

Molecular wires and devices: Advances and issues

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Substantial advances have been made in (a) our experimental and theoretical understanding of simple tunnel junctions based on molecules, (b) the role of contacts in tunneling and (c) experimental studies of redox-state gated transport. In addition, a new thermally-activated transport process has been discovered in a non-redox active system. Substantial challenges remain. The engineering of molecular contacts to technologically important electronic materials will stretch the ingenuity of synthetic chemists. The theory community must rise to the challenge of describing redox-mediated transport using first-principles, parameter free approaches. These advances will enable a new generation of devices that span the silicon (electronic) and carbon (bio-organic) worlds.

Introduction

The world of molecular electronics is, in some important ways, an unhappy one. Published experimental data have been all over the map. As just one example, DNA is reported to be an insulator,¹ semiconductor,² conductor³ and even superconductor⁴ (though the issue is now probably resolved⁵). This is a field where reasonable agreement between theory and experiment should have been achieved long ago, but with experimental disagreements like this, it is hardly surprising that this been a long time in coming.⁶ Hyperbole about imminent molecular computing has been compounded by the effects of outright fraud,⁷ leaving the field with little credibility in the eyes of many scientists. This meeting marked a milestone, in that broad quantitative agreement was reached by several laboratories about the magnitude of tunneling in simple systems.^{8,9} Redox gated transport, first reported by Tao nearly a decade ago,¹⁰ was the subject of reports by many of the discussants^{11–16} and many aspects of the process are in qualitative agreement with the proposals of Kuznetsov and Ulstrup.⁷ Interesting issues about contacts and environment remain to be clarified. Haiss and coworkers in the Liverpool group⁸ reported a remarkable temperature dependence to ‘tunneling’ in alkanedithiols and subsequent discussion suggested that this is a new process existing alongside the simple tunneling that is already quite well described by theory.¹⁸ These developments surely mark a turning point in this field. But difficult problems remain if molecular electronics is ever to make a real impact on technology. The key challenges are for the synthetic chemists in developing reliable contacts to materials that are more suitable than gold, and in finding ways to covalently attach devices at both sides of a junction. Theory of redox gated transport will present a major challenge, but it should become possible given the power of modern computers. We turn now to a more detailed review of these topics.

Simple tunneling processes in molecular junctions

Robust comparison with theoretical simulations, the only real measure of our degree of understanding, requires single molecule data. Reproducible single-molecule data requires both well-defined covalent contacts to molecules and statistical analysis of substantial data sets.¹⁹ Tunnel transport in alkanedithiols has now been studied with methods that incorporate these features by at least three groups.^{19–21} Data taken in this way is in broad agreement with first-principles simulation

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Table 1 Examples of some types of response in redox-mediated charge transport. The letters refer to Fig. 2

| Group | Molecule | Response | Ref. |
|------------|---------------------|----------------|------|
| Tao | Perylene derivative | c | 11 |
| Lindsay | Oligo-aniline | a | 16 |
| Rampi | Tethered Ru | a | 13 |
| Ulstrup | Os, Co complexes | a | 12 |
| Chi | Cu–azurin | a ^a | 14 |
| Haiss | Viologen | b | 32 |
| Wandlowski | Viologen | a and b | 15 |

^a Means intermediate response between a and b.

for a number of molecules as shown in Table 1 of a contribution elsewhere in this volume.⁹ (An exception is benzenedithiol, which presents both experimental and theoretical challenges as described by Avik Ghosh and co-workers in Condensed Matter Preprint cond-mat/0505375.) To take one example, values of the conductance reported for a single octanedithiol attached to gold electrodes are approximately 20 nS,^{9,21} 3 nS⁹ and 1 nS.^{19,20} This range of 20 : 1 may seem like a large disagreement, but measured on the scale of the disagreements prior to the introduction of these techniques,⁶ it is not. Furthermore, this set of features has been observed in several laboratories, suggesting that they are not spurious, but rather correspond to discrete types of arrangement in the tunnel junction.

Haiss and coworkers have shown that the 1 nS feature is strongly temperature dependent (an observation confirmed in as yet unpublished work from other labs). The 20 nS and 3 nS features are not temperature dependent (also unpublished data). We had suggested that differences in contact geometry could account for these different sets of conductances, although simulations of the difference between top-site and hollow-site attachments did not produce much difference.⁹ Recent (unpublished) simulations indicate that ‘pyramidal’ connection geometries (Fig. 1) might result in substantial reduction of the calculated 20 nS conductance, and so could account for the 3 nS feature. Thus there appear to be at least two distinct temperature independent processes that are described well by tunneling theory.

