

The study of charge transport through organic thin films: mechanism, tools and applications

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In this paper, we discuss the current state of organic and molecular-scale electronics, some experimental methods used to characterize charge transport through molecular junctions and some theoretical models (superexchange and barrier tunnelling models) used to explain experimental results. Junctions incorporating self-assembled monolayers of organic molecules—and, in particular, junctions with mercury-drop electrodes—are described in detail, as are the issues of irreproducibility associated with such junctions (due, in part, to defects at the metal–molecule interface).

Keywords: self-assembled monolayer; alkanethiolates; superexchange;
molecular junctions; defects

1. Introduction. Organic and molecular-scale electronics: the drive towards miniaturization, versatility and low-cost device fabrication

This paper describes some of the theoretical models and experimental tools used to characterize charge transport (CT) through films of organic molecules and polymers. The emergence of nanotechnology from fundamental science has been marked, in part, by the birth of the distinct fields of molecular-scale electronics and organic electronics (sometimes called ‘molecular materials for electronics’; Jortner & Ratner 1997) from the field of molecular conduction, which originated with studies of charge transfer complexes in the 1940s. A molecular-scale electronic device—the first of which, a molecular diode, was proposed by Aviram & Ratner (1974)—is one in which a single molecule performs an electronic function (or an array of molecules performs the function in parallel). Organic electronics (Farchioni & Grosso 2001; Malliaras 2003; Facchetti *et al.* 2005)—a field that originated with the discovery by Heeger, MacDiarmid and Shirakawa of electrical conduction in doped organic polymers (Chiang *et al.* 1977)—is the use of films of molecules and polymers as the semiconducting (charge transporting) materials, electrodes or dielectric materials within electronic devices such as light emitting diodes (Hutchison *et al.* 1999; Morteani 2003;

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Tseng *et al.* 2006), field effect transistors (Kudo & Yamashina 1984; Dimitrakopoulos & Mascaro 2001; Dimitrakopoulos & Malenfant 2002; Newman *et al.* 2004; Shankar & Jackson 2004; Panzer *et al.* 2005) and solar cells (Gregg 2003; Gledhill *et al.* 2005; Shaheen *et al.* 2005).

In general, efforts to incorporate molecules and polymers into electronic devices have been motivated by six major considerations (Cahen & Hodes 2002; Vilan & Cahen 2002a): (i) molecules (1–2 nm) are smaller than the smallest features in semiconductors (presently approximately 90 nm; with well-defined engineering development, less than 20 nm) and might therefore facilitate the packing of more computational power onto a smaller footprint, (ii) the electronic properties of molecules and polymers are tunable by organic synthesis; these procedures can, in principle, have very low cost, (iii) under certain conditions, molecules self-assemble into ordered monolayers (SAMs) and multilayers on surfaces, and into ordered arrays in solution, (iv) films of molecules and polymers can be deposited over large areas on flexible substrates, (v) the electronic and optical properties of many molecules can be controlled via modulation of temperature, electric and magnetic fields and other environmental parameters, and (vi) assemblies of molecules perform complex, high-efficiency electronic and optoelectronic charge and energy transport functions in nature (e.g. electron transport, photosynthesis, coupling of one- and two-electron processes in metabolism).

Molecular-scale electronics is, so far, a purely academic pursuit suffering from poor reproducibility among measurements of the same systems gathered using different techniques, a set of daunting experimental issues concerning the connection of fragile molecules to macroscopic leads, and an incomplete theoretical basis. Furthermore, this field now suffers from both a well-deserved lack of credibility (Service 2003) and an identity crisis: ‘Is the point of molecular-scale electronics to gain a detailed mechanistic understanding of CT through molecules or to build functional devices?’ The performance of systems suited to evaluate the electrical properties of individual molecules—for instance, break junctions and scanning tunnelling microscopy experiments under ultra high-vacuum conditions and low temperatures—does not easily translate to the performance of practical devices. In the immediate future, organic electronic devices (Malliaras & Friend 2005) are anticipated to find a place in commercial markets where mechanical flexibility, low cost, chemical sensitivity, optical properties and large-area applicability are valued over high performance, markets such as transaction cards, identification tags and large-area displays.

Potential applications aside, the fundamental studies of CT through organic molecules—especially at the interfaces between organics and metals or semiconductors—that define the field of molecular-scale electronics today are necessary for continued innovation in organic electronics. Self-assembled monolayers (SAMs) are an important tool in creating metal/semiconductor–molecule junctions that can be characterized electrically using a variety of instrumentation. In the following sections, we will discuss mechanisms of CT applicable to both molecular-scale and organic electronic devices, and give a qualitative description of non-resonant superexchange tunnelling, the widely accepted mechanism for the transport of charge over long distances in molecules in the solution phase, and a very useful framework to describe CT through SAMs of organic molecules. We will then describe some of the tools used to study CT through SAMs—in particular, the mercury-drop junction—and issues of

reproducibility of experiments using these techniques. Finally, we will give some concluding remarks and discuss future directions for the fields of molecular-scale and organic electronics.

2. Mechanisms of charge transport through organic films

The rate of long-distance (greater than 1 nm) CT is dictated by some combination of a strongly distance-dependent tunnelling mechanism and weakly distance-dependent incoherent transport (Jortner 1976; Marcus & Sutin 1986). The contributions of each of these mechanisms to CT through a metal–insulator–metal (MIM) junction or an organic film are dictated by the energy gap between the work function or energy band of the electrode that injects the charge carrier (electron or hole) and the energy of the orbitals of the insulating organic material. When this energy gap is on the order of $k_b T$, molecular orbitals are energetically accessible to the incoming charge carrier and a short-lived oxidation or reduction of the molecule or polymer occurs. In a molecular junction, this charge is then absorbed by the other electrode; in an organic film, it hops to another molecule until it reaches an interface with a collecting electrode or recombines with a complementary charge carrier. The type of CT that proceeds via real intermediate states that couple to internal nuclear motions of the bridge and the surrounding medium is called incoherent or sequential CT (Davis *et al.* 1998; Nitzan 2001; Berlin *et al.* 2002).

For MIM junctions where the work functions of the electrodes lie well within the energy gap between the highest occupied and lowest unoccupied molecular orbitals (the HOMO–LUMO gap) of the insulating material, CT proceeds by a non-resonant tunnelling process. The difference between tunnelling and real charge injection is the time the charge carrier spends in the organic layer. If the state in which the molecule is oxidized or reduced (the state in which the charge carrier resides on the bridge) is energetically unfavourable, then the time for which this state exists is vanishingly small, and is given by the Landauer/Buttiker contact time, τ_{LB} (Nitzan *et al.* 2000). In the limit of large energy gap for injection, E_G , this time is of the simple uncertainty principle form

$$\tau_{\text{LB}} \approx \frac{N\hbar}{E_G}, \quad (2.1)$$

where N is the number of bridge sites. For alkane wires, τ_{LB} is sub-femtosecond. This time is a great deal shorter than the period, $2\pi/\omega_\lambda$, of the environmental vibrations or polarizations (where the vibrational mode is designated λ) that localize charge. In this limit, then, the mechanism should be coherent tunnelling, where the only vibronic coupling is the very weak inelastic electron tunnelling signal (IETS) from intermediate (virtual) state nuclear reorganization (Wang *et al.* 2003a; Galperin *et al.* 2004; Kushmerick *et al.* 2004; Seminario & Cordova 2004; Selzer *et al.* 2004a; Troisi & Ratner 2004; Wang *et al.* 2004a,b, 2005).

