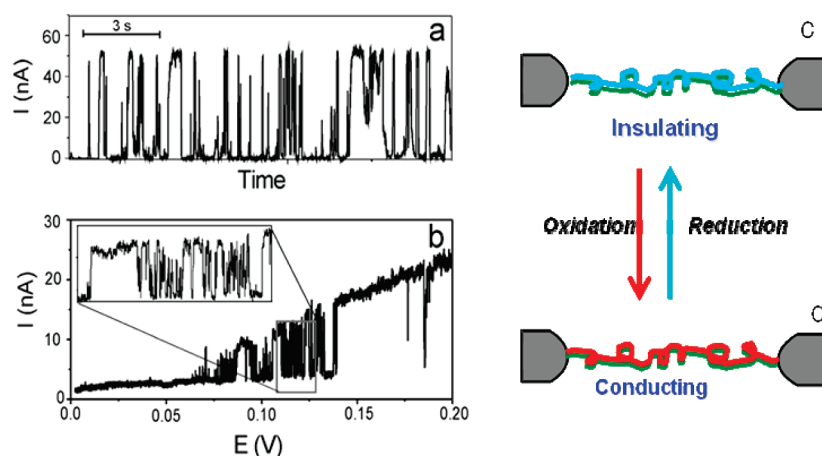


FIGURE 5. (a) On–off random switching in the conductance of polyaniline (potential = 0.2 V). (b) The dependence of the conductance switching on the potential of the electrodes. The inset is an enlargement of the conductance transient showing more clearly the on–off switching. (c, d) Illustration of oxidation and reduction of polyaniline.

ure 5c). As the gate voltage increases, the probability of oxidation increases. When the gate voltage is far greater than the redox potential, the molecule stays in the conductive oxidized state (Figure 5d). At the redox potential, the probabilities of oxidation and reduction are equal, so the conductance fluctuates between two levels as the molecule switches back and forth between the reduced and oxidized states. This stochastic switching appears to be a signature of single-molecule phenomena and has been observed in fluorescence spectroscopy and electrochemical luminescence of single molecules.⁶⁴

It is interesting to note that conductance fluctuations have also been observed in nanostructured devices including nanoscale MOSFET (metal oxide semiconductor field effect transistor)⁶⁵ and nanoconstrictions.⁶⁶ In a nano-MOSFET, electrons flow between source and drain electrodes via a conduction channel controlled by a gate voltage. When an electron traps in a defect site in the conduction channel, it introduces a new scattering center for electrons, which changes the conductance. When the electron escapes from the defect site, the conductance returns to the original level. The trapping and escaping of a single electron in the defect state of the nanodevices resemble closely the reduction and oxidation in redox molecules.

From Benzene to Graphene

Resonant tunneling does not seem to occur when one moves the LUMO or HOMO of a redox molecule close to the Fermi energy levels of the electrodes. Instead, an electron prefers to occupy the LUMO (or a hole occupies the HOMO) and reduce (oxidize) the molecule. The reduction (oxidation) of the molecule is accompanied by a structural reorganization (solvent polarization or structural distortion), which moves the molec-

ular energy level away from the Fermi level. If this is universally correct, then one will never be able to achieve the maximum conductance, $2e^2/h$, as in the atomic metal wires. However, nearly ideal ballistic transport in carbon nanotubes (number of carbon atoms $\rightarrow \infty$) has been observed, suggesting that one can in principle move electrons through a molecule as through an atomic metal wire.

Carbon nanotubes belong to the family of materials made of a conjugated network of aromatic rings. The smallest molecule in this family is benzene (Figure 6a). To connect a benzene molecule to two electrodes, linkers, such as thiols and amines, must be attached to two opposite ends of the molecule. One example is benzenedithiol,^{67,68} a model molecule for the proposed gate-induced resonant tunneling.^{49,69} Li et al.⁷⁰ have applied an electrochemical gate to benzenedithiol but observed only a small gate effect within the electrochemical gate voltage window (Figure 6b).

