

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

Elizabeth Tran<sup>a</sup>, Christian Grave<sup>b</sup>, George M. Whitesides<sup>a</sup>, Maria A. Rampi<sup>b,\*</sup>

<sup>a</sup> Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138, USA

<sup>b</sup> Dipartimento di Chimica, Centro di Fotochimica CNR, Università di Ferrara, Via L. Borsari 46, Ferrara 44100, Italy

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### 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  $\text{HS}(\text{CH}_2)_{n-1}\text{CH}_3$  ( $n = 8, 10, 12, 14, 16$ ), oligophenylene thiols  $\text{HS}(\text{C}_6\text{H}_4)_k\text{H}$  ( $k = 1, 2, 3$ ), or benzylic homologs of the oligophenylene thiols  $\text{HSCH}_2(\text{C}_6\text{H}_4)_m\text{H}$  ( $m = 1, 2, 3$ )]. 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  $[\text{HS}(\text{CH}_2)_{10}\text{CONHCH}_2\text{pyRu}(\text{NH}_3)_5](\text{PF}_6)_2$ . 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. The incorporated redox sites have energetically low molecular orbitals which can align with the Fermi levels of the electrodes. 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).

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### 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–molecule–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

\* Corresponding author.

E-mail address: [rmp@unife.it](mailto:rmp@unife.it) (M.A. Rampi).

and organometallic molecules are attractive as alternatives to solid-state materials at the nm-scale; these include the ease of tuning their electronic structure, and their potential for self-assembly.

Investigations on electron transfer reactions through molecules over the past 50 years have focused on measuring the rate of the transfer process between donor and acceptor species that exist in solution either as free solutes or as separate sites of larger molecules [1]. In particular, electron transfer studies between donor and acceptor units covalently linked through a molecular bridge in D–B–A systems (D = donor, A = acceptor, B = molecular bridge) have underlined the role of the chemical structure of the bridge in facilitating electron transfer from D to A.

In 1971, in a pioneer work Kuhn used two metal electrodes as electron donor and acceptor for measuring electron transport 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 theoretical paper in 1974 [14]. In the middle of the 1990s, the improvements in nanofabrication [15] and scanning microscopies [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 colloquially 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 molecular 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 ability 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 position 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 dominated 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 transfer mechanism changes regime and the electron transfer rate

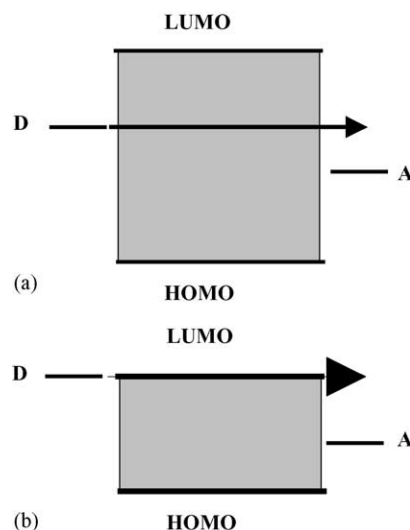


Fig. 1. Energy diagrams for donor–molecule–acceptor systems. D = donor, A = acceptor. The molecular orbitals and the Fermi levels of the electrodes are (a) not aligned; (b) aligned.

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 electrochemistry 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 parameter which determines the mechanism of the electron transfer process.

In D–B–A systems, processes of electron transfer operating 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 simply increasing the voltage applied to the electrodes. Several authors have measured a maximum peak (negative differential 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 interpretation, 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 particularly 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 designing molecular systems mimicking electronic functions and for basic electron transfer studies. For example, studies of electron transfer processes in donor–acceptor supramolecular systems incorporating redox centers have shown that they can be used to modulate or trigger the electron transfer processes between a donor and an acceptor [46]. Supramolecular

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  $J_{\text{Ag-SAM}(1)//\text{SAM}(2)\text{-Hg}}$ , 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,  $J_{\text{Hg-SAM-M//M-SAM-Hg}}$ , 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, $J_{\text{Hg-SAM}(1)//\text{SAM}(2)\text{-M}}$ (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) are 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  $\text{HS}(\text{CH}_2)_{n-1}\text{CH}_3$  ( $n = 8, 10, 12, 14, 16$ ), oligophenylene thiols  $\text{HS}(\text{C}_6\text{H}_4)_k\text{H}$  ( $k = 1, 2, 3$ ), or benzylic homologs of the oligophenylene thiols  $\text{HSCH}_2(\text{C}_6\text{H}_4)_m\text{H}$  ( $m = 1, 2, 3$ ) (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 ( $d_{\text{Ag,Hg}}$ ). The decrease in current,