When $E_G \sim k_B T$ (e.g. oligophenylenevinylene wires; Kubatkin *et al.* 2003), the Landauer formula fails because charges localize on the wire and move by a polaron-type mechanism (Segal *et al.* 2000, 2003; through vibronic coupling to the λ mode) that does not conform to the elastic-scattering limit assumed by

Landauer. In that case, far more general non-equilibrium Green's function techniques (Wingreen *et al.* 1993; Datta 1995, 2005; Damle *et al.* 2002; Xue *et al.* 2002; Seideman & Guo 2003) and other hopping models (Berlin & Ratner 2005) have been useful to characterize transport through junctions and films of molecules or polymers. We will discuss both tunnelling and hopping mechanisms in this section.

(a) *Non-resonant coherent superexchange tunnelling*

The calculation of the coherent, elastic conductance, g , across a molecule sandwiched between two continuous densities of states, and in the presence of a time-dependent voltage, is most often approached through the Landauer formula (Datta 1995, 2001, 2005; Emberly & Kirczenow 2000; Seideman & Guo 2003; Troisi & Ratner 2003),

$$g = \frac{2e^2}{h} \sum_i T_i, \quad (2.2)$$

where T is the scattering matrix, whose elements give the probability of scattering of the electron in channel i , and $2e^2/h = (12.8 \text{ k}\Omega)^{-1}$ is the quantum of conductance. The scattering matrix can be expanded in Green's function of the molecule (Liu *et al.* 2005) or estimated via superexchange formulation, as described below.

The form of the scattering matrix directly reflects the mechanism by which the charge moves through the junction, and there are two such mechanisms. The first is direct tunnelling, which takes place only if the wave functions of the two electrodes extend far enough into the junction to overlap such that they are *directly* electronically coupled. The second mechanism of non-resonant CT in molecular junctions (which almost always applies if we are, indeed, speaking of *molecular* conduction and not just chemical modification of a metal surface) is superexchange: superexchange is an indirect transfer of electrons or holes from donor to acceptor through an energetically well-isolated bridge, during which bridge orbitals are utilized solely as a coupling medium (Kramers 1934; Anderson 1950, 1959). The term superexchange was first used to describe the indirect exchange coupling of unpaired magnetic spins via orbitals having paired spins; diamagnetic orbitals acquire paramagnetic character through mixing with charge transfer excited state configurations. Superexchange is thought to be an important mechanism for efficient electron transfer within the photosynthetic reaction centre (Marcus 1987; Ogrodnik & Michel-Beyerle 1989) and has been studied in various biomimetic systems (Kilsa *et al.* 2001; Lukas *et al.* 2002).

In CT that occurs via superexchange, the charge carrier (either an electron or a hole) does not remain on the bridge long enough to experience dephasing by nuclear motions of the bridge (hence the nomenclature 'coherent superexchange'). The time spent in the states—'virtual excitations'—that the molecule occupies between the instance the electron leaves the donor and when it arrives at the acceptor is inversely proportional to the energy gap between the electronically coupled orbitals (equation (2.1)).

Figure 1*a,b* are schematics of the simplest cases of both electron and hole superexchange processes, where a single molecular orbital (either the LUMO in the case of electron conduction or the HOMO in the case of hole conduction) acts as the conduit for the charge carrier between electrodes 1 and 2. We will discuss

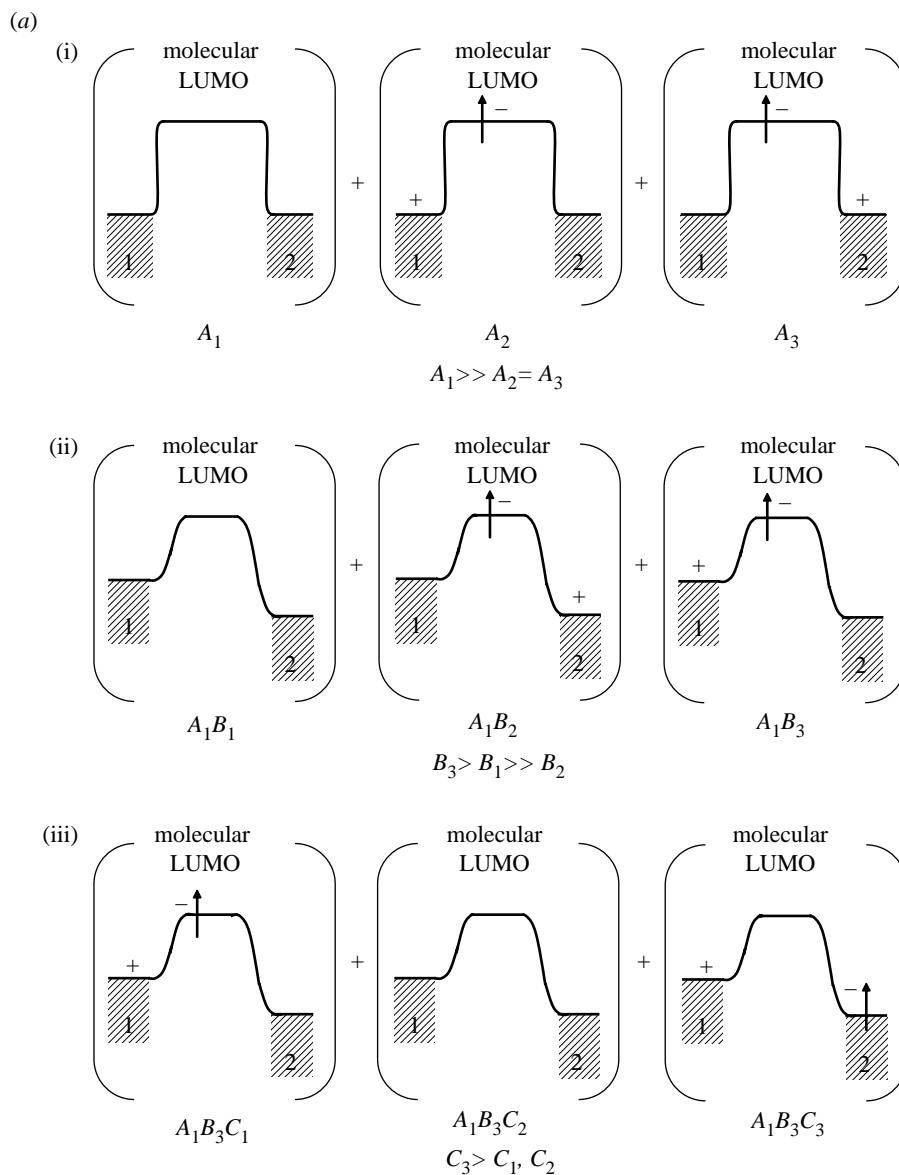


Figure 1. Diagrams of (a) electron and (b) hole multistep superexchange tunnelling processes within a metal–molecule–metal junction where all conduction takes place through either the (a) LUMO or (b) HOMO of the molecule. The shaded areas indicate occupied states of the metal electrodes and the arrows are electrons. The system is a statistical mixture of the configurations (where each diagram is a configuration), and the probability of the system being in a specific configuration is given by the letters below each diagram. The progression of both electron and hole superexchange is: $A_1 \rightarrow B_3 \rightarrow C_3$, with a total probability of $A_1B_3C_3$. (a) Electron conduction: (i) zero bias, (ii) step 1, electron injection, and (iii) step 2, electron absorption. (b) Hole conduction: (i) zero bias, (ii) step 1, hole injection, and (iii) step 2, hole absorption.