A new temperature-dependent transport process in alkanethiols

The 1 nS temperature dependent feature reported for octanedithiol by Haiss *et al.* in this discussion⁸ has several things in common with the system used in our original work on this molecule.¹⁹

- The low bias conductance of octanedithiol attached to gold electrodes is 1 nS in both cases.
- The tunnel decay constant, β , is *ca.* 0.45 Å⁻¹ in both cases (reports by Haiss *et al.*⁸ and Cui *et al.*²²). This contrasts with a value of *ca.* 0.8 Å⁻¹ for the 20 nS²¹ and 3 nS (unpublished) temperature-independent features.
- The current–voltage characteristic is linear over a ± 1 V range⁸ in complete disagreement with simple tunneling theory, but as observed for the 1 nS process when a small gold particle was used as an attachment.²³

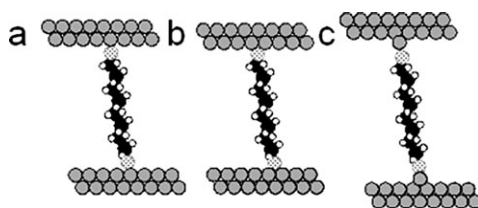


Fig. 1 Showing (a) on-top, (b) hollow site and (c) pyramidal connections of an octanedithiol molecule to gold electrodes. The precise connection geometry influences the tunnel transport significantly.

It is therefore tempting to suppose that that same process underlies the 1 nS feature in both cases. It is interesting to note that in the case of a gold nanoparticle contact^{19,23} no current is expected in the low-bias blocked region²³ but one flows anyway. The process may, or may not require the attachment of a gold cluster—this is not done deliberately in the work of Haiss *et al.*, but gold is undoubtedly picked up by thiolated molecules.²⁴ The temperature dependence suggests that a trap is involved, a factor that could also explain the anomalous value of β .²⁵ Further theoretical developments and experiments are eagerly awaited.

Resonant tunneling in vacuum

Simple tunneling theories suggest that when the bias applied to a junction aligns the Fermi level of the metal with a molecular orbital of the molecule, resonant tunneling should be manifested by abrupt steps in the current–voltage characteristic.²⁶ These have not, in general, been observed, presumably because environmentally relaxed and broadened electrochemical processes occur at a lower energy first (when the environment is not ultrahigh vacuum). Weber²⁷ reported data in this discussion that show these features clearly (and see also the reports by Bjørnholm's group²⁸). The energies at which the steps are observed are difficult to account for, because polarization, contact dipoles, image charges and potential distributions present formidable theoretical challenges.²⁸

Redox-state gated tunneling

Given the preceding remarks about the difficulty of locating molecular states in a vacuum experiment, one might think that conducting measurements in an electrolyte is nothing short of madness. But the great power of electrochemistry lies in the capability of *controlling the molecular potential* at the electrode with respect to the solution electrochemical potential precisely and reproducibly (though tethered molecular films present some challenges²⁹). Thus a molecular electronic process may be quantitatively associated with an oxidation state of a molecule if the measurement is made under potential control. This was first demonstrated by the pioneering work of Tao, who showed that the STM contrast of a protoporphyrin molecule containing an Fe(II) was a maximum near the formal potential for the Fe(II) \rightleftharpoons Fe(III) redox process.¹⁰ Work in this area has increased recently^{16,30–33} and this discussion marked a flurry of new reports.^{11–15} These are summarized in Table 1 and the types of response observed are illustrated in Fig. 2. We will discuss these responses in terms of electronic transitions, but at this early stage, it is important to note that chemical and structural changes could come into play. Thus, a molecule might undergo permanent structural or chemical changes that alter its electronic transmission, giving the appearance of a potential-dependent electronic phenomenon. One important test is to establish the reversibility of the process.^{16,33,34}

Most of the responses show a characteristic maximum in the conductance when the surface potential is somewhat above the formal potential for the redox process, E_0 (Fig. 2a). This is in line with the predictions made by Kuznetsov and Ulstrup¹⁷ for the case where the extra current is mediated by partial occupation of the redox state during transport. As the level fluctuates thermally between the Fermi energy on the left electrode ($E_F + V/2$) and the Fermi energy on the right

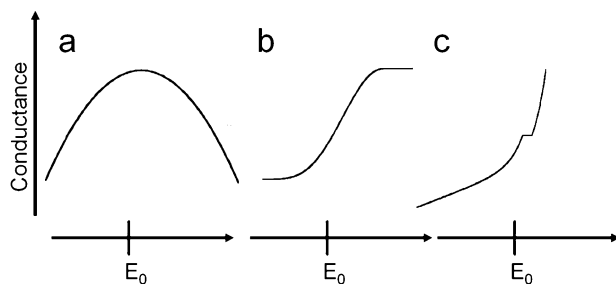


Fig. 2 Showing three types of dependence of the molecular conductance on surface potential. (a) Parabolic with a maximum a little above E_0 , (b) sigmoidal with the half-maximum conductance occurring near E_0 and (c) a rapid rise in current with step features reminiscent of resonant tunneling.