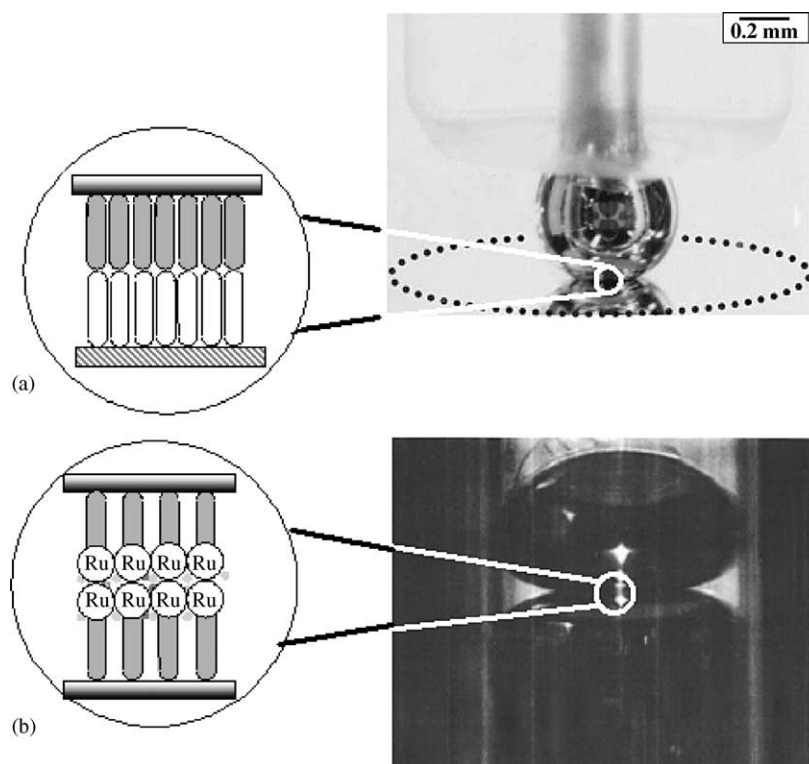


Fig. 2. Photography and schematic representation of the two types of junction. (a)  $J_{\text{Hg-SAM}(1)//\text{SAM}(2)\text{-Ag}}$ . (b)  $J_{\text{Hg-SAM//SAM-Hg}}$  with the SAMs carrying redox active sites in their periphery.

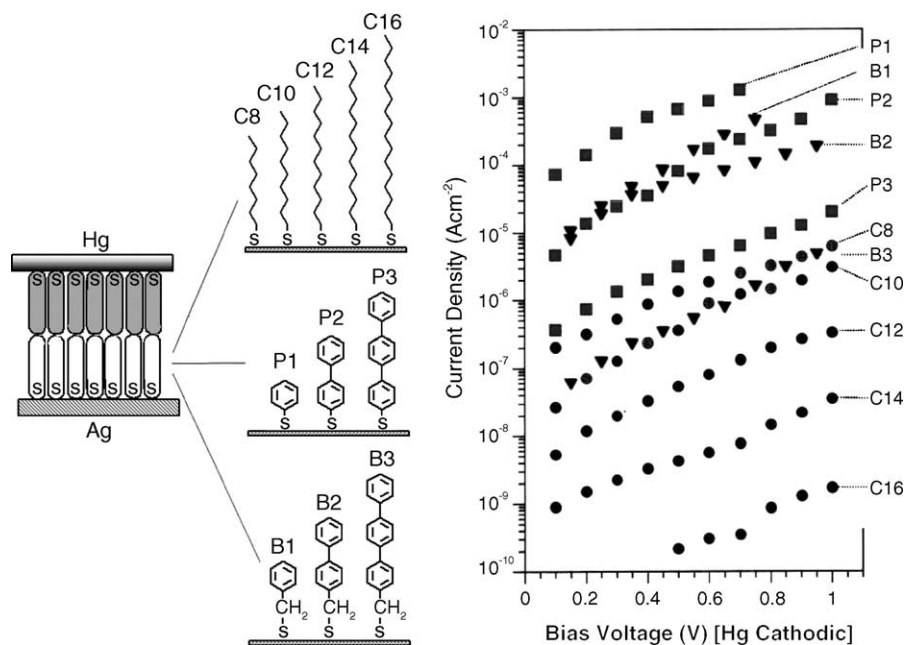


Fig. 3. Plots of current density as a function of the bias voltage between the mercury and silver electrodes for  $J_{\text{Hg-C16/SAM(2)-Ag}}$  junctions. The symbols used to represent different classes of compounds forming SAM(2) are: (●) aliphatic thiols  $\text{HS}(\text{CH}_2)_{n-1}\text{CH}_3$ ; (■) oligophenylene thiols  $\text{HS}(\text{C}_6\text{H}_4)_k\text{H}$ ; (▼) benzylic homologs  $\text{HSCH}_2(\text{C}_6\text{H}_4)_m\text{H}$ . The data were obtained using statistically significant populations ( $N=20$ ) of junctions [56,57].