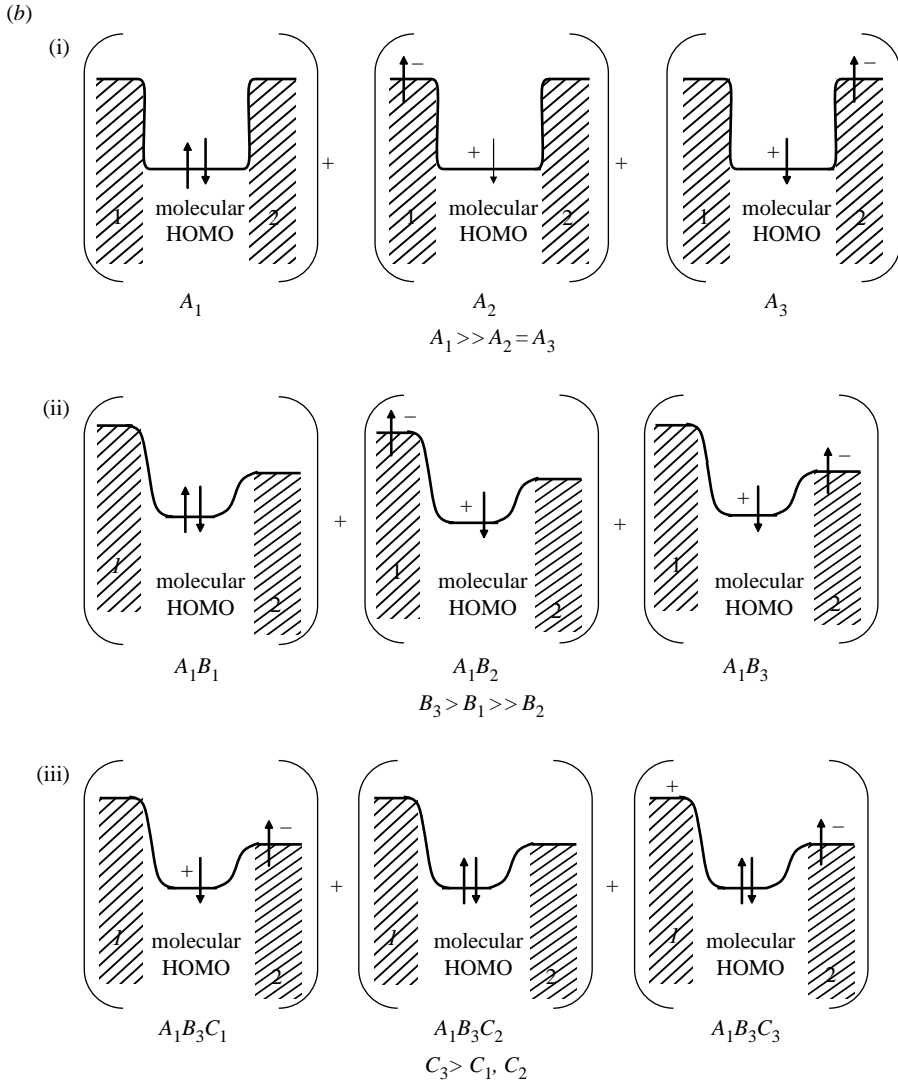


Figure 1. (Continued.)

these processes qualitatively. We assign each electronic configuration a coefficient (listed under each diagram) for a given set of initial conditions; the coefficients give the probability that the system exists in that configuration. We will refer to the configuration by its probability: configuration A_1 has probability A_1 , configuration B_3 has probability B_3 (given that the system is initially in configuration A_1), and so has a total probability A_1B_3 , etc. The total state of the system at any time is a statistical mixture of the possible configurations. The y -axis of these plots is the potential energy of the electron in the given electronic state, and the x -axis is the spatial coordinate along the dimension that charge travels through the junction. The up (spin-up) and down (spin-down) arrows indicate the presence of electrons in the molecular orbitals, and the Fermi level of the metal electrode is the line between occupied (shaded) and unoccupied states.

The positive and negative signs indicate charge-separated virtual intermediate states, *not* the oxidation or reduction of any of the components in the system. For the electron (hole) conduction case, we assume that the electrodes are not directly electronically coupled and that the only available channel for CT is the LUMO (HOMO) of the molecule. The molecular orbitals of the molecule are weakly electronically coupled to the electrodes, as indicated by the curved, connecting lines between the Fermi levels of the metals and the frontier orbitals of the molecule, but are energetically well separated from the Fermi levels of the electrodes, such that only non-resonant tunnelling processes may occur within the junction.

We will first consider the case of electron conduction (figure 1*a*). At zero applied bias, the electrodes are degenerate, and the small electronic coupling and large energy gaps between the orbitals of the molecule and the states of the metal render the configuration where the electrodes are initially filled to their Fermi levels and the molecular LUMO is empty (A_1) far more probable than the other two configurations, which are, in principle, allowed virtual states: $A_1 \gg A_2 = A_3$. By applying a bias to the junction, we introduce an electric field, which changes the interaction energy between the molecular and metallic levels by altering the energy gaps between these levels. At some applied voltage, this effect makes configuration B_3 (with a total probability equal to the product of starting in state A_1 , and then progressing to state B_3) favourable, i.e. the electron spends some amount of time on the bridge, and electron injection occurs. This transient intermediate configuration then couples with the more stable configurations, C_2 and C_3 . C_2 results from recombination of the charges at the metal–molecule interface, and C_3 results from absorption of the electron by electrode 2 (and, hence, passage of current through the junction). For a given applied voltage and metal–molecule combination, C_3 is most probable and there is net electron transport from electrode 1 to electrode 2.

Hole conduction proceeds in a similar manner, except that the first step must be an electron from the filled HOMO of the molecule occupies the most energetically accessible level of the electrode whose Fermi level has been shifted towards the HOMO by the applied bias (an electron *cannot* move into full HOMO). Again, the combination of the electric field resulting from the potential drop across the junction and the increased mixing between the HOMO of the molecule and the metallic states leads to population of the transient virtual intermediate configuration B_3 , which then couples with the more stable configurations C_2 and C_3 ; the latter configuration results from net electron transport from electrode 1 to electrode 2 via the molecular HOMO (i.e. net hole transport from electrode 2 to electrode 1).

The total probability of transmission of an electron or hole from electrode 1 to electrode 2 via indirect tunnelling (here, crudely represented by a product of coefficients of participating configurations) is the electronic superexchange coupling, t_{DA} (Marcus 1965). For CT that takes place through superexchange, this coupling determines the scattering matrix in the Landauer formalism (equation (2.1)). The superexchange coupling is the sum of the probabilities to transport charge through all available channels in the junction (figure 1*a,b* show just two of those channels: one through the molecular HOMO and one through the molecular LUMO, but CT is almost always a weighted sum of the conduction through multiple channels). McConnell gives a perturbation theory-based

expression for the magnitude of t_{DA} in terms of individual resonance integrals between molecular subunits and the energy gap between the degenerate donor and acceptor and the homologous bridge (McConnell 1961). The McConnell model predicts an approximately exponential dependence of t_{DA} on the through-bond distance between the electrodes, with decay parameter β^{SE} ; this approximation is verified by many experimental data (Closs & Miller 1988; Paddon-Row *et al.* 1988; Roest *et al.* 1997). Significant extensions of this model have been derived to accommodate non-nearest neighbour interactions (Lopez-Castillo *et al.* 1993), multiple geometry-dependent CT pathways (Liang & Newton 1992; Newton 2000) and a non-homologous bridge (Cave 1997).

