Controlling the electron transfer mechanism in metal–molecules–metal junctions

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Received 24 November 2004; received in revised form 10 April 2005; accepted 10 April 2005
Available online 5 July 2005

Abstract

We show how the mechanism of electron transfer through molecules can be switched between different regimes by using Hg-based metal–molecules–metal junctions. The junctions are easy to assemble and allow for hosting of self-assembled monolayers (SAMs) of a large variety of molecular structures. In this paper, we compare results from studies of charge transport across two different types of junctions. The first approach has been reported previously and involves the use of a two-electrode junction, Hg–SAM//SAM–Ag, to measure I–V curves through SAMs formed from different organic molecules [alkanethiols HS(CH 2 ) n−1 CH 3 (n = 8, 10, 12, 14, 16), oligophenylene thiols HS(C 6 H 4 ) kH (k = 1, 2, 3), or benzylic homologs of the oligophenylene thiols HSCH 2 (C 6 H 4 ) mH (m = 1, 2, 3)]. The molecules incorporated have a very large HOMO–LUMO energy separation and their orbitals cannot align with the Fermi levels of the electrodes under an applied voltage. The molecules therefore behave as insulators, and the electron transport mechanism is characterized by a non-resonant tunneling process. The second approach is new and involves the use of an electrochemical junction, Hg–SAM//SAM–Hg, with SAM formed by electroactive thiol molecules [HS(CH 2 ) 10 CONHCH 2 pyRu(NH 3 ) 5 (PF 6 ) 2 ]. Charge transport across the junction is measured using a conventional electrochemical technique, which allows the potentials of the Hg electrodes relative to that of a reference electrode to be controlled with respect to the redox potential of the incorporated redox-active molecules. We show that under this control of potential the electron transport mechanism can be switched to different regimes and the current flowing through the junction can be modulated. The current changes of order of magnitude (NDR effect) as a result of a change of the mechanism of electron transport from non-resonant to resonant tunneling (or hopping). © 2005 Elsevier Ltd. All rights reserved.

Keywords: Molecular electronics; Electron transfer mechanism; Metal–molecules–metal junctions; Self-assembled monolayers; Mercury

1. Introduction

Electron transfer is the single most important chemical reaction. It is (i) an elementary process amenable to detailed theoretical description and experimental investigation [1]; (ii) a key step in a number of important biological processes [2,3]; and (iii) a fundamental feature of many processes of great technological impact [4]. While at the molecular and bulk level charge transfer processes are now fairly well understood, at the nanoscale they still present several unanswered problems, like the role of the molecule–metal contact or the difficulty to calculate a priori the I–V behavior for a given metal–molecules–metal junction [5]. The control of the mechanism of charge transfer through molecules is a fundamental task both for theoretical studies and for applications in areas such as sensors [6], photonics [7], electrocatalysis [8], and solar conversion [9]. Whether or not molecular species are suitable as active components in electronic devices is a matter of discussion [4,10–12], but information gained from studies of molecular electronics will certainly increase our predictive capabilities for electron transport through organic matter at the nanometer scale. Several key features indicate that organic
and acceptor units are almost isoenergetic, the electron trans-
of the molecule. When the molecular levels and the donor
acceptor. The mechanism of electron transfer will be domi-
nated by a non-resonant tunneling regime, characterized by
the dependence of the electron transfer regime on the posi-
tion of the molecular bridge with respect to the energy of the
D and A units is a critical param-
er which determines the mechanism of the electron transfer
process.

In 1971, in a pioneer work Kuhn used two metal electrodes
as electron donor and acceptor for measuring electron trans-
port processes through Langmuir–Blodgett films [13]. The
possibility to use molecular properties for making electronic
devices was first envisaged by Aviram and Ratner in a the-
oretical paper in 1974 [14]. In the middle of the 1990s, the
improvements in nanofabrication [15] and scanning micro-
scopies [16], together with the possibility to interface in
a stable way molecules to a metal surface [17], triggered
the fabrication of metal–molecules–metal junctions and also
opened the door to experimental “molecular electronics”.

In electron transfer studies, the molecules that bridge
electron donor and acceptor units (either molecular units in
D–B–A systems or two metal surfaces in junctions), are col-
loquially called ‘molecular wires’ to emphasize the ability
of the molecular bridge to facilitate electron transfer from
A to B. It should be clear that the term ‘wire’ is in some
way misleading, since it implies ohmic conductivity. Such
a feature has not been observed with any of the molecu-
lar bridges discovered to date; studies of electron transfer
through “molecular wires”, in fact, have so far shown that
the process occurs through a tunneling mechanism. This
term therefore must be understood as referring to the abil-
ity of molecules to facilitate electron transport with respect
to vacuum.

