A critical perspective on molecular electronic junctions: there is plenty of room in the middle

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The promise of molecular electronic devices stems from the possibilities offered by the rich electronic structure of organic molecules. The use of molecules as functional components in microelectronic devices has long been envisioned to augment or even replace silicon. However, the understanding of what controls charge transport in these devices involves complexities stemming from numerous variables that are often interactive and exert a controlling influence on transport, confounding the role of the molecular component. This perspective discusses various aspects of molecular electronics, from the initial ''vision quests'' of single molecule, functional electronic elements, to the molecular tunnel junctions that have been studied and characterized in-depth. Aspects of energy level alignment are discussed in the context of charge transport mechanisms, as are important electronic interactions when molecules are bonded to conducting ''contacts''. In addition, integration of molecular components with microelectronic processing is considered, as are the prospects for functional, real-world devices.

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1. Introduction

The term ''molecular electronics'' (ME) generally refers to a range of structures and phenomena, all of which involve organic and/or inorganic molecules as components in an electronic circuit. The field emerged rather explosively in the late 1990's, stimulated by developments in scanning probe

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microscopy and nanofabrication techniques. An early driver was the familiar "Moore's law" based on the exponential increase in microelectronic device density which has continued for more than three decades, and the realization that its continuation would soon result in devices with molecular dimensions of a few nanometers. The prospect of electronic circuits composed of molecular components, possibly "self-assembled" into complex microelectronic systems caused intense excitement. Not only could such "molecular circuits" conceivably increase device density by a factor of $\sim 10^6$ compared to today's state of the art, but molecules might also add a wide range of functions and structures not possible with conventional semiconductors. The prospect of single molecule memory cells, self-assembled molecular circuits, and very high device density was indeed exciting, resulting in some examples of technological hyperbole in the popular press, such as: "Our goal is to make chips so cheaply and easily that any 12-year-old with a chemistry set could do it." (San Francisco Chronicle); "Processors 100 billion times faster than the most powerful ones available today" (ABC news), and "trillions of transistors, processors so fast their speed is measured in terahertz, infinite capacity, zero cost. It's the dawn of a new technological revolution – and the death of silicon" (http://www.wired.com/wired/archive/8.07/moletronics.html).

A large body of research was stimulated by this initial excitement, directed toward making and understanding devices containing single molecules or collections of molecules connected to electronic circuits. Obviously molecules have not replaced silicon in the past decade, but we have learned valuable techniques and concepts related to charge transport in molecules, "contacts" between molecules and conductors and semiconductors, and the theory which underlies molecular charge transport.[1] The discussion which follows is focused on the "molecular junction (MJ)", which is the basic building block of molecular electronic circuits, shown schematically in Fig. 1 for several experimental manifestations.

The important distinction between "molecular electronics" and "organic electronics" we will use herein is one of scale: at least one dimension of the devices shown in Fig. 1 is in the range of 1–10 nm, compared to the 100–1000+ nm organic films typical of organic field effect transistors, organic light emitting diodes, and other "organic" electronic devices. Obviously "molecular" electronics is a subset of "organic" electronics but the nanoscale dimension imparts fundamentally different electronic behaviour, as described in later sections. Although the rather wild promises cited above will likely never be realized, there remain several important electronic properties of molecules which have the potential to significantly enhance today's already sophisticated microelectronic technology. First, molecules are inherently electronic systems, with a wide range of orbitals and energies to exploit in possible electronic circuits. Second, there are millions of molecular structures available, and new molecules may be "made to order" once the factors controlling electronic behaviour are known. Third, non-silicon manufacturing is potentially much cheaper, since ultrapure crystalline silicon is not necessarily required, and printed and/or disposable formats are possible. Fourth, molecules are capable of chemical and/or biochemical recognition, raising the prospect of sensors located directly on electronic circuits for biomedical or environmental monitoring. Since molecular electronics represents a new "platform" for devising microelectronic circuits, there are likely many other novel features of ME which may emerge in the future.

In this Perspective, we provide a selective review of the current state of molecular electronic junctions, with particular attention to the electronic properties that distinguish a molecular junction from conventional semiconductor-based microelectronic devices. Although many excellent theoretical approaches have been developed for predicting electronic behaviour of molecular junctions,[6–11] we focus here primarily on experimental investigations. An important conclusion is the realization that a molecular junction is a system that must be considered in total, including the properties of the contacts and how the molecules are connected to them. Then we will consider some novel physics and electronic behaviours available with molecular junctions, and how they might be exploited in practical devices. The significant practical problems of integration of molecular junctions with commercially viable microelectronics will also be considered, since they must be solved before practical ME devices become widely available. Closely coupled to the issue of commercial viability is consideration of the economic driving force for developing molecular electronics, particularly: what can be done with ME that is not already possible with silicon? Finally, some emerging areas and techniques of ME will be considered, particularly those related to unusual transport mechanisms over distances larger than molecular dimensions.

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2. Molecular junction paradigms

The possibility that molecules could be used as microelectronic circuit components was stated in the 1974 often-cited Aviram and Ratner article on "Molecular Rectifiers".[12] This theoretical proposal involving unidirectional electron transport between donor and acceptor levels in a single molecule was an early stimulus for the field of ME, but direct experimental evidence
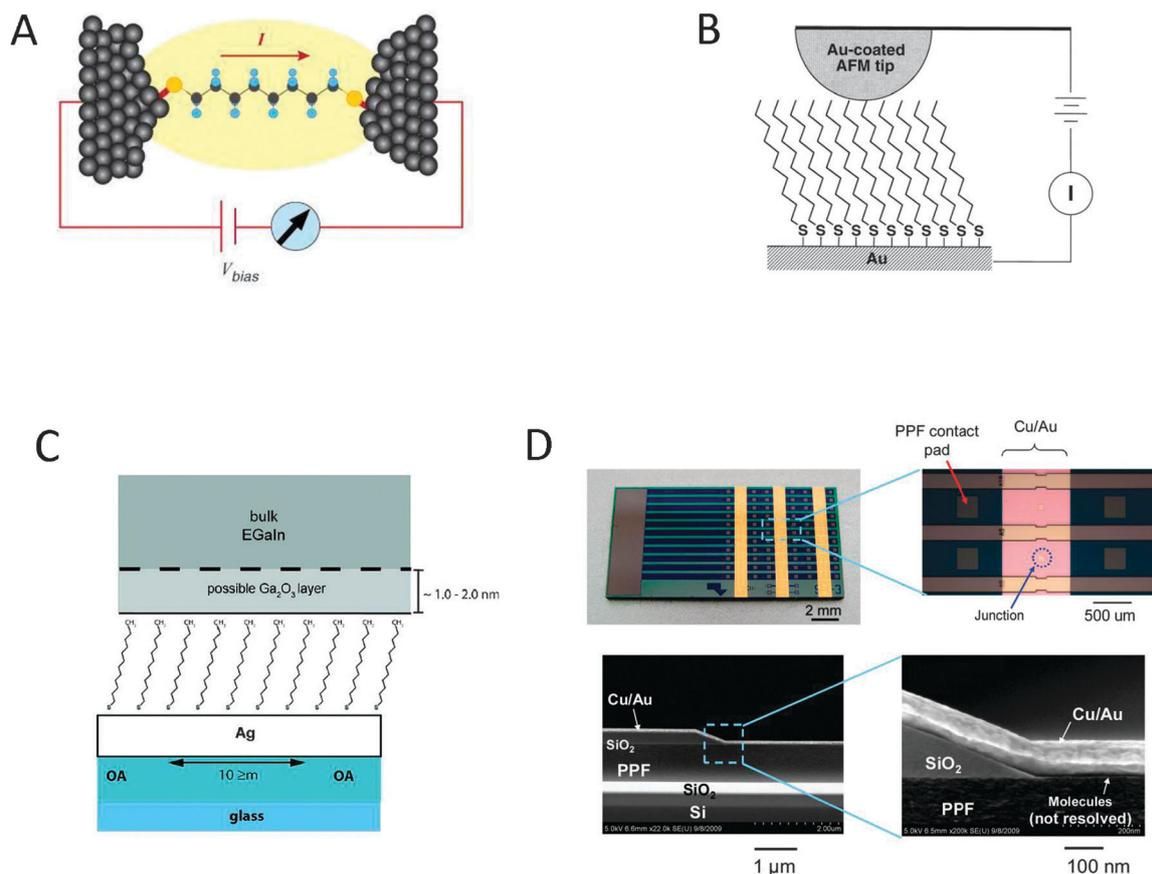
Fig. 1 (A) Schematic of a single molecule break junction. The molecule forms between a molecule-size gap formed after a metallic tip is withdrawn from the surface of a conductor. Reproduced with permission from ref. 2. (B) Schematic of a CP-AFM junction formed by bringing a conducting AFM probe into contact with a conductor modified with a molecular layer. Reproduced with permission from ref. 3. (C) A junction made by dispensing a liquid metal onto the molecular layer. In this case, a skin of oxide is present. Reproduced with permission from ref. 4. (D) Example of a cross-bar junction made by wafer-scale photolithography. Reproduced with permission from ref. 5.