(b) *The barrier model for non-resonant tunnelling and the β parameter*

The superexchange model accounts for the explicit electronic structure of the molecular bridge and the metal–molecule contact. There are, however, simpler approaches to calculate the magnitude of the current through a molecular junction; these approaches consider the molecule to be a homogeneous dielectric layer (a single tunnelling barrier) between two metal electrodes and are used to describe both direct (overlap of electrode wave functions) and indirect (no direct coupling between electrodes) tunnelling. For a rectangular barrier, one can obtain an analytical solution for the coefficient for transmission of an electron. A semiclassical expression (the WKB approximation; Cohen-Tannoudji *et al.* 1977) is necessary to describe non-rectangular barriers. In both cases, as for superexchange, the transmission probability decays exponentially as the length of the barrier increases.

The most popular approach for estimating the magnitude of the tunnelling current through a barrier of arbitrary shape is the Simmons model for elastic tunnelling (Simmons 1963*a,b*; Lee *et al.* 2003*a*). In this model, a system of two equipotential metals with an insulating layer between them at zero applied bias is in thermal equilibrium such that the Fermi level is uniform throughout the system. If a bias is applied, current can flow. At small applied voltages (V) (where the size of the injection barrier $\gg V$), the current density depends linearly on V . At higher voltages (the intermediate regime), when the barrier is on the same order as the applied voltage, there is a hyperlinear dependence of current density on V .

Equation (2.3) gives the dependence of the magnitude of the current density (the current divided by the area of the junction, J) on the length of a potential barrier,

$$J = J_0 e^{-\beta d}; \quad J_0 = j_0 e^{-\alpha d_0} \quad (d, d_0 \geq 0), \quad (2.3)$$

which we have partitioned into a portion whose length (d_0 , Å) is constant as we vary the molecular structure of the insulating layer, and a portion whose length (d , Å) changes as we vary the molecular structure of the insulating layer. A plot of $\ln J$ versus d has slope $-\beta$ (Å⁻¹), which quantifies the decay of the tunnelling probability with increasing d and does not depend on the choice of d_0 , and intercept $\ln J_0$ (Å cm⁻²), the value of which depends on three factors: (i) j_0 , the current that would flow through the junction if the two metals were in contact (i.e. if the thickness of the insulating layer were zero), (ii) the choice of d_0 , and (iii) α , the characteristic decay of the tunnelling probability with increasing d_0 . The factor $e^{-\alpha d_0}$ is sometimes called the ‘contact resistance’ because it

quantifies the characteristics (height and length) of the tunnelling barrier that the electron encounters at interface between the metal and the molecule (Engelkes *et al.* 2004).

An electron may tunnel through the junction via multiple pathways, some that follow the carbon backbone of the molecule and some that involve multiple molecules. For close-packed SAMs of *n*-alkanethiolate, for example, the magnitude of the tunnelling current appears to correlate with the molecular length, i.e. the distance between the electrodes along the molecular axis, and not with the average shortest physical distance between the electrodes.

The parameter β has been used as a benchmark for the suitability of a molecule as a wire: the smaller the value of β , the longer the distance over which charge can be transferred without penalty. The β parameter is often used to characterize all types of transport, although from its very definition it only applies to exponentially decaying processes. The range of β values found for identical bridge units measured in solution and through SAMs of organic thiols on the surface of metal electrodes (e.g. $\beta=0.6\text{--}1.2 \text{ \AA}^{-1}$ for alkanes (Leland *et al.* 1985; Oevering *et al.* 1987; Closs & Miller 1988; Chidsey 1991; Finklea & Hanshewm 1992; Paulson *et al.* 1993; Paddon-Row 1994; Slowinski *et al.* 1997; Klan 1998; Holmlin *et al.* 2001; Cui 2002*a,b*; Selzer *et al.* 2002; Xu & Tao 2003; Weiss *et al.* 1998), $\beta=0.32\text{--}0.66 \text{ \AA}^{-1}$ for oligophenylene (Kim & Lieber 1989; Osuka *et al.* 1990, 1993; Helms *et al.* 1991, 1992; Barigelletti *et al.* 1994, 1996; Holmlin *et al.* 2001; Weiss *et al.* 2004), $\beta=0.06\text{--}0.5 \text{ \AA}^{-1}$ for oligo(phenyleneethynylene)s (OPEs) and oligo(phenylenevinylene) (OPVs) (Sachs *et al.* 1997; Creager 1999; Sikes *et al.* 2001), $\beta=0.04\text{--}0.2 \text{ \AA}^{-1}$ for oligoenes (Benniston *et al.* 1994; Osuka *et al.* 1996) and $\beta=0.04\text{--}0.17 \text{ \AA}^{-1}$ for oligoynes (Marczinke 1994; Grosshenny *et al.* 1995; Osuka *et al.* 1995)) reflects the fact that the most fundamental aspects of transport, including length dependence, are sensitive to the environment in which the measurement is performed.

The Simmons model (and variations) have been used successfully to fit experimentally measured current densities in a variety of systems (Cui 2002*b*; Chen 2003; York & Slowinsky 2003; Lee *et al.* 2004), but this model ignores the details of the electronic structure of the molecule and the geometry of the contacts and neglects electron–electron interactions that are captured by more sophisticated electronic structure theory (Nitzan 2001; Reimers *et al.* 2002; Xue *et al.* 2002). The model, therefore, gives no real insight into either the mechanism of CT through the junction or modifications that might be made on the molecular level to optimize the performance of the junction. Furthermore, while the single-barrier model may adequately describe electron conduction in some cases, it does not lend itself to the description of hole conduction (an inherently multi-step process), which is thought to be the dominant mechanism of CT through many saturated and conjugated molecular bridges. In contrast, the inputs for calculations of superexchange coupling can, in principle, incorporate everything known about the electronic structure of the junction because these inputs are taken from the Hamiltonian of the system.

(c) Thermally activated hopping transport

If the Fermi level of the injecting electrode and the energy of the relevant bridge orbital(s) are within several $k_{\text{B}}T$ of resonance, such that thermal injection is relatively facile (as is often found for π -systems and high temperatures), the

conduction of electrons or holes will occur through the molecular orbitals, either via resonant tunnelling (for weak vibronic coupling, as in carbon nanotube wires) or localized hopping, if the vibronic coupling is stronger (Cave & Newton 1997; Berlin *et al.* 2002; Weiss *et al.* 2004; Berlin & Ratner 2005). For long distances, the incoherent, ‘wire-like’ channel is generally more efficient than the coherent one (because, for processes whose rate decays exponentially with distance, the total rate of a series of very short-distance processes is greater than the rate of one very long-distance process; Davis *et al.* 1997, 1998; Jortner *et al.* 1998). Incoherent hopping is the dominant mechanism of efficient hole and electron transport over long (approx. 1–1000 nm) distances within films of undoped, conjugated polymers and molecular crystals.

The transition from tunnelling-type transport (weakly temperature dependent and strongly length dependent) to incoherent hopping (strongly temperature dependent and weakly length dependent) has also been observed in single molecule break junctions (Anariba & McCreery 2002; Selzer *et al.* 2004*a,b*, 2005; Haiss *et al.* 2006). In the case of single molecules, the mechanism switch most often results from the thermal activation of vibrational or torsional modes; this activation improves conjugation within the molecule and stabilizes its oxidized or reduced state. Charge is then injected into the newly thermally accessible molecular orbital, where it may hop along the molecular bridge until it is absorbed by the counter electrode.