Mechanisms of electron transfer through organic
molecules both in D–B–A systems [5,18–21] and in junctions
[5,22–29] have been discussed in detail in several theoretical
and experimental studies. In Fig. 1, we show schematically
the dependence of the electron transfer regime on the posi-
tion of the energy levels of a molecular bridge with respect
to the energy levels of the electron donor or acceptor units,
regardless of the nature of these units (molecular systems or
electrodes). Fig. 1a represents a system where the molecular
levels are very high in energy with respect to the donor and
acceptor. The mechanism of electron transfer will be domi-
nated by a non-resonant tunneling regime, characterized by
a “through-bond” mechanism, and the electron transfer rate
will exhibit a negative exponential decay with d, the length
of the molecule. When the molecular levels and the donor
and acceptor units are almost isoenergetic, the electron trans-
fer mechanism changes regime and the electron transfer rate
is expected to have a “shallow” dependence on d (Fig. 1b)
[30,31]. Whether the electron transfer process takes place via
one-step resonant tunneling or two-step single molecule elec-
etrochemistry has been discussed theoretically [32–35], but is
difficult to determine experimentally [36–39]. Fig. 1 clearly
indicates that the position of the molecular energy levels with
respect to the energy of the D and A units is a critical param-
eter which determines the mechanism of the electron transfer
process.

In D–B–A systems, processes of electron transfer oper-
atating through different mechanisms can be achieved only
through the synthesis of specific D, B, and A units [40]. A
metal–molecules–metal junction, on the other hand, offers
the advantage that it is, in principle, possible to bring the
energy of the Fermi levels of the electrodes in resonance with
the energy of the LUMO (or HOMO) of the molecule by sim-
ply increasing the voltage applied to the electrodes. Several
authors have measured a maximum peak (negative differen-
tial resistance, NDR) in current density when increasing the
voltage [40], and interpreted this effect as due to the alignment
of the Fermi level with the molecular states. This interpre-
tation, however, has been clearly proven in only a few cases
[36,41]. In other studies [42–45], the observed NDR effect
has been related to a conformational change of the molecules
and to other effects.

Incorporation of redox sites in molecular bridges is par-
ticularly suitable for studying this kind of effects. Because
of their well-defined, easy to reach, tunable energy states,
redox centers have been extensively used both for design-
ing molecular systems mimicking electronic functions and
for basic electron transfer studies. For example, studies of
electron transfer processes in donor-acceptor supramolecu-
lar systems incorporating redox centers have shown that they
can be used to modulate or trigger the electron transfer pro-
ces between a donor and an acceptor [46]. Supramolecular

![Energy diagrams for donor-molecule-acceptor systems](image-url)
systems with multiple redox centers organized at a metal electrode have been shown to exhibit rectification effects that depend on the relative redox potential of the redox centers [47]. Electroactive polymers sandwiched between microelectrodes have been shown to mediate the current flowing between the electrodes [48–50]. In other studies, several groups [36,37,41,51,52], using STM technique, have measured current mediated by the accessible states of redox centers. Lastly, sophisticated junctions, incorporating single redox center between the two electrodes, have shown transistor-like behavior and Kondo effects at low temperature (100 K)[53,54].

In this paper, we use a versatile junction that allows for easy incorporation of different molecular systems to demonstrate (i) that organic molecules with a large HOMO–LUMO separation (so that under an applied potential of the electrode, the Fermi levels cannot match the LUMO or HOMO), behave as insulators, and (ii) that a change in the electron transfer process and, therefore, in current density can be achieved when the incorporated chemical system has molecular orbitals which can easily align with the Fermi levels of the electrodes. More specifically, we show that in the latter case the junction exhibits electronic functions like “on–off” switching by controlling the potential of the electrodes with respect to the energy of the molecular levels.

We have assembled, characterized, and studied two different types of junctions, using Hg-based electrodes (Fig. 2). The first type J$_{Ag}$–SAM$\langle 1 \rangle$/SAM$\langle 2 \rangle$–Hg, which has been described elsewhere [55–57], consists of a solid silver electrode and a liquid mercury drop electrode, each of which is covered with a SAM of a different type of organothiol. The second type, J$_{Hg}$–SAM$\langle 1 \rangle$/SAM$\langle 2 \rangle$–Hg, consists of two Hg drop electrodes covered with organothiol SAMs that are terminated with redox-active metal centers [58]. Recent work on Hg-based junctions is also available by others [59–63].