electrode ($E_F - V/2$) it serves as a transient resting place for a partially-localized electron that completes its transition by a series of hops, from the left electrode to the molecule, and from the molecule to the right electrode. As the molecule is driven towards its stable (oxidized or reduced) end point above E_0 , the molecular state relaxes below the two Fermi levels, cutting off the current channel and causing the fall-off in conductance as the potential is raised. V is the bias applied across the junction, and it is usually small. Note that the width of the response is controlled by thermal fluctuations, so that it should be some small multiple of 25 meV (as it generally is). As an aside, redox processes are conventionally discussed in terms of the (potential-dependent) fraction of the total population of molecules that has undergone an electron transfer process, but if the Kuznetsov–Ulstrup fluctuation-model is correct, then the individual molecules are highly dynamic, so that the change in population with potential occurs through fluctuations of *individual* molecules that move between oxidation states rapidly until the overpotential is sufficiently large to trap the population in its final redox state, well below the lower Fermi level.

Another type of response is sigmoidal, the conductance rising near E_0 , and then saturating above it (Fig. 2b). This type of response might occur in a system with densely spaced unoccupied states so that the redox gating sweeps a ‘conduction band’ into the gap. This might be the case for long oligomers that form highly conductive oxidized states.³⁵ Wandlowski has shown a given molecule (a viologen derivative) can be switched from the parabolic response (when it is weakly coupled to one electrode) to the sigmoidal response (when it is strongly coupled to one electrode). The response reported for a perylene derivative¹¹ (Fig. 2c) is unusual, and reminiscent of a resonant tunneling process.

Contacts, environment and voltage-induced changes

Contacts

It is remarkable that such common behavior is found in such disparate experiments as those described above, but it is a testament to the power of electrochemistry. The potential at which a conduction maximum occurs is independent of the means used to contact the molecule because the potential is controlled by the double-layer, which is, in turn, established with respect to a non-polarizable reference electrode. This will not be the case for current–voltage characteristics, where the potential change at the molecule owing to the applied bias is critically-dependent on the microscopic details of the connections to the electrodes and the electrode geometry (this is, of course, precisely the problem that potential control circumvents in the low-bias experiments described above).

Fig. 3a shows i – V data for a double-mercury drop junction containing tethered Ru complexes.¹³ Coupling to the electrodes is weak, with the molecules located in the middle of the junction by rather long tethers, with no direct covalent linkage across the junction. The current follows the

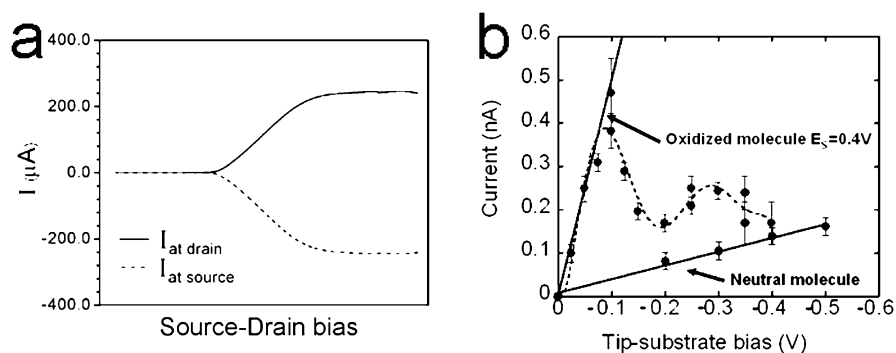


Fig. 3 Showing (a) current–voltage characteristic for a double-mercury drop junction containing redox active molecules¹³ and (b) single molecule data for an aniline oligomer covalently tethered to gold electrodes.¹⁶ Data are shown both for the molecule immersed in H_2SO_4 electrolyte with the substrate poised at the potential for maximum conductance (labeled ‘oxidized molecule’) and for the molecule immersed in toluene (labeled ‘neutral molecule’).

classical redox-mediated behavior. It rises exponentially with overpotential, saturating when limited by the maximum turn-over rate of the redox centers. This behavior should be contrasted with that of an oligoaniline molecule covalently tethered between gold electrodes and poised at a potential near its peak conductance¹⁶ (Fig. 3b). As the bias is increased in a direction that opposes the surface double layer field (that maintains the molecule near the formal potential) the molecule is driven back towards its less conductive neutral form, resulting striking negative differential resistance. This behavior is accounted for semi-quantitatively using the measured dependence of conductance on surface potential.¹⁶

Environment

Fig. 3b also illustrates the critical role of environment in charge transport. Measurements made in toluene, lacking the electrolyte and protons that stabilize the oxidized state, show only a linear current–voltage behavior. The applied bias cannot drive changes in oxidation state.