3. Tools for the study of charge transport through organic molecules: SAMs and the mercury-drop junction

The measurement of a current–voltage response on a single molecule within a junction is, in principle, the ideal method of characterizing the electrical properties of single molecules. Indeed, the conductances of single molecule transport junctions—usually within mechanically controllable or electrochemical break junctions (Reed *et al.* 1997; Reinerth *et al.* 1998; Xu & Tao 2003; Selzer *et al.* 2004*a,b*, 2005; Gupta *et al.* 2004; Xiao *et al.* 2004)—have displayed the characteristic fluctuations that are analogous to the ‘blinkings’ observed in single-molecule spectroscopy, probably due to different geometries of the molecule or surrounding molecules (Donhauser 2001; Xiao *et al.* 2004). The collection of many data using sophisticated single-molecule measurements is, however, challenging experimentally. An alternative strategy is to arrange macroscopic quantities of molecules in ordered SAMs (Barigelletti *et al.* 1994; Benniston *et al.* 1994; Osuka *et al.* 1995; Cave & Newton 1997; Sachs *et al.* 1997; Jortner *et al.* 1998; Sikes *et al.* 2001; Reimers *et al.* 2002; Chen 2003), and then electrically address these molecules *en masse*, in small groups, or individually. SAMs of saturated hydrocarbons (Troughton *et al.* 1988; Bain & Whitesides 1989; Bain *et al.* 1989; Nuzzo *et al.* 1990; Labinis *et al.* 1991*a*; Dubois & Nuzzo 1992; Allara 1995; Ulman 1996; Reed *et al.* 1997; Zhou *et al.* 1997; Reinerth *et al.* 1998; Bumm *et al.* 1999; Wold & Frisbie 2000; Cui 2001; Holmlin *et al.* 2001; Beebe *et al.* 2002; Rampi & Whitesides 2002; Wold *et al.* 2002; Love *et al.* 2003; Naaman & Vager 2003; Wang *et al.* 2003*a*; Engelkes *et al.* 2004; Tran *et al.* 2004, 2005; Lewis *et al.* 2005; Selzer *et al.* 2005; Weiss *et al.* 1998) and conjugated oligomers (oligophenylenes (Liao *et al.* 2000; Heister *et al.* 2001; Anariba & McCreery 2002; Lee *et al.* 2003*b*; McCreery 2004; Shaporenko *et al.* 2005),

oligophenylenevinylenes (Joachim 1999; Dudek *et al.* 2001; Sikes *et al.* 2001; Reichert *et al.* 2002), oligophenyleneethylenes and carotenes (Leatherman 1999; Ramachandran 2003)) have been the basic building block for the majority of MIM junctions. The chemistry of the formation of SAMs on many metal, semiconductor (Selzer & Cahen 2001; Selzer *et al.* 2002; Vilan & Cahen 2002*b*; Salomon *et al.* 2003; Haick *et al.* 2004) and carbon (Ranganathan *et al.* 2001; Anariba & McCreery 2002) substrates is well understood, and the structure of SAMs—both within the film and at the substrate–organic interface—has been characterized via X-ray diffraction, X-ray photoemission spectroscopy and infrared spectroscopy.

The very first MIM junction (MIM) used to study the electrical properties of monolayer films was assembled by condensing evaporated metal (Pb, Ag and Al) on top of a Langmuir–Blodgett (LB) film deposited on an Al surface (Honig 1976). Several researchers still use the same technique to study the electrical behaviour of molecules incorporated in a LB film. In recent years, a large variety of conceptually new junctions have been designed to measure the current densities through a single molecule or few molecules within a SAM, including STM (Han 1997; Bumm *et al.* 1999; Zeng *et al.* 2002; Monnell *et al.* 2005; Haiss *et al.* 2006; Weiss *et al.* 1998), conducting AFM (cAFM; Kelley *et al.* 1999; Leatherman 1999; Wold & Frisbie 2000; Beebe *et al.* 2002; Cui 2002*a*; Rawlett *et al.* 2002; Wold *et al.* 2002; Ramachandran 2003; Engelkes *et al.* 2004; Engelkes *et al.* 2005), gold nanoparticle-mediated cAFM (Cui 2001, 2002*b*), nanopore (Zhou *et al.* 1997; Chen *et al.* 1999; Lee *et al.* 2003*a*; Wang *et al.* 2003*a,b*), crosswire (Blum 2005) and in-wire junctions (Kratochvilova *et al.* 2002*a*; Blum *et al.* 2004). Each type of junction has specific advantages and disadvantages with respect to fabrication, reproducibility and application. In many cases, the interpretation of the results of STM experiments is difficult due to the convolution of the tip–substrate distance with the conductance. Conducting AFM obviates this problem by controlling the position of the metal-coated tip with respect to the substrate using force feedback. Nanofabrication results in junctions able to trap a much smaller number of molecules: the evaporation of gold through a nanopore mask on top of a SAM reduces the area of the junction to less than $300\ \mu\text{m}^2$, and therefore reduces the probability of incorporating defects in the junctions (but also the current). Although these systems have demonstrated interesting functionalities, there has been little characterization (Zhu *et al.* 2006; Walker *et al.* 2007) of the nature of the interface formed by the evaporation of metal atoms onto organic films, and electrical shorts due to the percolation of Au atoms through the film (and probably other types of defects) have limited the reproducibility of the results.

Junctions designed to incorporate a large number of molecules usually consist of a metal surface electrode supporting a SAM of organic molecules, and a second electrode that is formed by deposition of evaporated gold onto the organic layer (Wang *et al.* 2004*b*). The evaporation of the second electrode without damaging the fragile molecular layer and inducing electrical shorts between the two electrodes still presents a challenge. In an attempt to circumvent this problem, a number of different strategies such as lift-off float-on Au pads (Xu *et al.* 2002) or deposition of cold gold (Xu *et al.* 2002) have been employed successfully. Although these approaches have produced laboratory test structures, they are difficult to scale up for the fabrication of circuits or molecular devices because they are highly specialized and time consuming. Recently, nano-transfer printing

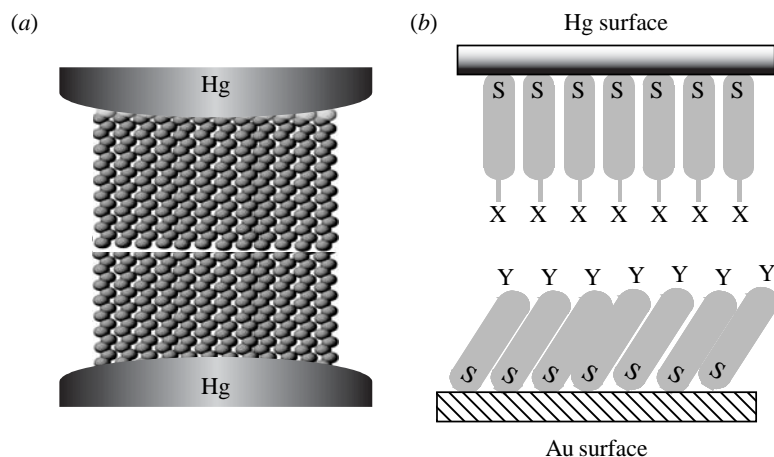


Figure 2. Schematic diagrams of two types of solid-state, bilayer mercury-drop junctions: (a) Hg-SAM₁//SAM₂-Hg and (b) Hg-SAM₁//SAM₂-M (M=Au in this case). The SAMs are chemisorbed to the metals and form a van der Waals interface with each other. Two SAMs within a single junction may or may not be equivalent, or, as shown in (b), can be functionalized with different terminal groups.

of gold electrodes for efficient fabrication of junctions based on semiconductors (Ga/As-SAM-Au; He *et al.* 2006) was introduced, and functionalized single-walled carbon nanotubes have been used as electrodes for assembling test-bed junctions (He *et al.* 2006).