2. Results and discussion

2.1. The tunneling junction, J$_{Hg}$–SAM$\langle 1 \rangle$/SAM$\langle 2 \rangle$–M (Fig. 2a)

The fabrication of these junctions has been described previously [64]. To compare the electron transport characteristics of different molecules, we have used junctions wherein SAM(2) is incorporated with molecules of different length and structure and the composition of SAM(1) on Hg is kept constant (being hexadecanethiol). Three series of junctions with different SAM(2) were assembled: SAM(2) was formed either from alkanethiols HS(CH$_2$)$_n$CH$_3$ ($n = 8, 10, 12, 14, 16$), oligophenylene thiols HS(C$_6$H$_4$)$_k$H ($k = 1, 2, 3$), or benzylic homologs of the oligophenylene thiols HSCH$_2$(C$_6$H$_4$)$_m$H ($m = 1, 2, 3$) (Fig. 3) [56,57]. We observe that the current density decreases with increasing length of the molecules forming SAM(2), and, therefore, with the distance separating the electrodes ($d_{Ag,Hg}$). The decrease in current,
Fig. 3. Plots of current density as a function of the bias voltage between the mercury and silver electrodes for $J_{\text{Hg-C16//SAM(2)-Ag}}$ junctions. The symbols used to represent different classes of compounds forming SAM(2) are: (●) aliphatic thiols $\text{HS(CH}_2\text{)}^n\text{CH}_3$; (■) oligophenylene thiols $\text{HS(C}_6\text{H}_4\text{)}^k\text{H}$; (▼) benzylic homologs $\text{HSCH}_2\text{(C}_6\text{H}_4\text{)}^m\text{H}$. The data were obtained using statistically significant populations ($N = 20$) of junctions [56,57].

$I_{et}$ with increasing length of the molecules forming SAM(2) followed the relation

$$I_{et} = I_0 e^{-\beta d}$$

(1)

where $d$ is the length of the bridge, and $\beta$ the so-called “decay factor” that correlates the rate of electron transfer with the chemical structure of the bridge. For a tunneling mechanism, the rate of electron transfer depends exponentially on the distance between $D$ and $A$ according to Eq. (1).

Our data, interpreted according to Eq. (1), thus gives for alkanethiols $\beta = 0.87 \pm 0.10 \text{Å}^{-1}$; for oligophenylene thiols, $\beta = 0.67 \pm 0.10 \text{Å}^{-1}$; and for the benzylic derivatives of oligophenylene thiols, $\beta = 0.66 \pm 0.10 \text{Å}^{-1}$ (Fig. 4) [26]. The values of $\beta$ are approximately independent of $V$ (over the range of 0.1–1 V). We observe that these values are in good agreement with corresponding values obtained by photoinduced electron transfer in molecular D–B–A systems [56].

2.2. The electrochemical junction, $J_{\text{Hg-SAM-M/M-SAM-Hg}}$

This junction is composed of a bilayer of the redox-active thiol, $[\text{HS(CH}_2\text{)}^n\text{CONHCH}_2\text{pyRu(NH}_3\text{)}^5\text{PF}_6]^2$ [65,66], sandwiched between two Hg drop electrodes (Fig. 2). The SAMs were formed in a single-compartment electrochemical cell by immersing freshly extruded Hg drops into a 1 mM acetonitrile solution of the thiol compound and incubating for 5 min before rinsing successively with acetonitrile and water. After removal of the washing solvents, the cell was filled with an aqueous solution of $\text{Na}_2\text{SO}_4$ that had been adjusted to pH 4 and the mercury–SAM surfaces were then brought into contact in the presence of this solution using a micromanipulator as described previously for the $J_{\text{Hg-SAM(1)//SAM(2)-M}}$ junction. The diameter of the contact area between the two Hg drops was ca. 0.5 mm. In order to control the potentials of the Hg electrodes with respect to the electrochemical potential of the redox site, an Ag/AgCl reference electrode and a platinum counter electrode were also added to the cell and all the electrodes were connected to a bipotentiostat. The potentials of the Hg electrodes can be controlled independently relative to that of the reference electrode (Fig. 5). Thus, one
Hg electrode acted as an electron donor (cathode, C) and the other as electron acceptor (anode, A).

**Fig. 6a** shows the *I–V* characteristics of the junction when the potential of the cathode is fixed with respect to the reference electrode so that the attached ruthenium is in its +2 oxidation state (i.e., \( V_{CR} \) is fixed at \( -0.20 \text{ V} \)), and the potential of the anode is varied with respect to the reference (i.e., \( V_{AR} \) is varied). For \( V_{AR} \leq V_{CR} \), the currents are negligible and the junction is non-conducting. When \( V_{AR} \) is increased to values more positive than \( -0.14 \text{ V} \), a current flows at both the anode and the cathode, corresponding to the oxidation of \( \text{Ru}^{II} \) to \( \text{Ru}^{III} \) and the reduction of \( \text{Ru}^{III} \) to \( \text{Ru}^{II} \), respectively.