did not emerge until the late 1990's. Since that time, the concept of a molecular junction developed along two parallel but distinct paths, which remain active today. The "single molecule" paradigm shown in Fig. 1A was pursued primarily with scanning probe techniques in air, ultrahigh vacuum, or solution, and represents the lower limit of molecular device size, with all three dimensions of the active region being <10 nm. Bonding between the molecule and a conducting "contact" may range from relatively weak physisorption or electrostatic interactions to covalent bonds such as Au–S and Si–C. The "ensemble" approach (Fig. 1B–D) involves collections of molecules usually oriented in parallel between two conducting "contacts". The number of molecules may vary from a few hundred in conducting probe Atomic Force Microscopy to several thousand in crossed wire geometries and 10^5 to 10^{10} in "large area" molecular junctions with active areas of <10–10^5 μm^2. The merits and disadvantages of "single" vs. "ensemble" approaches have been reviewed previously[1,13] but are summarized briefly here. Single molecule devices indeed represent one limit of miniaturization, are much simpler to treat theoretically and are amenable to well established scanning probe microscopy (SPM) techniques. SPM is capable of visualizing device structure as well as molecular orbitals, and inelastic tunneling may be used as a vibrational

probe of molecular conduction. However, single molecule devices of a particular molecule usually vary significantly in bonding geometry at the contacts, and such variations may strongly affect observed charge transport. Furthermore, thermal fluctuations of molecular conformation result in stochastic variation of conductance, resulting in an often erratic current–voltage response. A popular method to average such variations in contact structure and conformation is the repetitive "break junction" method[14,15] in which an STM tip repeatedly makes contact with the substrate, then is withdrawn to a point where a single molecule bridges between tip and substrate, as shown in Fig. 2A and described in more detail below. Collection of thousands of such contacts permits construction of a histogram of conductance such as the example shown in Fig. 2B. In the long term, a major question about single molecule paradigms is integration into practical microelectronic devices.[16] Nearly all of today's microelectronic products involve massively parallel fabrication and operation of billions of active devices, so the problem of how to "wire up" a large number of single molecule devices must ultimately be addressed.

Several of the "ensemble" paradigms are amenable to massively parallel fabrication, but also complicate the theoretical problem by greatly increasing the number of variables,
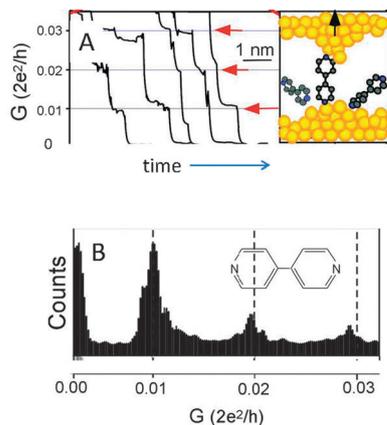
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Fig. 2 (A) Schematic of repetitive break junction technique for measuring single molecule conductance. (B) Histogram of conductance of single bipyridine molecules. Reprinted with permission from ref. 14.

and introduce possible lateral interactions between adjacent molecules. The "large area" devices (*e.g.* Fig. 1C and D) may be probed with optical spectroscopy (Raman, infrared, UV-Vis) to both characterize the device during fabrication and monitor its structure during operation.[17] Such information is very valuable for confirming device structure and observing structural changes accompanying bias application and/or current flow. There may be a range of molecular conformations and bonding geometries in ensemble junctions, but the electronic response represents the aggregate behaviour averaged over a large (usually) number of molecules. By analogy to the vast majority of chemical systems which usually involve billions of molecules, the observed response or behaviour is a time- and space-averaged phenomenon which represents the aggregate behaviour of the individual molecules. Ensemble MJs are based on a variety of substrate/molecule bonding, including Au/thiol self-assembled monolayers (SAMs), Langmuir–Blodgett films on conductors, covalent bonding between substrate and molecular layer, and electrodeposition. A significant issue with ensemble junctions is the "top contact" necessary to incorporate the molecular layer into an electronic circuit, and many of the reported methods for completing ensemble junctions are listed in Table 1. There have been numerous reports of structural changes in the molecular layer during formation of the top contact, sometimes resulting in drastic alteration of the FTIR spectrum or other indication of layer integrity.[18–23] Given the few nm thickness of the molecular layer, structural changes

often lead to direct contact between substrate and top contact and formation of a "short circuit" which usually obscures any molecular effects. While several methods have been developed to avoid such damage, structural changes in the molecular layer are responsible for much of the variation in reported experimental results.

3. Scientific questions

Before considering results from particular MJ designs, it is useful to consider the "big questions", both scientific and practical, about the phenomena which control charge transport in either single-molecule or ensemble molecular junctions. First and foremost, does electron transport (ET) in MJs differ fundamentally from that in organic electronics and semiconductors? Second, does MJ electronic behaviour depend directly on the orbitals and energy levels in the molecule, and can that connection be used for rational design of electronic function? Third, how does the molecule/contact interaction affect MJ behaviour, and what is the barrier, if any, to transport of electrons between the molecule and the contact? Fourth, is ET in an ensemble MJ a linear combination of single molecule ET, or do lateral interactions between molecules significantly affect device conductance?[6] Fifth, can molecular electronic devices achieve higher density than possible with current lithographic techniques, possibly *via* self-assembly? Sixth, a "show stopper" in terms of possible economic value: can MJs and related molecular electronic devices be integrated into commercially viable products, with acceptable stability, temperature tolerance, and compatibility with microelectronic manufacturing? Finally, the big one: does molecular electronics provide sufficient promise to justify the major scientific and development effort required to realize practical applications? These questions provide a context for the sections which follow, and we hope they will help illustrate the progress, challenges, and promise of molecular electronics.

4. Insights from single molecule paradigm

Although most of the "big questions" just listed remain to be answered conclusively, the first two decades of experimental molecular electronics have resulted in new physical insights into charge transfer in molecular devices. We consider now an illustrative but not comprehensive review of the main scientific achievements toward understanding molecular junctions,

Table 1 Examples of ensemble molecular junctions

Substrate/molecule	Surface bond	Top contact method	Area range (cm^2)	Ref.
Ag/alkane	Au–S	Hg (liquid metal)	3×10^{-4} to 3×10^{-3}	116
Au/alkane	Au–S	CP-AFM	2.5×10^{-13}	111
Carbon/molecule	C–C	E-beam evaporation	9×10^{-8} to 3×10^{-3}	36,65,69,71,72,130
Hg/alkane	Hg–S	Hg (liquid metal)	3×10^{-3}	134
Ag/alkane	Ag–S	EGaIn (liquid metal)	10^{-6} to 10^{-4}	73,74
Si/alkane	Si–C	Hg (liquid metal)	3×10^{-3}	135
Si/alkane	Si–C	Au (soft deposition)	2×10^{-4} to 3×10^{-3}	135
Al/AlO$_x$/alkane phosphonate	Al–O–P	Hg (liquid metal)	$\sim 2 \times 10^{-3}$	136

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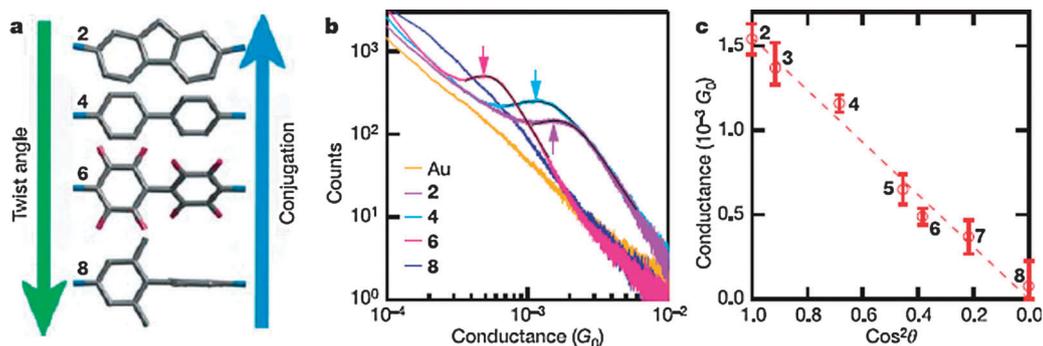
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Fig. 3 Single molecule conductance for diaminobiphenyl derivatives as a function of dihedral angle. (a) Relationship between twist angle and conjugation for four of the structures studied; (b) examples of histograms obtained from the break junction technique; (c) observed single molecule conductance dependence on twist angle. Reprinted with permission from ref. 32.

with the single molecule and ensemble paradigms discussed separately. Following this brief review, some pressing current questions will be discussed in more detail, notably the molecular junction as a "system" comprised of electronically interacting contacts and molecules, transport mechanisms beyond tunneling, integration of molecular devices, and new physical phenomena.