We and Majda have developed a MIM junction based on liquid Hg electrodes (Slowinski *et al.* 1997; Rampi *et al.* 1998; Slowinski *et al.* 1999*a,b*; Rampi & Whitesides 2002; Tran *et al.* 2004, 2005; Sek *et al.* 2004). In the following discussion, we describe four types of Hg-drop junctions. We use ‘//’ to indicate a van der Waals interface, and ‘-’ to indicate a chemisorbed contact.

(a) Hg-drop junctions

(i) Hg-SAM₁//SAM₂-Hg

This junction is formed by contacting two drops of Hg, each covered by a SAM of alkanethiolate (the two SAMs may or may not be equivalent, figure 2*a*). It has the advantage of using the same metal for the two electrodes but presents the following inconveniences associated with using two liquid surfaces: (i) the contact area is difficult to evaluate and changes with potential, (ii) intercalation may be possible at high voltages, (iii) the influence of mechanical deformation on the structure of surface films is not characterized, and (iv) the Hg-SAM drop is no longer compliant when the SAM is composed of rigid conjugated molecules.

(ii) Hg-SAM₁//SAM₂-M

The junction comprises a Hg drop with a SAM (SAM₁) and a solid metal surface (M=Au, Ag, Pt, Pd, Cu, Hg, Ti, Hg/Au alloy) with a SAM (SAM₂), where SAM₁ may or may not be equivalent to SAM₂ (figure 2*b*). The presence

of a solid surface increases the versatility of the junction dramatically because: (i) one can characterize the organization of the molecules forming the SAM on a solid surface using infrared spectroscopy or other methods, (ii) the supramolecular structure of a SAM can be adjusted by changing the metal substrate: both saturated and conjugated chains have different tilt angle on Ag than on Au surfaces, and (iii) the contact area can be evaluated easily.

(iii) *Electrochemical junctions: Hg-SAM₁-R//R-SAM₂-Hg and Hg-SAM₁//R//SAM₂-Hg*

Two-electrode systems suffer from an ambiguity in the relative positions of the Fermi levels of the electrodes and the energy levels of the redox molecules sandwiched between them. In an electrochemical cell, however, a reference electrode relates the potential of a working electrode to energy levels of molecules in solution. We have assembled an electrochemical junction, [figure 3a](#), that allows us to fix the potential of the electrodes with respect to the oxidation potential, E° , of the incorporated redox centre, R (equal to a ruthenium-terminated thiol, HS(CH₂)₁₀CONHCH₂pyRu(NH₃)₅). We placed the Hg electrodes, together with an Ag/AgCl reference electrode and a platinum counter electrode, in an electrolyte solution, and controlled the potentials of the electrodes by connecting them to a bipotentiostat.

We have designed, assembled and studied two different electrochemical junctions that incorporate redox sites. [Figure 3](#) shows schematically the interfaces of the two junctions: one where the Hg electrodes are functionalized by thiolate monolayers that are covalently bound to redox sites (Hg-SAM₁-R//R-SAM₂-Hg, [figure 3b](#)), and one where the redox sites are incorporated into the inter-electrode gap (Hg-SAM₁//R//SAM₂-Hg, [figure 3c](#)). In both junctions, the potentials of the mercury electrodes are driven in such a way that one electrode (the cathode) acts as the electron donor and the other one (the anode) as the electron acceptor. We measured the current between the electrodes by keeping the potential of one electrode constant and sweeping the potential of the other electrode across the oxidation potential of the Ru^{II/III} redox couple.

The redox sites, R, are incorporated between the electrodes within the Hg-SAM//R//SAM-Hg junction ([figure 3c](#)) by trapping them via electrostatic interactions at the interface of the SAMs of alkanethiolate terminated with carboxylic acid groups. We selected the carboxylic acid functionality as the head group for two reasons: (i) carboxylic acid tail groups can be ionized at pH > 4, so COO⁻ moieties attract the positively charged Ru(NH₃)₆³⁺ ions at the surface of the SAM and (ii) the defects caused by electrostatic repulsion between the COO⁻ terminating groups allow the Ru(NH₃)₆³⁺ ions to access the surfaces of the electrodes. To assemble the junction, we extruded two Hg drops from two microsyringes, both of which are immersed in a solution of 11-mercaptodecanoic acid (HSC₁₀COOH) to form the carboxylic-terminating SAMs. After rinsing, they are placed in a solution of Ru(NH₃)₆³⁺. When they are brought in contact by a micromanipulator, the redox sites are trapped between the two electrodes.

[Figure 4](#) shows a plot of log J for Hg-drop junctions incorporating SAMs of n -alkanethiolates versus the total number of carbons in the alkyl chain(s) between the electrodes in the junction ([Weiss *et al.* 2007](#)). A linear least-squares fit ($R^2=0.971$) to the largest dataset—that collected at $V=0.4\text{--}0.5$ V—yields

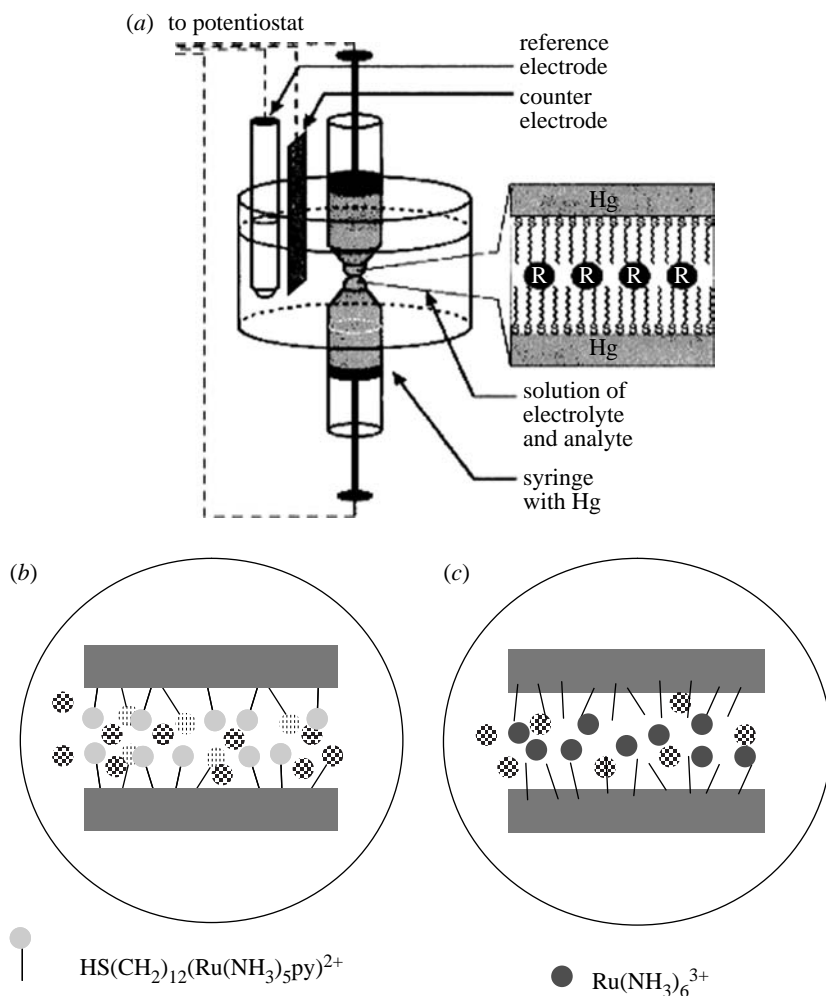


Figure 3. (a) Diagram of the electrochemical mercury-drop junction. The inset is a close-up of redox centres that are trapped at the interface of the two SAMs (each chemisorbed to mercury) to form the junction Hg-SAM₁//R//SAM₂-Hg. A less-idealized cartoon of this type of interface is shown in (c). (b) A cartoon of the interface formed when two SAMs on mercury, each covalently bonded to a redox centre, are contacted to form the junction Hg-SAM₁-R//R-SAM₂-Hg.