One reason for the weak gate effect in benzenedithiol is that its HOMO and LUMO are separated with a large gap (~ 5 eV) and they are far away from the Fermi levels of the electrodes. In order to move the HOMO or LUMO close to the Fermi levels, one must apply a large gate voltage. Unfortunately, the range over which one can apply the electrochemical gate voltage is limited. The upper limit is determined by the oxidation of gold, and the lower limit is set by the reductive desorption of thiol monolayer from Au surface. For benzenedithiol, we cannot align its HOMO or LUMO with the Fermi level of electrodes. An additional reason for the weak gate effect in benzenedithiol is the screening of the gate electric field by the proximity of the two electrodes. This issue arises also in conventional field effect transistors when decreasing the gate channel length. In order to achieve effective gate control, the gate oxide thickness must be smaller

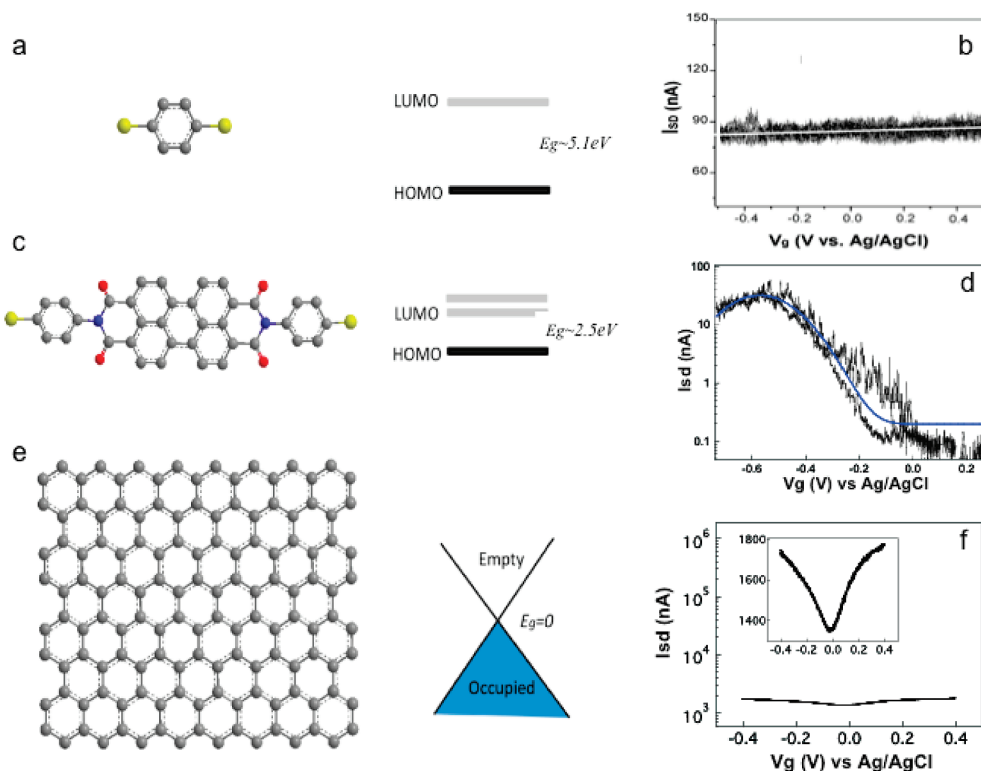


FIGURE 6. Molecular structures, energy diagrams, and electrochemical gate effects of benzenedithiol, PTCDI, and a graphene sheet: (a) Benzenedithiol (containing a single benzene ring) has a large LUMO–HOMO gap (5.1 eV) and is “insulating” with a weak gate effect (b). (c) The LUMO–HOMO gap of PTCDI (containing seven rings) is ~ 2.5 eV, and the molecule is “semiconducting” with a large gate effect (d). (e) Graphene (containing a large number of rings) has a zero energy gap between the conduction and valence bands and shows semimetallic behavior with a weak gate effect (f).

than the gate length. In the case of electrochemical gating, the gate thickness is determined by the double layer and the diffuse layer. The former thickness is about the size of solvated ions in the electrolyte, while the latter is the Debye screening length. At high electrolyte concentrations, the Debye length is small and the gate thickness is determined primarily by the double layer thickness, which is comparable to the size of benzenedithiol (~ 0.7 nm). This may cause substantial screening of the gate field, so the actual shift of the HOMO or LUMO is smaller than the shift of the gate voltage.

As the number of aromatic rings increases, the HOMO–LUMO gap of an aromatic hydrocarbon decreases. A good example is perylene tetracarboxylic diimide (PTCDI) derivatives, terminated with different linker groups (Figure 6c). The core structure of the molecules is essentially a piece of graphene consisting of seven aromatic rings. The energy gap between the LUMO and HOMO is only 2.5 eV, much smaller than that of benzenedithiol. Such a small energy gap implies a semiconductor-like behavior and also redox activity.⁷¹ The molecule can indeed be easily reduced with a redox peak near -0.6 V (vs Ag/AgCl), indicating that the LUMO is close to

the Fermi levels of the electrodes. If the LUMO is moved downward to the Fermi levels, one may expect resonant tunneling.