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

$$I_{\text{et}} = I_0 e^{-\beta d} \quad (1)$$

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  $\beta = 0.87 \pm 0.10 \text{ \AA}^{-1}$ ; for oligophenylene thiols,  $\beta = 0.61 \pm 0.10 \text{ \AA}^{-1}$ ; and for the benzylic derivatives of oligophenylene thiols,  $\beta = 0.66 \pm 0.10 \text{ \AA}^{-1}$  (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,  $[\text{HS}(\text{CH}_2)_{10}\text{CONHCH}_2\text{pyRu}(\text{NH}_3)_5](\text{PF}_6)_2$  [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

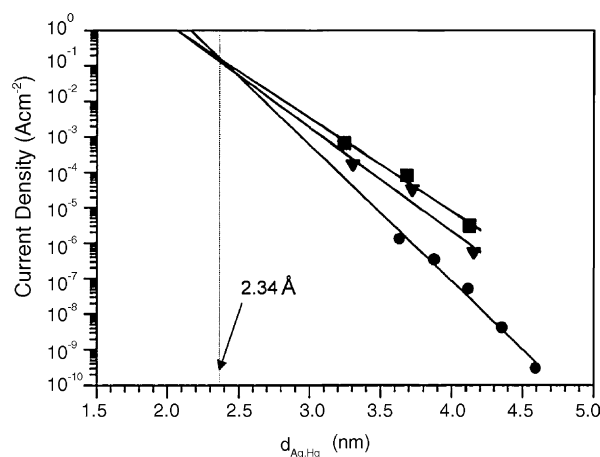


Fig. 4. Plot comparing the distance dependence of current density in  $J_{\text{Hg-C16/SAM(2)-Ag}}$  junctions: (●)  $\text{HS}(\text{CH}_2)_{n-1}\text{CH}_3$ ; (■)  $\text{HS}(\text{C}_6\text{H}_4)_k\text{H}$ ; (▼)  $\text{HSCH}_2(\text{C}_6\text{H}_4)_m\text{H}$ . Current densities were obtained at 0.5 V bias. The error in  $\beta$  is  $\sim 0.1 \text{ \AA}^{-1}$  [56,57].

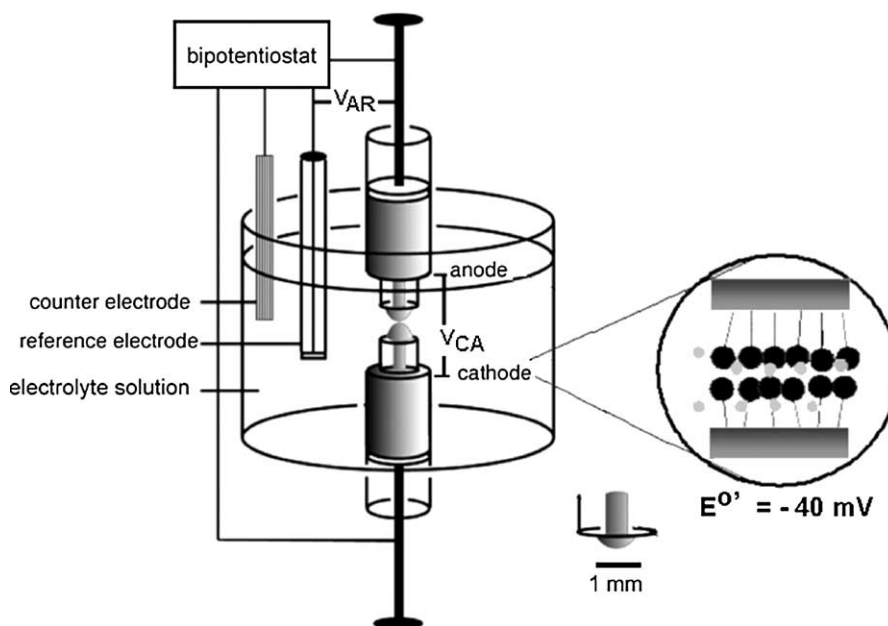


Fig. 5. Schematic representation of the electrochemical  $J_{\text{Hg-SAM/SAM-Hg}}$  junction with the SAMs carrying redox active sites in their periphery. For explanation, see text [58].