$\beta = 1.1/\text{carbon}$ (0.85 \AA^{-1}). Aggregated dataset 2 (the solid circles) contains values of J measured at $V = -1.5 \text{ V}$ (in an electrochemical setup). For this dataset, $\beta = 0.86/\text{methylene group}$ (0.69 \AA^{-1}), and $J_0 = 1.7 \times 10^2 \text{ Acm}^{-2}$.

4. Reproducibility of measurements of charge transport

Efforts to interpret and use several types of remarkable phenomena that have been observed in organic and molecular-scale devices—phenomena such as molecular rectification (Ranganathan *et al.* 2001; Chabynec 2002; Vilan *et al.* 2003) and negative differential resistance (Esaki 1958; Gunn 1963; Sollner *et al.* 1983; Rawlett *et al.* 2002; Chen & Reed 2002; Kratochvilova *et al.* 2002b)—have

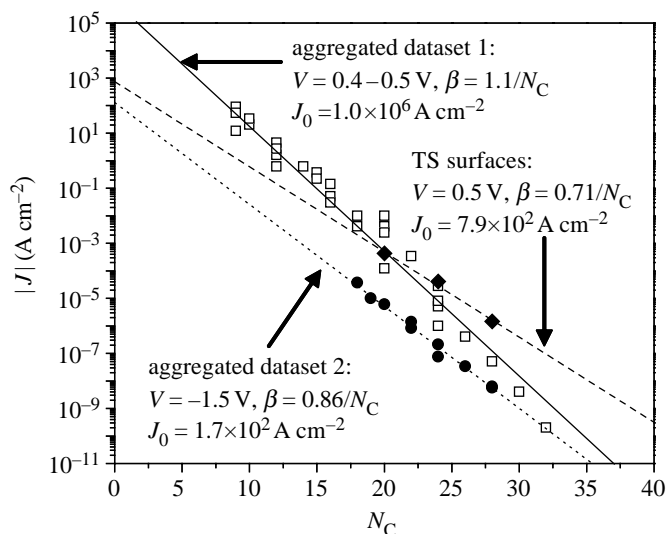


Figure 4. Log J for Hg-drop junctions incorporating SAMs of n -alkanethiolates versus the total number of carbons in the alkyl chain(s) between the electrodes in the junction. The slope of the linear least-squares fit to these data is $\beta/2.3$. In the calculation of β , all points are weighted equally. Aggregated dataset 1 (the solid diamonds and open squares) includes values of J measured at $V = 0.4$ or 0.5 V (the solid diamonds are data acquired using template-stripped surfaces, see text). For this dataset, $\beta = 1.1/\text{methylene group}$ (0.85 \AA^{-1}), and $J_0 = 1.0 \times 10^6 \text{ A cm}^{-2}$. Aggregated dataset 2 (the solid circles) contains values of J measured at $V = -1.5 \text{ V}$. For this dataset, $\beta = 0.86/\text{methylene group}$ (0.69 \AA^{-1}), and $J_0 = 1.7 \times 10^2 \text{ A cm}^{-2}$. (Reprinted with permission from the *Journal of the American Chemical Society*)

been hampered by the inability of researchers to duplicate each other's results or even construct identical devices and junctions on which to obtain these results. Differing degrees of both intramolecular disorder within the organic film and defects at the metal–organic interfaces (caused by defects in or impurities on the electrodes or the use of different methods of film deposition) are two major sources of irreproducibility of electrical measurements. For devices where current is limited by transport through the bulk, i.e. organic devices where the film is hundreds of nanometers thick, variation in intermolecular order (usually due to variation in the morphology of the polymer film) is a major cause of discrepancies in performance from device to device. For molecular-scale electronic devices, where the organic film is, at most, tens of angstroms thick, CT across the metal–molecule interfaces is often the rate-limiting step; furthermore, the currents through these devices may be masked by defect-mediated current (caused by filaments between the electrodes or contact of the electrodes with disordered sections of the SAM).

(a) Survey of defects in SAMs formed on metal substrates

Many of the defects that occur at the metal–organic interface of a SAM on a metal substrate have the potential to contribute to (or even dominate) the current through the SAM. For instance, migration of metal atoms from the surface of one electrode to the second electrode may result in a highly conductive

pathway (or filament) between the electrodes through which electrons can travel (Haynie *et al.* 2003). In the case of SAMs of *n*-alkanethiolates, step edges and grain boundaries in the metal surface probably result in ‘thin areas’ of the SAM, where the molecules are not *trans*-extended and the top electrode contacts a disordered region of the SAM; this type of defect may result in a reduced length of the through-bond pathway between the electrodes and increased current (compared with that through the all-*trans* molecules). Vacancy islands form when individual metal (usually silver) atoms dissociate from the plane of the metal surface upon formation of the thiolate bond and migrate to form raised islands (Laibinis *et al.* 1991*b*; Bucher *et al.* 1994; Dhirani *et al.* 1995). The reorganization process leaves behind vacancies of one or a few metal atoms that are one atomic step (approx. 0.5 nm for silver) below the surface; isolated vacancies may also anneal into larger vacancy islands (Bucher *et al.* 1994; Dhirani *et al.* 1995; Yamada *et al.* 2000). Raised vacancy islands form when metal atoms do not migrate to step edges, but rather form small clusters on the surface that are one atomic step above the surrounding atoms. The molecules on raised vacancy islands are not stabilized by the molecular lattice and may become disordered (or perhaps deformed) under the pressure of the top electrode (Love *et al.* 2005). If solvent is present in the junction (such as in the case of many mercury-drop junctions; Chabinye 2002; Tran *et al.* 2005), solvent molecules may become trapped within a gap at metal//SAM or SAM//SAM (in the case of bilayer junctions) van der Waals interfaces when a molecule ‘kinks’, i.e. bends over within the SAM and curls away from the top contact. If one chain bends, another chain will bend on top of it, and packing of the terminal ends of the chains of the few surrounding molecules will be disordered relative to that of *trans*-extended chains. Molecules may kink due to, for example, the presence of grain boundaries or step edges in the metal film or impurities in solvents and reagents that deposit on the metal surface during SAM formation and cause irregularities in the metal lattice (Hieber 1976; Laibinis *et al.* 1991*b*; Hoogvliet & van Bennekom 2001).