Figure 6d shows an example of source–drain current vs electrochemical gate voltage for a PTCDI derivative. When the gate voltage is >0 V, the current is rather small with the corresponding conductance at $10^{-5} \times 2e^2/h$. When the gate voltage is decreased toward the redox potential, the current increases rapidly and reaches a maximum value near the redox potential. The corresponding conductance at the maximum is $\sim 10^{-2} \times 2e^2/h$, nearly 3 orders of magnitude greater than that at positive gate voltages. The large gate effect and the conductance peak are consistent with the resonant tunneling model, but the maximum conductance is still 100 times smaller than $2e^2/h$. Furthermore, a temperature-dependence experiment shows that the electron transport in these molecules is a thermally activated process involving nuclear degrees of freedom.⁷²

It has long been recognized that the electronic states of a redox molecule couple to nuclear degrees of freedom, including the polarization of the surrounding solvent molecules and

vibration modes in the molecule. The energy involved in the structural reorganization is denoted as λ . Upon reduction of the molecule, the "LUMO" is occupied by an electron and lowered by 2λ associated with the structural reorganization. From the temperature dependence of the conductance, thermal activation energy of PTCDI molecules as a function of gate voltage has been extracted. When the activation energy was fitted with the Marcus theory, the reorganization energy of PTCDI was found to be ~ 0.47 eV.⁷²

Due to the coupling between the electronic and the nuclear degrees of freedom, simple resonant tunneling does not take place even when the LUMO of PTCDI is moved to the Fermi energy level of the electrodes. If we continue to increase the number of aromatic rings, this coupling strength is expected to weaken because electrons can spread over a larger volume, which decreases both the reorganization energy and HOMO–LUMO gap. An extreme case is a graphene sheet (Figure 6e), a two-dimensional atomic layer containing an infinite number of aromatic rings.^{73–75} Graphene has zero gap, and the gate effect is relatively small (Figure 6f).⁷⁶ This small gate effect is due to a rather large conductivity at zero gate voltage, which is generally attributed to charge impurity-induced scattering near the Dirac point.⁷⁷ One way to increase the gate efficiency is to open up an energy gap between the conduction and valence bands, for example, by cutting a graphene sheet into nanoscale pieces, that is, nanoribbon, in which quantum confinement along the short axis becomes pronounced.^{78,79} Large gate effect has indeed been observed in graphene nanoribbons, but edge disorders and other impurities prevent one from achieving perfect transmission.^{80,81} In contrast, a short single-walled carbon nanotube (SWNT), made of a graphene sheet rolled up into a tube, exhibits nearly perfect transmission with the conductance reaching $4e^2/h$.^{82–84} In this case, the edge effect in graphene sheets is removed and other defects are minimized by reducing the length of the nanotubes. Apparently, one can achieve nearly perfect electron transmission in molecules by eliminating defects/impurities and the coupling between the electronic and nuclear degrees of freedom.

Conclusions

A single molecule is probably the smallest unit of materials that can possess sophisticated functions for device applications. It can be synthesized in large quantities with atomic precision and with functional groups that can recognize other molecules for sensor applications and interface with external electrodes for devices. An important step toward device applications is to study electron transport in mole-

cules and correlate the molecular conductance with their electronic states.

A small molecule, such as benzene, is often found to be "insulating" because of the large LUMO–HOMO gap. A larger molecule (e.g., PTCDI) containing multiple benzene rings has a smaller LUMO–HOMO gap and behaves like a "semiconductor" with a large gate effect. However, due to the strong coupling between the electronic states and the nuclear degrees of freedom, electron transmission via the molecule is still far from perfect. Further increasing the number of benzene rings eventually leads to carbon nanotubes and graphene sheets that have small or even zero energy gaps. The coupling between the electronic and nuclear degrees of freedom in these large aromatic materials is weak, and the transmission becomes nearly perfect when defects and impurities are minimized.

Controlling the size of these polycyclic aromatic materials has a profound effect on the electron transport properties, which has been achieved via top-down and bottom-up approaches. The top-down approach relies on mechanical breakdown or lithographic etching of large graphene sheets, by which it becomes increasingly difficult to create a structure below a few tens of nanometers. The bottom-up approach is based on chemical synthesis, which can create a large quantity of molecules with atomic precision but currently faces difficulties at scales above a few nanometers. Lying in the middle are many molecular structures with rich electronic properties, which are waiting to be explored.

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BIOGRAPHICAL INFORMATION

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N. J. Tao joined the ASU faculty as a professor of electrical engineering and an affiliated professor of chemistry and biochemis-

try in August 2001. Before that, he worked as an assistant and associate professor at Florida International University. His research interests include molecular electronics, nanostructured materials and devices, chemical and biological sensors, interfaces between biological molecules and solid materials, and electrochemical nanofabrication.

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