Among the earliest experimental observations of electron transport through single molecules used a scanning tunneling microscope (STM) tip to probe molecules bonded to a conducting surface.[24,25] Many examples followed, but the most commonly used variant today is the repetitive "break junction" described earlier in Fig. 2.[10,15,26–32] This approach has the attractive aspect of providing statistics for a large number of junctions but also the disadvantage of uncertainty in the structure and details of what is sampled. Alternatives include UHV experiments with well-defined surfaces, notably silicon.[33–35] Together with numerous theoretical treatments, these experiments provide important physical insights into transport through single molecules. First, conductance through molecules is governed in part by the fundamental quantized conductance through conductors with dimensions on the order of the Fermi wavelength of electrons. For a chain of single metal atoms, this conductance (G_0) equals $2e^2/h$, or 77 μS (*i.e.*, 1/12.9 kΩ). This conductance limit has been verified experimentally for a variety of structures, including single quantum point contacts formed by diffusing Au atoms on carbon surfaces.[36,37] When a single molecule bridges the Au–carbon contact, the observed conductance is smaller than 77 μS by a "transmission" term between 0 and 1, which depends strongly on molecular structure and contact geometry. Although typical molecular conductance values at low bias are 10^{-6} to 10^{-2} in units of G_0, molecules can nevertheless transmit many electrons per second (*e.g.* 1.0 V across a molecule with $G = 10^{-3}$ G_0 corresponds to ~4000 e^- s^{-1} through the molecule). Second, the conductance (G) through a single molecule decreases exponentially with the length of the molecule (d), according to an empirical relation:

$$G = A_0\ e^{-\beta d} \qquad (1)$$

where A_0 is a constant, and β is the attenuation factor, typically with a value between ~0 and 10 nm^{-1}, depending on molecular structure. The exponential decrease of current with molecular

length is a strong indication of transport controlled by quantum mechanical tunneling, and β is considered in more detail below.

Third, single molecule experiments have clearly established the dependence of junction conductance on molecular structure, of which the aforementioned variation in β with conjugation is an example. An elegant case is shown in Fig. 3 for diaminobiphenyl molecules with substituents which forced a range of dihedral angles between the phenyl rings.[10,26,32] The conductance decreased by a factor of 20 when the dihedral angle ranged from 0° to 88°, which was attributed to the reduced conjugation between the rings for the larger angles. Polyolefin derivatives related to carotene exhibit much higher conductance than alkanes of similar length,[8,38] with β = 2.2 nm^{-1}. Single molecules of oligothiophene and porphyrin chains exhibit exceedingly low β values of <1 nm^{-1}, implying ET is possible over distances much greater than those characteristic of tunneling, and perhaps a change in mechanism as discussed in Section 7.

Fourth, a third "terminal" has been added to single molecule molecular junctions, in the form of a solution which permits control of the local redox potential,[39–43] or by field effects from adjacent charged sites on silicon.[33,44] For the latter case, an adjacent charge center modulated the conductance of a single molecule bonded to a silicon surface in UHV, thus forming a single molecule transistor.[44] Redox events have been investigated more extensively in ensemble junctions, as discussed below, but have also been reported for single molecules suspended between Au contacts in an electrolyte solution. As shown in Fig. 4, the current through a molecule containing a ferrocene center could be recorded as a function of the redox potential imposed *via* a solution-phase "gate".[40] Although the stochastic fluctuations of the single molecule made the response very noisy, changes in the conductance were observed near the redox potential of ferrocene. Later work on an anthraquinone derivative showed that the single molecule conductance changed significantly when the anthraquinone was reduced to its hydroquinone state, and the effect was offered as evidence for quantum interference during single-molecule transport.[39]

Fifth, optical and tunneling spectroscopies have been used to provide structural information about single molecule junctions. Inelastic electron tunneling spectroscopy (IETS) provides
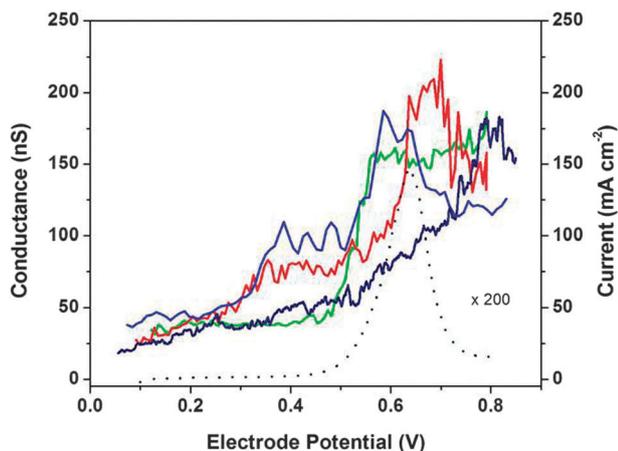
Fig. 4 Four successive scans of the conductance (at 0.1 V) of a ferrocene derivative while the molecule's redox potential was scanned between 0 and +0.8 V relative to a reference electrode in solution (solid lines). The dotted curve (and right-side *Y* axis) is a conventional voltammogram of the same molecule dissolved in solution, showing the expected redox peak for ferrocene. Reprinted with permission from ref. 40.

vibrational information about single molecules, and has the attractive feature of directly connecting electron transport to spectroscopic signature.[45] Enhanced Raman spectroscopy at an STM tip permits simultaneous monitoring of conduction and molecular vibrations in single molecules,[46] and in small collections of molecules oriented between crossed wires.[45] Finally, the non-equilibrium Green's function (NEGF) approach has provided reasonable agreement between theory and experiment for single molecules, both in terms of the magnitude of the conductance and the observed β values for aliphatic and aromatic MJs.[8] The NEGF approach includes the contacts as well as the molecule in geometry and electronic optimization, and permits calculations of time-dependent parameters such as the current and charge density under the influence of an external electric field.[47–51] Space constraints prevent a more detailed discussion of MJ theory, but it will clearly be an essential component in future progress toward rational design of electronic behaviour.

5. Insights from ensemble molecular junctions

Ensemble or "large area" molecular junctions are often made by applying a top contact onto a molecular layer formed on a flat conductor. Most of the wide range of techniques for forming the top contact have been reviewed previously,[1,52] and several examples are listed in Table 1. A major concern regarding formation of the top contact is damage or structural rearrangement of the molecular layer, with likely major effects on the electronic behaviour of the finished junction. In some prominent cases, such as vapor deposition of Au or Ti on thiolate monolayers, Au penetration and destructive reactions of Ti have been clearly demonstrated,[18,20,22,23,53–55] indicating that the structural integrity of the molecular layer must be verified following top contact application. Successful approaches that yield reproducible results include: "soft" deposition techniques that deposit room temperature metal atoms,[36,37,56,57] liquid metal contacts,[58–62] a conducting polymer buffer layer;[63,64] "direct" vapor deposition onto thermally stable, irreversibly bonded molecular layers on flat carbon or silicon surfaces;[23,65] crossed wire junctions;[45,66] and conducting probe atomic force microscopy (CP-AFM).[67,68] CP-AFM and crossed wire junctions contain a few hundred to several thousand molecules in parallel, while "soft" vapor deposition can yield junctions ranging from single molecules to >10[6] molecules oriented in parallel. Electron beam (e-beam) deposition of Cu,[69,70] Si,[65] and carbon[71] onto diazonium-derived molecular layers bonded to flat carbon surfaces results in reproducible, high yield molecular junctions with no changes in the molecular film detectable by FTIR or Raman spectroscopy. Examples are shown in Fig. 5, for e-beam deposition of several top contact materials on nitroazobenzene multilayers (thickness ~4 nm) bonded to flat carbon surfaces. Au penetrates the molecular layer to result in a higher proportion of Au/C "short circuits" (and less reproducible junction behaviour), while the other three materials result in qualitatively similar response and a high yield of non-shorted junctions (>90%). The β values observed for Cu, e-C, and Si were similar, in the range of 2.5–3.0 nm^{-1}, although the current magnitudes were significantly
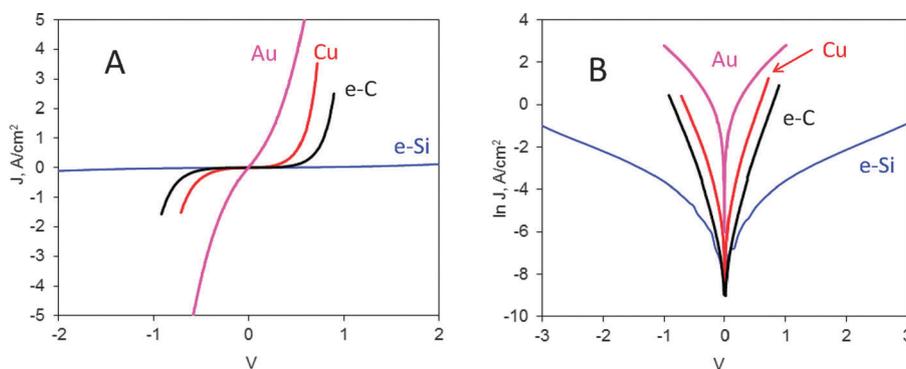

Fig. 5 Current density–voltage curves for carbon/nitroazobenzene (NAB) MJs made by vapour deposition of the indicated top contacts on linear (A) and semilog (B) scales. Electron beam deposited silicon and carbon are denoted by e-Si and e-C, and included an additional Au layer for electrical contact. NAB thickness was 4.5 nm in all cases except e-Si, where it was 3.8 nm. Original data appears in ref. 65, 71, 72.