The anodic and cathodic currents are equal and increase to a plateau with a half-wave (half-maximum) potential, \( E^{0'} \), of the \( \text{Ru}^{II}/\text{III} \) couple. In control experiments, where the cathode was either bare or covered with a non-electroactive thiol SAM, negligible current was observed at the cathode. This shows that redox centers at both electrodes are necessary for the current to pass from one electrode to another. The total charge transport through the junction is therefore proposed to occur via the following key steps: oxidation of \( \text{Ru}^{II} \) to \( \text{Ru}^{III} \) at the anode, electron exchange between \( \text{Ru}^{III} \) at the anode and \( \text{Ru}^{II} \) at the cathode, and reduction of \( \text{Ru}^{III} \) at the cathode back to \( \text{Ru}^{II} \) monolayers.

The process can also be explained in terms of an energy diagram relating the potential of the mercury electrodes on the Ag/AgCl scale to vacuum and to the corresponding Fermi energy (Fig. 6b). When both the anode and cathode are at potentials very positive or negative relative to \( E^{0'} \), no current flows and the junction is non-conducting. The current flows only when the electronic states of the \( \text{Ru}^{II}/\text{III} \) couple fall between the Fermi energies of the mercury electrodes.

**Fig. 7a** shows the *I–V* characteristics of the junction when the potentials of the cathode and the anode are fixed with respect to each other (i.e., \( V_{CA} = +0.10 \text{ V} \)), and, again, the...
Fig. 7. (a) Current voltage characteristics ($I_A$ as a function of $V_{AR}$) of the $\text{J Hg–SAM}/\text{SAM–Hg}$ junction for $V_{CA}$ fixed at $+0.10 \, \text{V}$, scan rate $50 \, \text{mV s}^{-1}$. (b) Interpretation of the process in terms of an energy diagram.

Potential of the anode with respect to the reference electrode (i.e., $V_{AR}$) is varied. The anodic current is negligible for $V_{AR}$ less than $-0.25 \, \text{V}$ and greater than $+0.15 \, \text{V}$. Upon scanning $V_{AR}$ from $-0.25$ to $+0.15 \, \text{V}$, the current increases from zero to a maximum value near the $E^{o}$ of the redox couple and then decreases again to zero. Charges therefore pass from one electrode to another only when $V_{AR}$ is at or close to the Ru$^{II}$/Ru$^{III}$ redox potential. This process can be explained in terms of an energy diagram (Fig. 7b) analogous to the one in Fig. 6b. Again, the current flows only when the electronic states of the Ru$^{II}$/Ru$^{III}$ couple fall between the Fermi energies of the mercury electrodes. The observation that the current scales with $V_{AR}$ is indicative of transistor-like behavior (the electrolyte in this case being the gate) [67].

Unlike conventional solid-state devices which exhibit linear and saturation regions for a given applied gate bias, however, the current passing through the Hg–SAM–M/M–SAM–Hg junction described here increases nonlinearly with increasing $V_{CA}$. Similar current–potential curves have been reported for a number of systems [68], where charge transport has also been proposed to occur via an electron hopping mechanism. Such behavior has been attributed to field-dependent charge mobility.

3. Conclusions

We have used a Hg-based metal–molecules–metal junctions that allows (i) for easy assembly and (ii) for hosting of SAMs of a large variety of molecular systems. In particular we have demonstrated that by using an electrochemical four-electrode junction, that allows for controlling the energy of the Fermi levels of the electrodes respect to the energy of the molecular orbitals of incorporated molecules, it is possible to modulate the current flowing through the junction. When the Fermi levels of the electrodes align with the molecular orbitals, the current flowing through the junction increases by orders of magnitude (NDR effect). Under these conditions, the electron transport mechanism switches to a different regime, that is from a non-resonant to a resonant tunneling. Whether the mechanism responsible for such an increase in current is a one-step resonant tunneling or a two-step hopping mechanism [38–41] is under analysis. On the other side, we compare these results with previous experiments performed by using a two-electrodes junction, where the molecules incorporated have a very large HOMO–LUMO energy separation and their molecular orbitals cannot align with the Fermi levels of the electrodes, and the molecules behave as insulators. In this case the electron transport mechanism is characterized by a through-bond non-resonant tunneling. Comparisons of these results indicate that only by using an electrochemical junction it is possible (i) to control the amount of current flowing through the junction; (ii) to predict the potential at which the increase in current will occur; and (iii) to address different electron transport mechanisms.

Acknowledgments

This work was supported by the ONR, DARPA, and the NSF (IICS-9729405) (USA), by the CNR (Italy) and the European Union (Grants G5RD-CT-2002-00776 MWFM and IST-2001-35503 LIMM).

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