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.,  $V_{\text{CR}}$  is fixed at  $-0.20$  V), and the potential of the anode is varied with respect to the reference (i.e.  $V_{\text{AR}}$  is varied). For  $V_{\text{AR}} \leq V_{\text{CR}}$ , the currents are negligible and the junction is non-conducting. When  $V_{\text{AR}}$  is increased to values more positive than  $-0.14$  V, a current flows at both the anode and the cathode, corresponding to the oxidation of  $\text{Ru}^{\text{II}}$  to  $\text{Ru}^{\text{III}}$  and the reduction of  $\text{Ru}^{\text{III}}$  to  $\text{Ru}^{\text{II}}$ , respectively. The anodic and cathodic currents are equal and increase to a plateau with a half-wave (half-maximum) potential,  $-0.04$  V, that is near the formal potential,  $E^{\circ}$ , of the  $\text{Ru}^{\text{II/III}}$  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  $\text{Ru}^{\text{II}}$  to  $\text{Ru}^{\text{III}}$  at the anode, electron exchange between  $\text{Ru}^{\text{III}}$  at the anode and  $\text{Ru}^{\text{II}}$  at the cathode, and reduction of  $\text{Ru}^{\text{III}}$  at the cathode back to  $\text{Ru}^{\text{II}}$  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  $E^{\circ}$ , no current flows and the junction is non-conducting. The current flows only when the electronic states of the  $\text{Ru}^{\text{II/III}}$  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.,  $V_{\text{CA}} = +0.10$  V), and, again, the

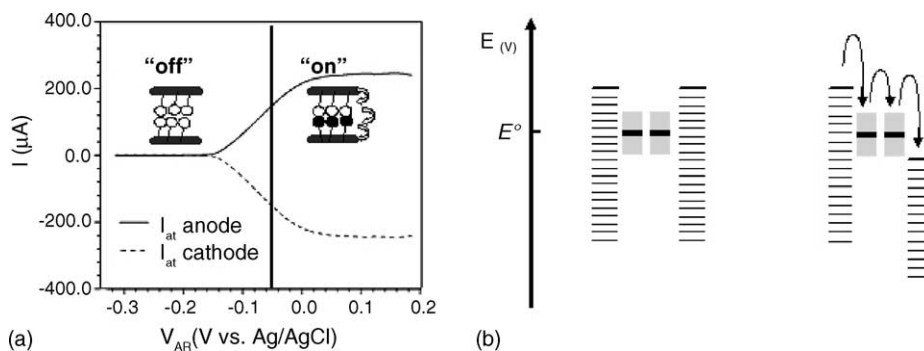


Fig. 6. (a) Current voltage characteristics ( $I_{\text{C}}$  and  $I_{\text{A}}$  as a function of  $V_{\text{AR}}$ ) of the  $J_{\text{Hg-SAM/SAM-Hg}}$  junction for  $V_{\text{CR}}$  fixed at  $-0.20$  V, scan rate  $50 \text{ mV s}^{-1}$ . (b) Interpretation of the process in terms of an energy diagram.



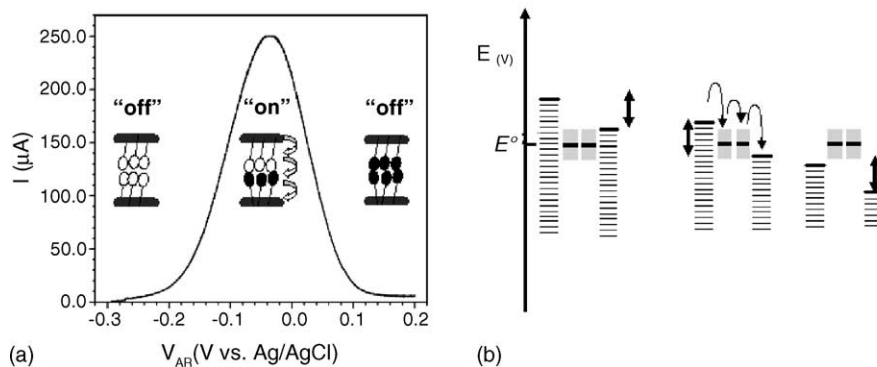


Fig. 7. (a) Current voltage characteristics ( $I_A$  as a function of  $V_{AR}$ ) of the  $J_{Hg-SAM/SAM-Hg}$  junction for  $V_{CA}$  fixed at +0.10 V, scan rate  $50 \text{ mV s}^{-1}$ . (b) Interpretation of the process in terms of an energy diagram.

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  $\text{Ru}^{II/III}$  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  $\text{Ru}^{II/III}$  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  $\text{Hg-SAM-M/M-SAM-Hg}$  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.

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