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lower for disordered silicon (e-Si). For the case of the Cu top contact, the shape and magnitude of the current–voltage response for devices made by direct deposition were very similar to those made by a "soft" technique, in which room-temperature Cu atoms diffused onto the molecular layer to make contact.[37] The differences between the Cu, Si, and e-C devices are likely due to the electronic properties of the contact materials, with Cu and e-C being essentially metallic, while e-Si is an amorphous semiconductor.[65,71] The merits and potential pitfalls of many approaches to "ensemble" molecular junctions were reviewed recently by Whitesides *et al.*,[73] in addition to our 2009 review.[1]

Despite the rather wide range of experimental paradigms and molecules studied in ensemble junctions, some important observations and conclusions are available. First, one cannot escape the importance of high yield and reproducibility when attempting to understand the relationship between structure and charge transport in molecular junctions. Since there are not yet any standards or "well-known" phenomena, it is very risky to rely on selected responses from individual devices, however interesting those may be. Only when a particular device can be made reproducibly can its structure be reliably characterized and its electronic behaviour determined. Reus *et al.* recently presented a statistical analysis of the common case of large standard deviation and the presence of outliers, noting its importance in reaching conclusions,[74] and there are several examples of ensemble junctions made with nearly 100% yield and <20% relative standard deviation of the current–voltage response.[5,64,69,72,75] Second, characterization during fabrication and operation is critical to verifying the finished junction integrity.[17,23,76] The examples already noted of damage to the molecular layer during vapor deposition can obviously lead to erroneous conclusions about the relation of junction structure to electronic behaviour.

Third, significant differences in electronic behaviour have been demonstrated for ensemble devices with differing molecular structure, in agreement with single-molecule observations. The most prominent and consistent example is the value of the attenuation factor, β, when the molecular layer thickness is varied. The reported β values of $\sim$8–9 nm^{-1} for aliphatic and 2–3 nm^{-1} for aromatic molecules are consistent with those observed for single molecules, and for ensemble junctions having different contacts and geometries. Similar values have also been observed for electron transfer in donor–acceptor complexes in solution and through monolayer films on electrodes in electrochemical cells. While the difference between aliphatic and conjugated β values may not be surprising given the extensive literature on electron transfer in molecules in solution, it does clearly establish a "molecular signature" relating structure to electronic behaviour in molecular junctions. Fourth, optical spectroscopy has been used to characterize finished junctions, by using a partially transparent substrate or top contact. FTIR through a transparent silicon substrate provides direct structural information about the molecular layer before and after top contact deposition,[20,77] and Raman spectroscopy through thin carbon layers has been reported for carbon/molecule/metal MJs.[23,76] IETS of ensemble

junctions has been reported, permitting observation of vibrational features in intact MJs.[78,79] Fifth, redox activity in ensemble molecular junctions has been demonstrated directly with optical spectroscopy,[80–84] and associated with major changes in device conductance. Conducting polymers which exhibit large changes in conductivity upon oxidation or reduction have been exploited in ensemble junctions[85] and as redox "switches" in solution.[86–91] Redox reactions with accompanying structural change may have utility in molecular memory applications,[92,93] and represent phenomena which are fundamentally distinct from those occurring in conventional silicon semiconductors. Finally, the origin of the "scaling problem" between single molecule and ensemble junctions remains unknown, despite many comparisons and analyses. The predicted conductance for ensembles containing >10^6 molecules determined by simply adding single-molecule conductances in parallel is consistently 2–3 orders of magnitude higher than that observed for the ensemble junctions. Whether this discrepancy is due to an experimental problem such as contact area or a fundamental issue related to intermolecular interactions or interference effects is simply unknown, to our knowledge. Some additional major conclusions from the study of ensemble junctions are discussed in greater detail next, particularly the concept of a molecular junction "system", charge transport mechanisms, and integration with commercial microelectronics.

6. Molecular junctions as systems

As already stated, a major goal of the investigation of molecular junctions is determining how molecular structure affects electronic behaviour. However, many details of the molecular junction can affect the electronic properties to a greater extent than intuition might predict. For example, depending on the details of doping level and voltage bias, a metal–molecule–semiconductor junction can have current density that does not depend at all on molecular length, while changing only a single variable (*e.g.*, bias or doping) can result in exponential dependence on molecule length.[94] Such dramatic variation of molecular junction conductance with alteration of the details of device construction is not an isolated case, and may occur even with good reproducibility of junction fabrication. Instead, it illustrates a problematic situation for the interpretation of experimental results: often, a difference in the conductance of two molecular junctions is attributed to systematic variation of molecular properties when in fact there is insufficient evidence to determine what actually caused the difference. It has become clear in recent years that the electronic properties of a molecular junction should be considered to result from the whole system, the details of which must be considered in order to understand the variables that impact charge transport.

While the energetic features that control the transport of electronic charge in a molecular junction are simple in principle, in practice detailed knowledge is required in order to understand the factors that control the system energy levels. A simplified model can be constructed as shown in Fig. 6, which shows the Fermi energy of carriers in the contacts off-set
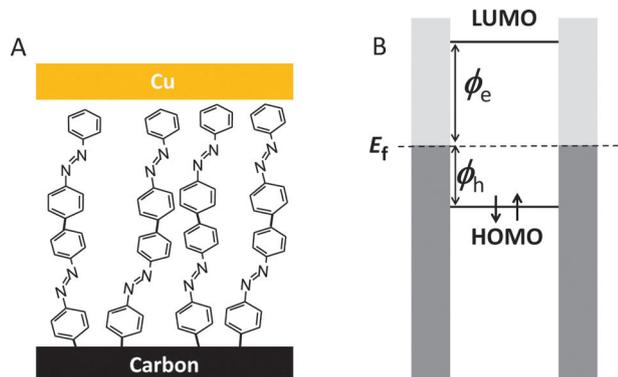
Fig. 6 Schematic of a carbon/azobenzene/Cu molecular junction (A) and its associated energy levels (B). Dark shading in B represents filled states in the metallic contacts, while light shading indicates empty states. ϕ_e and ϕ_h are the energy barriers for tunnelling by electrons and holes, respectively. E_f is the system Fermi level. Adapted with permission from ref. 72.

from the filled or empty molecular orbitals (HOMO and LUMO) of the molecule. This offset occurs in any non-resonant charge transport mechanism and is often called a charge injection barrier or a tunneling barrier (and here, more generally, the transport barrier, ϕ). As shown in Fig. 6, the relative values of the contact Fermi levels (E_f) and the molecular orbital energies (*e.g.*, HOMO and LUMO) can be used to define ϕ for electron or hole tunneling. However, knowledge of these energies in a completed junction is not easy to obtain. Often, molecular orbital energies are calculated using density functional theory (DFT), and in some cases are estimated from experimental data, generally involving optical spectroscopy or electrochemistry of the molecule in solution. The value of E_f for a contact material is often determined by various experimental measurements of

the material work function (WF). In some cases, the WF is taken from literature values determined using highly purified materials with clean surfaces. Regardless of how the WF and orbital energies are determined, there are several pitfalls in using the measured or reported WF of the isolated contact material and E_f in the molecular junction. As discussed in more detail below, the validity of calculating ϕ using isolated material energy levels depends on how well the vacuum levels of the two components align when the materials are brought into contact, and thus, how well the system obeys the Schottky–Mott rule.

The Schottky–Mott rule was developed in the last century based on theoretical descriptions of metal-semiconductor contacts.[95,96] In the limit where no changes occur in the energy levels of two components when they are brought into contact, the value of the interfacial barrier will be given by:

$$\phi_h = E_f - E_{HOMO} \qquad (2)$$

The Schottky–Mott rule has been applied to organic semiconductor films in contact with a metallic conductor and is also referred to as "vacuum level alignment", meaning the energy levels of the two components have a common vacuum level. In the field of organic electronics, the applicability of this rule has been shown to follow for systems in which there are either no or only weak electronic interactions between the metallic contact and the organic film (or as stated by Mott, "If the two do not influence each other in any way…").[95] On the other hand, it frequently fails (as expected) for systems with strong electronic interactions between the substrate and molecular component.[97,98] Thus, the validity or failure of the Schottky–Mott rule in organic and molecular electronics can be attributed to how closely the vacuum levels of the substrate and molecular entity line up.[97–99] Fig. 7 shows the effect of modifying a conductive substrate with
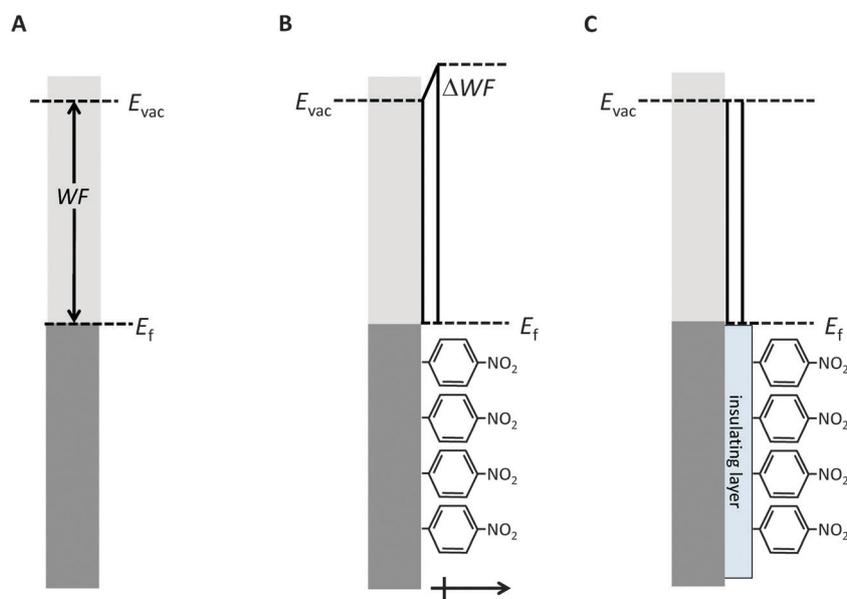

Fig. 7 Effect of surface modification on the energetics of an interface between a conductor and a molecule. (A) Fermi level and work function of a bare metallic surface in vacuum. (B) Effect of bonding a nitrophenyl layer to the conductor surface. (C) Effect of preventing electronic interactions between the conductor and nitrophenyl layer. Dark gray regions represent filled electronic states in the conductor, light gray is empty states.