(*b*) *Formation of ultrasmooth substrates using template-stripping*

One way to minimize the frequency of defects at the electrode–organic interface and within the bulk of the organic layer is to start with an atomically smooth electrode. Ultrasmooth metal substrates—those with low root-mean-squared (RMS) roughness and large, flat grains (compared with that of the films characterized as deposited, AS-DEP, by e-beam evaporation)—produced with the general method of template stripping (TS; Wagner *et al.* 1995) have proven to be useful in the study and application of well-ordered SAMs (Wagner *et al.* 1995; Hsaio *et al.* 1996; Diebel *et al.* 2001; Unal *et al.* 2002; Naumann *et al.* 2003; Ragan *et al.* 2004; Zhou *et al.* 2004; Engelkes *et al.* 2005; He *et al.* 2005). Recently, we developed a procedure (Weiss *et al.* in preparation) by which we prepared ultrasmooth metal films by evaporating the metal onto a silicon wafer supporting a native oxide layer (the ultraflat ‘template’; Hegner *et al.* 1993; Samori *et al.* 1999; Ederth 2000; Diebel *et al.* 2001; Unal *et al.* 2002; Naumann 2003; Rossetti *et al.* 2003; Gupta *et al.* 2004; Ragan *et al.* 2004; Engelkes *et al.* 2005), attaching a mechanical support—either a composite of a glass slide and optical adhesive (glass/OA), a composite of polydimethylsiloxane and optical

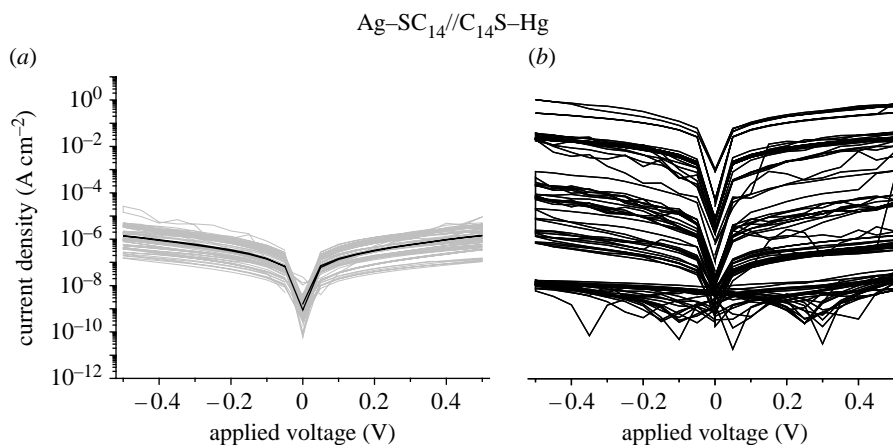


Figure 5. (a) Plot of the average $|J|$ - V curves (bold black line) and all $|J|$ - V curves (light grey lines) measured on the TS junctions Ag-SC₁₄//C₁₄S-Hg, except for the initial traces that had a current density several orders of magnitude below the remaining traces, and traces directly preceding and following amalgamation. (b) The same set of traces for the corresponding junction using AS-DEP silver. (No averages were calculated for these data.) (Reprinted with permission from the *Journal of the American Chemical Society*)

adhesive (PDMS/OA), or a drop of solder—to the top of the evaporated metal film, and cleaving the metal film from the template to expose the face of the film that had been adjacent to the Si/SiO₂ surface. The template-stripping method produces, as a precursor to the ultrasmooth film, a ‘sandwich structure’ that is composed of the template, the film and the mechanical support. In this sandwich structure, the template protects the functional surface of the metal film from any environmental contaminants and from oxidation (even for readily oxidized materials like silver); thus, we are able to store the films for at least two months between the evaporation of the film and use (or structural characterization) of the film, without contamination (Diebel *et al.* 2001; Ragan *et al.* 2004). We can also separate the TS film from the protecting template by immersing the sandwich structure in a solution of thiols (chemical template stripping), such that the film never comes into contact with O₂.

We observed (through infrared spectroscopy) that the SAMs formed on the ultrasmooth template-stripped silver surfaces were more crystalline than those on the AS-DEP substrates. The low frequency of defects on the TS surfaces and the high degree of order of the SAMs formed on these surfaces, relative to the AS-DEP surfaces, significantly enhanced the electrical stability of the mercury-drop junction incorporating the TS samples. Junctions with SAMs on AS-DEP substrates failed (by amalgamation of the Ag and Hg electrodes), on average, 4.6 times more often during I - V traces 1–3, and 3.5 times more often during I - V traces 1–5 than did SAMs on TS substrates (where $V=0\text{ V}\rightarrow 0.5\text{ V}\rightarrow -0.5\text{ V}\rightarrow 0\text{ V}$, in steps of 0.05 V). The template-stripping procedure also produced junctions whose electrical characteristics were substantially more reproducible (Weiss *et al.* 2007). For example, figure 5a shows all of the $|J|$ - V curves (light grey lines) measured on the TS junctions Ag-SC₁₄//C₁₄S-Hg except for: (i) initial traces that had a current density several orders of magnitude below the remaining traces and

(ii) traces directly preceding and following amalgamation. Figure 5*b* contains the same set of traces for the corresponding AS-DEP junctions. Use of ultraflat Ag as the substrate for the SAM decreased the range in measured values of J by 10^6 .

5. Future directions and additional remarks

There are three especially promising directions for the mercury-drop junction as follows. (i) The junction has proven useful for the measurement of current–voltage characteristics (both dark and under illumination) of ordered films of semiconductor nanocrystals. Glass coated with indium tin oxide (ITO) is a common substrate for these films because it allows the films to be incorporated into solar cells and photodetectors; ITO is also a convenient ‘bottom contact’ within the mercury-drop junction because it does not amalgamate with mercury. Preliminary experiments indicate that I – V curves for these films with mercury as a top contact are reproducible. (ii) We are designing and constructing a system by which pressurized flow of mercury through microchannels positions hundreds to thousands of mercury drops above SAMs that have been patterned on a common substrate; these drops are then extruded simultaneously and individually electrically addressed in order to parallelize the I – V measurement. In this way, we can gather meaningful statistics on current densities and efficiently screen organic molecules for their potential as components in electronic devices. (iii) Much of the irreproducibility in the measurements of current density using the mercury-drop junction comes from the fact that the mercury drop consistently amalgamates with the bottom electrode if the measurement is not performed under solvent (usually hexadecane) or a solution of thiol. Solvent molecules then become trapped at the SAM//SAM interface and cause heterogeneity in the topography of this interface. The replacement of mercury, which is also problematic owing to its high reactivity with environmental contaminants, with a eutectic metal—specifically, an indium/gallium alloy that is a liquid at room temperature—alleviates many of these problems. In/Ga does not amalgamate with the metals commonly used as substrates for SAMs, it does not (to our knowledge) react readily with thiol contaminants, and it may be ‘pulled’ to create a junction with a diameter approximately 10 times smaller than that which may be formed with the mercury drop. We can, therefore, perform these measurements ‘dry’, i.e. in the absence of a solvent bath, and smaller junctions, in general, incorporate fewer defects and lead to a smaller range in values of current density measured for a given junction than do larger junctions. Currently, we are pursuing all three of these directions.

A final, more general, note is that in the fields of both organic and molecular-scale electronics, there still exists a major difference in philosophy between chemists and engineers. Chemists often concentrate on molecular properties of the organic bulk within a device or junction without considering the effect of interfacing the organic material with the metal electrodes. Engineers understand the properties of interfaces (tunnelling barriers, diodes, etc.) but often do not pay attention to the fact that organic molecules cannot always be treated as bulk dielectric layers. A molecule is a spatially and energetically diverse (and environment-sensitive) landscape, and the electronic structure of a molecule is,

by definition, responsible for its electronic properties, both within the bulk and at an interface with another material. Both characteristics—the molecular and supramolecular structure of the organic material and the nature of the metal–organic interface—are equally important in determining the performance of the device. Theorists have recognized this fact and have designed programmes to incorporate explicit electronic structure in the bulk and at the interface, but do not yet have the tools to predict the characteristics of junctions with more than a few molecules and a few metal atoms.

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