The environment itself can modify the transport dramatically through specific electrochemical reactions. For example, negative differential resistance in ferrocenylundecyl monolayers was recently shown to be a consequence of an irreversible reaction with ambient oxygen.³⁴

Voltage-induced changes

McCreery's Raman-scattering studies of molecules in optically-thin junctions³⁶ show that significant structural changes occur in molecular monolayers sandwiched in a junction when high (*ca.* 3 V) biases are applied. Changes may occur even at small applied bias. For example, we have reported current–voltage data for oligoaniline molecules, both as taken point-by-point using the method of repeated break-junctions, and as obtained by sweeping the bias with a single molecule trapped in the gap. The characteristics are similar, but an additional rising background current is visible in the data taken by sweeping the bias applied to a fixed gap. As pointed out by Haiss during these discussions, potential induced distortions in the gap geometry might be expected to alter the transport over and above any effects owing to molecules in the gap, and this could account for the somewhat different characteristics we obtain using the two methods.¹⁶

Challenges

Theory

The observation of redox gated charge transfer makes molecular electronics much more interesting: We now have a robust way to build non-linear devices. But understanding these processes at a fundamental level presents many theoretical challenges. A parametric theory of these phenomena is complex¹⁷ as might be expected, and a full-blown first principles simulation might appear to be beyond the range of current techniques. However, much was learned about ion-gated polaron motion in DNA from a 2 ns molecular dynamics simulation combined with electronic structure calculations.³⁷ It would seem feasible therefore to capture the states of molecule, water and ions that generate the transition states for charge transfer, provided that the molecules are small enough so that nanosecond scale simulations are adequate.

Chemical synthesis

Only a small part of the discussion touched on the issue of contacts, but they are the key to many developments (*cf.* Fig. 3). Even the simple problem of contact to just one electrode needs much more work. How does one make stable attachments of molecules to materials such as silicon that form (easily hydrolyzed) oxides? The same is true for even more complex (and important) electronic materials like the optically-transparent ITO and FTO. Can one engineer contacts to anchor the molecule in a desired orientation with one, and only one type of desired contact bonding?

These are difficult problems, but even more challenging is the problem of putting molecules into *fixed* gaps of sort that might be used to make an integrated circuit. van der Zant³⁸ alluded to the problems of doing this in a laboratory research setting (much more forgiving than device manufacturing). Our experience with these junctions has not been encouraging, and we see little

correlation between the state of the molecules put into fixed gaps (made by electromigration) and the measured characteristics.³⁹ One might think that distinctive signatures like the Kondo effect would be clear indicators of the presence of a molecule in the gap^{40,41} yet Houck *et al.*⁴² report observation of a Kondo-type response in up to 30% of bare gold junctions (*i.e.*, containing no molecules). The problem is that not only must the gap be just the right distance to be spanned by a molecule, but it must also accommodate the accompanying relaxation of the metal surface when covalent bonding occurs.

One remarkable recent development is the catalytic growth of alkenes directly onto a ruthenium surface in a process that should be capable of self-termination in a covalent bond at a second electrode.⁴³

Other issues in synthesis include materials to replace liquid electrolytes to enable electrochemical gating in manufacturable devices, and materials for passivation of devices to avoid undesired reactions with, *e.g.*, oxygen and water vapor.

Future directions

Molecular electronics is often touted as a potentially revolutionary technology for the next generation of compact electronic devices. While, of course, it is already part of computer hardware (LCDs, OLEDs) the high density applications are fraught with pitfalls. Power is a major problem already, and conventional semiconductor platforms develop apace with feature sizes based on lithography that would have been regarded as impossible a few years ago. Yet there is an obvious and potentially revolutionary application in the interfacing of the carbon and silicon worlds. The completion of the Human Genome Project will drive the development of personalized medicine, with a need for complex *molecular* diagnostic devices that are widely available and cheap (the so-called 'doc-in-a-box'). These will require clever engineering of the electronic materials to molecule interface. Perhaps even more critically, the energy needs of the future might be met by photovoltaics and hydrogen generators based on cleverly engineered interfaces between electronic materials and molecules. These would be noble outcomes of the present research.

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