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a molecular layer on the energy levels of the system. Fig. 7A shows energy levels for a generic conductor, with the top of the filled states in the metal defining E_f. The energy difference between carriers at E_f and the vacuum level (E_{vac}) is therefore the work function (WF) of the material. Modifying the conductor with a strongly coupled molecular layer is shown in Fig. 7B. In this case, a surface dipole results from electron inductive effects, with the magnitude and direction of the dipole determined by the electron donating/withdrawing character of the molecular layer.[100,101] For a nitrophenyl layer shown in Fig. 7B, the nitro group acts as a withdrawing group, causing the local vacuum level to shift to higher energy. This shift is manifested as an increase in the WF of the modified surface in the energy level diagram in 7B, and can be envisioned as being due to the higher binding energy of electrons residing in the nitrobenzene moiety.[102] In any case, the lack of vacuum level alignment means that the energy levels of the components change due to charge transfer between the conductor and the molecule, leading to a value of ϕ that can be very different from that predicted from the Schottky–Mott limit (eqn (2)). As shown schematically in 7C, addition of an insulating layer such as an oxide on silicon prevents electronic coupling and restores the energy levels to those predicted by the Schottky–Mott rule.[103]

A rather dramatic consequence of molecule-contact interactions in MJs is shown in Fig. 8 for molecules bonded to a carbon substrate. It is often assumed that a change in molecular structure, which would result in a change in the molecular energy levels, will result in control over the energetic transport barrier. In the example of Fig. 8, the HOMO levels of the eight aromatic molecules studied vary from -5.29 to -7.59 eV,

based on DFT calculation of the free molecules. For a substrate WF of -4.6 eV, the Schottky–Mott rule predicts a barrier for hole tunneling ($E_f - E_{HOMO}$) ranging from 0.69 to 2.99 eV, which should produce a large variation in tunneling probability and junction conductance. However, carbon/molecule/Cu MJs made from the eight molecules show little variation in either current magnitude or β, as shown in Fig. 8B. Measurement of the HOMO levels by UPS and fitting a Simmons tunneling model to the current–voltage curves revealed that the actual tunneling barrier for all eight aromatic molecules is 1.3 ± 0.2 eV, as shown in Fig. 8C.[72] This "leveling" of a 2.3 eV range of HOMO levels to a <0.4 eV range of tunneling barriers results from breakdown of the Schottky–Mott rule due to strong electronic coupling between the aromatic molecules and the aromatic, conducting carbon surface. Stated differently, electron donating and withdrawing groups affect the energy levels of both the molecule and the contact, thus decreasing the effect on the tunneling barrier. Such behaviour can be explained by equilibration of the energy levels through the polarizable surface bond,[72,103] or through the influence of interface states.[103,104] In any case, it is critical that for any system, it is first determined if Schottky–Mott applies before drawing any conclusions regarding the value of ϕ or what factors influence it. A similar effect may be responsible for the relatively small effects of variations in molecular structure on conductance in single molecule MJs[105] and in ensemble MJs made from a series of thiols on Au.[106]

One way in which it can be determined if a given system resides in the vacuum level alignment regime (where the Schottky–Mott rule applies) is measurement of the interface parameter, S. Experimentally, the work function of samples of different metals with a molecular layer adsorbed at the surface are measured. S is determined as the slope of the measured WF versus the WF of the unmodified metals. For systems that do not interact strongly, often a change in the WF of the substrate will lead to a corresponding change in modified sample WF, and $S \sim 1$. On the other hand, for strong electronic interactions, the modified sample WF can be invariant with underlying substrate WF, resulting in Fermi level pinning, and $S \sim 0$. The main consequence of a system where S is near zero is the failure of the Schottky–Mott rule, and, as described above, the resulting inability to control ϕ by simply changing the value of the electrode work function or the molecular orbital energies.[11] This can be expected for systems where strong contact-molecule interactions are suspected, leading to the formation of interface states[107] or polarized chemical bonds.[108] Interestingly, there need not be an obvious pathway for interactions: non-covalent interactions are sufficient to cause S to deviate from unity.[109,110] In these cases, energy level alignment will be determined by the potential energy differences between the organic component and the conductive substrate.

Detailed investigations by Frisbie et al. using CP-AFM on Au/thiol monolayers reveal and confirm strong effects of the contacts and bonding on electronic behaviour.[111,112] Oligoacene molecules on Au were probed with CP-AFM tips of Ag, Au, and Pt, with the resulting junctions having either one or two metal–S bonds.
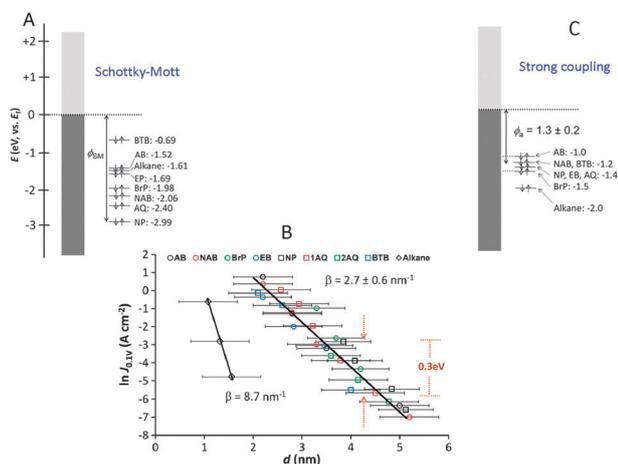

Fig. 8 Electronic behaviour of eight aromatic molecules and an alkane in carbon/molecule/Cu ensemble MJs. (A) Energy levels of free-molecule HOMOs relative to the carbon Fermi level, assuming the Schottky–Mott limit. (B) Observed attenuation plots for completed junctions, constructed from over 400 individual junctions, with $\beta = 2.7$ nm^{-1} for aromatic molecules and 8.7 nm^{-1} for aliphatic. (C) System energy levels for molecules bonded to carbon deduced from electronic conductance and UPS results. AB = azobenzene, NAB = nitroazobenzene, BrP = bromophenyl, EB = ethynyl benzene, NP = nitrophenyl, AQ = anthraquinone, BTB = bis(thienyl)-benzene. Modified and reprinted with permission from ref. 72.

UPS was used to assess work function changes and the extent of Fermi-level pinning, and the number of acene rings was varied to determine the attenuation coefficient, β. While the metal on the AFM tip did not greatly affect β for Au-SR, the magnitude of the current and contact resistance varied by a factor of $\sim 10^3$. Furthermore, a second metal–S bond between the AFM tip and the molecular layer decreased the contact resistance by factors of 10–100, and decreased β from ~ 5 to ~ 2 nm^{-1}. These strong effects of contact material were attributed to changes in energy level alignment between the molecular orbitals and the contacts, based on UPS determination of work functions and HOMO levels.[111] To confirm the conclusion that the entire junction system affects conductance, we point out that much smaller variations in current density ($\sim 10\times$) were observed for physisorbed Au, Cu, and Pt contacts on aromatic molecules bonded to carbon, using a different junction paradigm.[36,37]

It is clear from these and other examples that the value of ϕ and the resulting conductance of a molecular junction in many cases cannot be predicted from a simple analysis that assumes vacuum level alignment. Such predictions will only be possible if S is close to unity. Even in this case, the actual value of ϕ might differ from the prediction due to a number of other effects, including the specific orientation of the molecule,[32] contact resistance effects,[111] and the density of states of the contact materials.[109] From these observations it has become exceedingly clear that the entire system in a molecular junction needs to be considered, often in significant detail, in order to predict and control transport. The contact properties, the way in which the molecules interact with the contact (including electronic coupling and orientation), and many other factors need to be considered before a complete energy landscape can be constructed. The most important implication of these insights is that the conductance of different molecules cannot be compared without regard to the rest of the system. It is true that certain parameters derived from electronic measurements show some characteristics that are apparently less dependent on the paradigm and contacts (e.g. the attenuation factor described below), but great care must be taken when comparing absolute conductance values, which are controlled by the entire energy landscape.

Given that many factors affect MJ conductance and many experimental paradigms are in current use, it is often difficult to compare results from different labs and paradigms. As noted above, the repetitive break junction technique has proven valuable for single molecules, and led to useful insights from comparisons across different labs. Variations in molecular structure in the break junction technique have shown the importance of conformation,[32] bonding,[26,113,114] and energy levels,[10,114,115] and high conductance has been associated with resonant transport in single porphyrin molecules.[27,29] For ensemble junctions, however, there is no accepted "standard", and the different contact materials, MJ geometries, and bonding methods often confuse comparisons. As with single molecules, structural variation within a given MJ design can reveal strong structural effects such as the difference between aromatic and aliphatic molecules apparent in Fig. 8B. Although substrate–molecule

interactions suppress the effects of electron withdrawing groups on tunneling rate, there is a clear effect of conjugation in both single molecule and ensemble MJs. Regardless of whether a particular system follows the Schottky–Mott rule, the variation of conductance with molecule length is an informative parameter which has been applied successfully across experimental paradigms. Although the pre-exponential term in eqn (1) depends strongly on MJ design and geometry, the attenuation factor β is less sensitive to these variables. Electronic coupling can affect the relative orbital energies and tunneling barrier, but transport still depends exponentially on molecular length in the tunnelling regime. Several examples of attenuation plots are shown in Fig. 9, for ensemble MJs observed with several different paradigms for both aliphatic and aromatic molecules. An extensive comparison is available for alkane thiols which showed a consistent β of 8–9 nm^{-1} despite differences in bonding to the two ends of the alkyl chain.[117] Examples of reported β values for MJs are listed in Table 2, for both single molecule and ensemble junctions. These can be separated into three groups: alkanes (8–9 nm^{-1}), conjugated molecules (2–5 nm^{-1}), and systems with $\beta = 0$–2 nm^{-1}. For the cases where $\beta > 2$ which have been studied over a wide temperature range, conductance is independent of temperature in the range 5–250 K, consistent with a tunneling mechanism. In addition to the electronic coupling effects illustrated by Fig. 9, image charge and effective mass factors are important in comparisons of junction conductance with tunneling theory.[69,72] For example, delocalization in aromatic molecules results in effective electrons masses less than or equal to 0.3 m_e where m_e is the mass of a free electron. While there is general agreement on coherent tunneling as the transport mechanism for MJs with molecular layers with 1–5 nm thicknesses with β in the range of 2–10 nm^{-1}, the mechanism for cases with β in the range of 0–2 nm^{-1} is less well established, and is the subject of the next section.
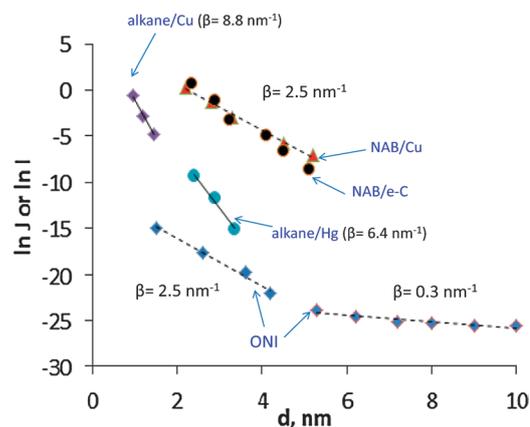

Fig. 9 Selected attenuation plots for aromatic and aliphatic molecules in ensemble molecular junctions. NAB = nitroazobenzene on carbon with Cu[69] or e-beam carbon[71] contacts, ONI = oligonaphthalenefluoreneimine on Au using CP-AFM.[67] Y axis is the natural log current density (A cm^{-2}) except for the ONI data which is stated as current due to unknown device area. Alkane/Au and alkane/Hg data are from ref. 37 and ref. 116, respectively.

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Table 2 Attenuation coefficient (β) values for several paradigms

Junction	Method	β (nm^{-1})	Ref.
C–C-conjugated molecules/Cu, e-C[a] or e-Si[a]	Ensemble/vapor deposition	2–3	65,69,71,80
Metal–S-conjugated oligoacene/metal	Ensemble/c-AFM	5.0	111
Metal–S-conjugated oligoacene–S–metal	Ensemble/c-AFM	2.0	111
C–N–alkyl/Au	Single molecule/SDMD	8.8	37
Metal–S–alkyl/metal	Ensemble/c-AFM	8.8	112
Au–S–alkyl–S–Au	Single molecule STM	8.1	137
Au–S–alkyl/PEDOT:PSS/Au	Ensemble/conducting polymer	5–7	75
Au–S–(porphyrin)$_n$–S–Au	Single molecule STM	0.4	30
Au–N(pyridine)–porphyrin–N(pyridine)–Au	Single molecule STM	0.4	29
Au–S–MCMW/Hg	Ensemble/hanging mercury	0.01;0.3	138
Au–N–(phenyl)$_n$–N/Au	Single molecule/STM	4.0	32
Au–SCN–(thiophene)$_n$–SCN–Au	Single molecule/STM	1.0	139
Au–N–OPE–N–Au	Single molecule/STM	0.3, 2.0	140

[a] "e-C" and "e-Si" refer to electron-beam deposited carbon and silicon.

7. Transport beyond tunneling

Since tunneling is governed by quantum mechanics, it is operational only over distances in which the electron wavefunction of a material extends into space, typically no further than $\sim$5 nm. The magnitude of the (non-resonant) tunneling current is controlled by the energetic situation illustrated in Fig. 6. As discussed in Section 6 and Fig. 8, failure of the Schottky–Mott rule can significantly decrease the effect of electron withdrawing or donating groups on MJ conductance. Unfortunately, this means that in many cases, the molecular layer acts as a simple tunneling barrier with limited variation in the barrier height, and the versatility of molecular properties is partially "washed out". Early excitement about ME was based on the hypothesis that the function of a molecular device would be tunable using a wide range of energy levels available from the great variety organic molecules, i.e., molecular structure would have a large impact on charge transport. Even in a system where control over the value of the tunneling barrier is exhibited, it is rare to modulate the tunnel barrier by more than $\sim$1 eV.[103] We could describe a tunneling mechanism with limited control of barrier height to be "barrier electronics", exhibiting an exponential dependence which limits conduction to distances less than approximately 6 nm.

As the transport distance extends beyond the tunneling regime, electrons or holes must reside in the molecular layer, usually long enough to dephase. We distinguish here between tunnelling and "injection", in which charge resides in a molecular energy level, possibly with reorganization of molecular structure. Any observable current across thick molecular layers ($>\sim$5 nm) must involve alternate mechanisms from coherent tunneling, with distinct distance dependences and energetics. For example, "hopping" involves electron transfer across the molecular layer by a series of transitions between neighboring sites consisting of localized and often stable redox states. Unlike coherent tunneling, hopping often involves nuclear motion and reorganization accompanying a redox reaction; therefore, it is incoherent (electron spin and phase are not conserved) and usually thermally activated. "Hopping" is a common but not terribly precise term in the literature, while "redox exchange" is often used by electrochemists. Importantly, hopping does not exhibit the exponential distance dependence of tunneling, but instead a d^{-1} dependence and other characteristics of ohmic conduction. An example is shown in Fig. 9, for a series of oligonaphthalenefluoreneimine (ONI) molecules with lengths from 1.5 to 10 nm, using a CP-AFM as the top contact. The β value changed from 2.5 nm^{-1} for $d < 5$ nm to 0.3 nm^{-1} for $d > 5$ nm, and the observed resistance of the molecular layer increased linearly with length for the longer molecules. The region exhibiting $\beta = 0.3$ nm^{-1} was temperature dependent, while the $\beta = 2.5$ nm^{-1} region was not, leading to the conclusion that hopping was operating in the thicker films, where tunneling was a negligible contribution.[67,68]

Alternatives to hopping have been proposed to explain observations of $\beta < 1$ nm^{-1}, some of which are listed in Table 2. A quite interesting possibility occurs when an orbital energy in the molecules approaches the Fermi level of the contacts. For example, suppose the HOMO shown in Fig. 6 shifts to higher energy, thus decreasing the barrier to hole tunneling (ϕ_h) to near zero. One possibility for this case is "resonant transport" in which charge carriers rapidly transport through molecular orbitals rather than tunnelling through barriers. It is also possible that occupation of orbitals results in reorganization and formation of a reduced or oxidized form of the molecule (i.e. a "polaron"), and this process should depend directly on the transport time across the junction.[118–120] Nichols et al., reported β values of 1.1, 0.42, and 0.19 nm^{-1} for single molecules of oligoporphyrins with different linkages between porphyrin centers,[27] and attributed transport to coherent tunneling through the HOMO of the molecules. An additional factor in conjugated molecules is the change in HOMO level with molecule length, due to more extensive delocalization.[27,69] Since $\beta < 1$ can also occur with thermally activated hopping mechanisms, it is important to consider temperature dependence of MJ conduction when investigating transport mechanism. The distinction between hopping and resonant transport is important, since the former is activated and the latter is not. If transport across distances greater than the $\sim$6 nm reported for coherent tunneling depends on hopping, conduction will be temperature dependent and will also involve reactive intermediates,

namely radical ions or related polarons. The activation barrier can result in slow charge transport, reflected, for example, by the low mobilities typical of organic semiconductors. Resonant or other non-activated transport can occur near absolute zero, and does not generate radical ions. As noted below, fast, activationless transport should be possible in molecular junctions due to their very short dimensions compared to today's organic electronics.

In addition to hopping and resonant transport, at least three other mechanisms can operate across large distances. First, field emission (FE), which is a special case of tunneling when the effective applied bias exceeds the energy of the tunnel barrier, can operate over very long distances as long as a sufficient electric field is reached. A transition from direct tunneling to field emission has been claimed for Au/SAMs/Au molecular junctions and is the basis of a technique termed "transition voltage spectroscopy".[111,121,122] Field emission is independent of temperature but decreases exponentially with distance. A second mechanism that was originally developed to describe DC conduction across insulating films is Poole–Frankel (PF) transport.[123] While PF is traditionally used to describe charge transport through "traps" in inorganic semiconductors, a similar situation may apply in some organic films. Traps in the PF context usually refer to "Coulombic" states with an energy offset relative to the conductive states that depends on the electric field. The depth of a potential well can vary between tens of meV to hundreds of meV, depending on the nature of the traps and the magnitude the applied electric field. Like hopping, PF usually exhibits an Arrhenius temperature dependence, with the current also varying exponentially with the square root of the electric field. PF transport has been reported in detail for organic semiconductors with thicknesses greater than 100 nm.[124,125] Schottky emission is another possible transport mechanism beyond tunneling, which has a temperature and field dependence similar to that for PF transport. The fundamental difference is that Schottky emission is an interfacial phenomenon and the so called Schottky barrier is usually formed by partial charge transfer across an electrode/material interface. While all these mechanisms are possible for MJs with molecular layers thicker than 6 nm, identification of a specific mechanism requires a full investigation of dependence of charge transport on molecular layer thickness, applied bias, applied electric field and temperature.

8. Integration of molecular devices

The amazingly rapid growth of microelectronics was achieved not only by miniaturizing components, but also by massively parallel fabrication, leading to many examples of consumer electronics containing billions of devices which cost a few dollars to manufacture. Assuming that useful electronic functions can be realized with molecules that are not already available with silicon, their practical value will depend on integration of molecular devices into commercially viable products.[1] While an electronic device consisting of a single molecule may represent the ultimate limit of device density,

many applications will require massively parallel manufacturing in fabrication facilities similar to those in today's microelectronics industry. No matter how interesting the behaviour of a given molecular junction (ensemble or single molecule) is in the laboratory, any commercial application will require a robust and reproducible format that can be made in exceedingly high yield and at low cost. In addition, the devices must be stable under the conditions required for wiring, packaging, and operation, which can often involve aggressive environments, including temperature extremes. As noted in Section 5, an early problem in the fabrication of molecular junctions was damage to the molecular species when attempting to evaporate metal top contacts onto the molecular layers.[53,54] These initial challenges resulted in several techniques for so-called soft contacting methods[126–128] and also raised awareness of the importance of proper analytical characterization of the molecular component.[17] Verification of molecular layer integrity not only helps to ensure that the structure of the molecule is intact within the junction, but can also reveal any problems that might be encountered during integration procedures. A recent review[17] discusses the various techniques that can be used to characterize molecular layers used in junctions, including *in situ* methods for analysis of components within a completed junction. Here, we will focus on cases where integration of molecular junctions has been demonstrated through a few examples.

Massively parallel fabrication of ensemble molecular junctions was demonstrated in 2008 using a conducting polymer top contact on Au/thiolate assemblies.[64] The polymer is spun onto the surface of the molecular layer, and circumvents degradation during the deposition of Au metal. This buffer layer enabled yields near unity for 20 000 parallel fabricated junctions. In addition, the devices showed excellent temporal stability, with the electrical characteristics remaining essentially unchanged upon storage in air for 2.5 years.[129] However, devices that utilize Au–thiol linkages begin to degrade when the temperature is raised to 50–60 °C.[77,129] This limitation poses a serious challenge in real world applications involving modern computing, where the operating temperatures of current CPUs often exceed this threshold significantly. This temperature instability demonstrates that at least three elements are needed in order for a molecular device to serve in a hybrid circuit: massively parallel fabrication, excellent operational stability in a variety of environments, and satisfactory functional performance metrics. While a device platform that meets all of these has yet to be demonstrated, progress has been made in each individual area.

Most molecular junctions have been made using thiolate self-assembled monolayers on metallic substrates due to the relative ease with which well-defined molecular layers can be generated. As noted, this platform has extended the state of knowledge about molecular devices greatly, and if a conductive polymer is used as a buffer layer, can even be made in massively parallel processing. However, devices that rely on self-assembly require a labile molecule–substrate bond in order to reach the minimum in free-energy that represents the ordered state. This necessarily limits the stability of the layers when subjected to

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temperature and other stimuli. One way to overcome this limitation is the use of strongly bound layers employing covalent bonds between the surface and the molecular layer. While this increases the stability of the surface bond, it also typically requires the use of irreversible surface bonding that results in less ordered layers and often produces multilayer films. The weak intermolecular interactions which result in ordering of thiolate monolayers are not able to create order in more strongly bonded surface layers, so essentially one is trading long-range order in Au/thiol layers for thermal stability in irreversibly bonded molecular layers. One example of irreversible bonding which produces robust junctions utilizes flat graphitic carbon with diazonium-derived molecular layers.[62,69,71,130–132]

The use of radical-mediated molecular layer growth results in high stability and the ability to withstand the direct evaporation of various top contact materials, including copper,[23] carbon,[71] and silicon,[65] as described in Section 5. The integrity of the molecular layer after top contact deposition was demonstrated using Raman spectroscopy through transparent contacts. Fig. 10 shows that minimal changes occur in the molecular layer bonded to a carbon surface during vapor deposition of Cu (Fig. 10A), silicon (Fig. 10B), and carbon/Au (Fig. 10C). These results illustrate the importance of verifying molecular layer integrity during fabrication, and together with Fig. 5 indicate nanoscopic molecular layers on graphitic carbon can withstand the direct deposition of contact materials without structural changes detectable by Raman spectroscopy. In addition, such molecular layers are intact after exposure to a complete photolithographic process consisting of spin-coated resist, exposure to UV light, and developing.[23]

In addition to verifying that diazonium-derived molecular layers survive top contact depositions intact, these molecular junctions have also been produced on a wafer scale[5] and packaged in commercial format, as shown in Fig. 11. Finished MJs made by diazonium reduction showed negligible changes in electronic behaviour after 10^9 voltage cycles to with current densities exceeding 0.5 A cm^{-2}, and withstood temperature excursions above 150 °C in air[5] and 400 °C in vacuum.[23] While there is clearly a long way to go before MJs are integrated in commercial microelectronics, these results demonstrate MJ compatibility with at least that some of the conditions encountered in commercial microelectronic processing. The example of the "Damascene" copper plating technique[133] which replaced aluminum conductors demonstrates that the microelectronic industry is willing to embrace "wet chemistry" involving organic molecules in microfabrication if there is a commercial advantage to doing so.

9. Conclusion: there is plenty of room in the middle

One answer to the often-posed question of "when will we see molecular electronics in the real world" is "as soon as molecular devices can do something not currently possible with silicon." The existing experimental and theoretical results on molecular junctions are sufficient to conclude that electron transport through 1–20+ nm molecular layers has distinct properties from that in traditional semiconductors or thick organic films. The special transport properties of molecular
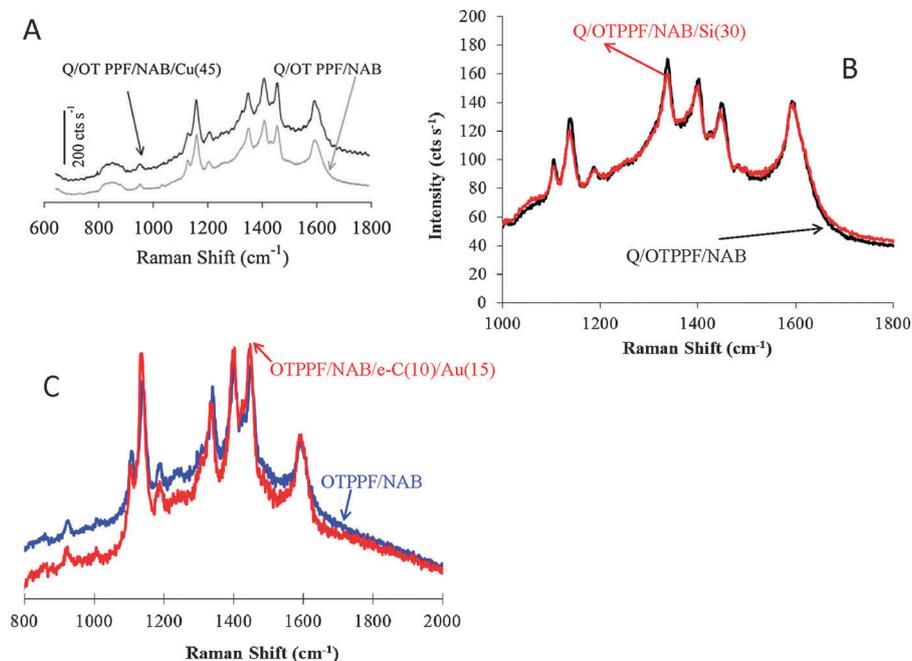

Fig. 10 Raman spectra obtained through a partially transparent carbon substrate to which a 5 nm layer of nitroazobenzene was bonded by diazonium reduction. Two spectra are shown in each case, one taken before and one after electron-beam deposition of 45 nm of Cu (A),[23] 30 nm of silicon (B), or 10 nm of carbon followed by 15 nm of Au.[71] Figures reprinted with permission from ref. 23 (A), ref. 65 (B), and ref. 71 (C).
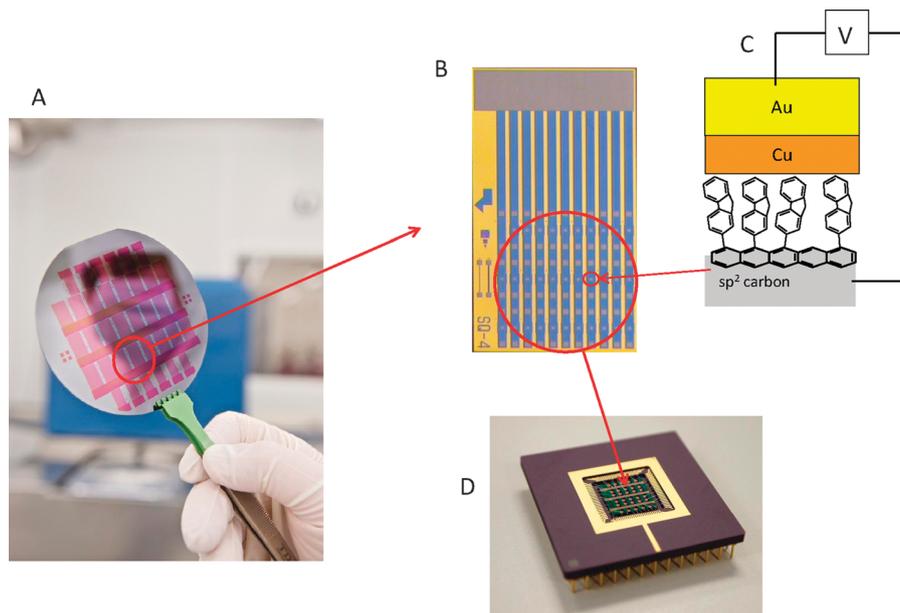
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Fig. 11 Several steps in parallel fabrication of carbon/molecule/Cu/Au ensemble molecular junctions. (A) A 100 mm Si/SiO$_2$ wafer after photoresist patterning and pyrolysis; (B) individual chip with 32 junction ''pads'' and contact areas; (C) schematic of a fluorene molecular junction; (D) completed chip after packaging. Details are in ref. 5.

junctions are illustrated by the comparison of characteristic length scales in Fig. 12. The right end of the scale approaches "macro" dimensions of >100 nm, for which redox exchange is the main mode of transport in organic films. The often strong temperature dependence of organic semiconductors is a consequence of the reorganization energy involved in redox exchange. In metallic conductors and in the conduction band of crystalline semiconductors, electrons move in bands without redox exchange, but are scattered by impurities, grain boundaries, *etc.*, resulting in transport by a series of steps between scattering events. The mobility characteristic of both organic and inorganic conductors is a consequence of the rate of redox exchange and the scattering length, as well as the "energy landscape" in the (semi)conductor. The tunneling observed in molecular junctions and single molecules occurs at the left end of the scale in Fig. 12, occurs without scattering, and is independent of temperature. Tunneling is "non dissipative," often coherent, generates no heat and is potentially very fast. Considering the simple case of an electron accelerated across a 5 nm molecular junction by a 1 V potential yields a transit time of <20 fsec, implying a maximum frequency response above 1 THz. For length scales between coherent tunneling and activated "hopping" some potentially valuable phenomena may be exploited, some of which do not have analogs in conventional electronics. If the junction thickness is less than the scattering length, electrons travel "ballistically", Ohm's law does not apply, and no heat is generated within the molecular layer. Scattering lengths in metals at low voltage (<10 V) are ten's of nm, and in organics are ~10 nm. Therefore, ballistic transport across a molecular junction containing one or more organic layers should be possible. Modern field effect transistors are approaching ballistic transport through their channels, but it is

possible that such transport is the norm for many molecular devices, given their typically 1–10 nm active regions.

As noted in Sections 7 and 8, most of today's molecular junctions represent "barrier electronics" in which transport is determined by tunneling length and barrier height. As shown for both Au/thiol/EGaIn and carbon/molecule/Cu junctions, variations in molecular orbital energies have only modest effects on the tunneling barrier, often due to the "leveling effect" noted in Section 6. Furthermore, coherent tunneling through barriers is short range, and will limit transport to well below 10 nm if it is the only mechanism operative. However, for *resonant* transport, the situation should be very different and β may approach zero, presumably limited only by the scattering length or molecular reorganization. Redox events in MJs represent a fundamental departure from the behaviour of conventional conductors and semiconductors, whether they occur in "thick" films of organic electronics or <20 nm layers in molecular junctions. However, redox exchange must occur in many steps to traverse a >100 nm organic film, with attendant low mobility and positive temperature dependence. In molecular junctions, it is conceivable that a polaron formed by a redox event could bridge the entire molecular layer, resulting in band transport and metallic behaviour. Conjugation lengths in conducting polymers can approach 20 nm or more, so presumably the "band" could bridge the gap between contacts. Furthermore, an electron generated during polaron formation may traverse the junction ballistically, essentially in one "hop" with minimal temperature dependence. The short distances involved in molecular junctions result in fundamentally different transport than that observed in either crystalline or organic semiconductors with dimensions greater than a few tens of nm. For the range of MJ thicknesses between those for coherent
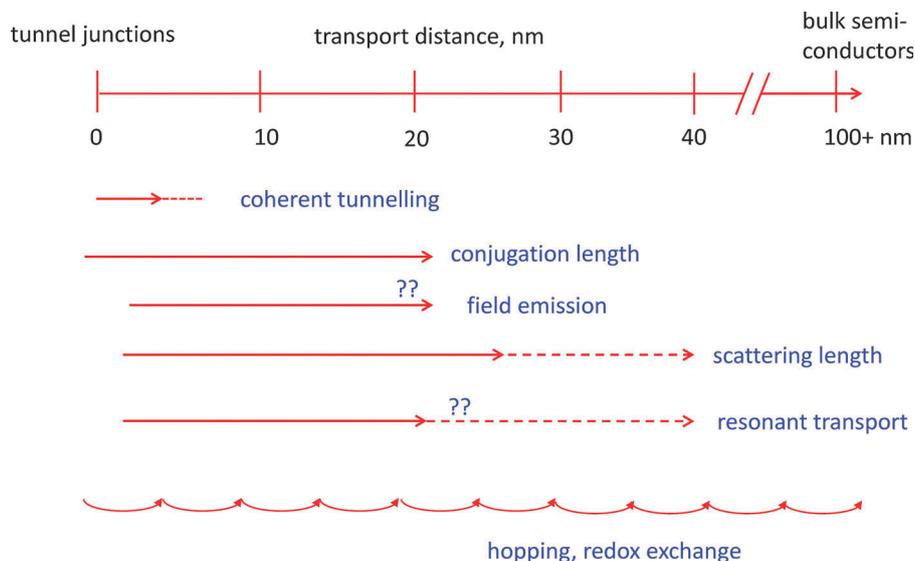
Fig. 12 Characteristic length ranges for transport mechanisms possible in molecular junctions, from a few nm tunnel junctions to bulk films >50 nm thick where transport is primary by a hopping mechanism. Dashed lines and question marks indicate that the phenomenon can occur over a range of distances depending on the material and conditions involved.

tunnelling (<6 nm), and those requiring activated hopping (>50 nm) there may be useful phenomena inherent in molecules which may be exploited without scattering or hopping. These observations lead to a modification of the 1959 Feynman quote that "there is plenty of room at the bottom". Given that "barrier electronics" is restricted in the range of possible barrier heights and transport distances (*i.e.* <5 nm), we could say that "there is plenty of room in the middle", meaning there are phenomena operative between 5 and 50 nm which may be unique to conjugated molecules and may be exploited for novel electronic functions.

In addition, chemical and biological recognition are potentially valuable attributes of molecules which could conceivably be realized in molecular junctions. There is already a vast existing literature on sensors which use chemical interactions between target analytes and sensor molecules to generate electrochemical, optical and electronic responses. In the context of a molecular junction, the question is whether recognition events can modulate conductance across the short distances where unusual transport phenomena are operative, *i.e.*, 1–50 nm. That possibility is as yet untested, but it is certainly an example of a situation where molecular components differ fundamentally from silicon or metals.

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