

Gating current flowing through molecules in metal–molecules–metal junctions

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Received 27th April 2005, Accepted 28th June 2005

First published as an Advance Article on the web 11th October 2005

DOI: 10.1039/b505860k

We have assembled two junctions that incorporate redox sites between Hg electrodes by different interactions. In the first junction, Hg–SAM–R//R–SAM–Hg, the redox site (R) are covalently linked to each electrode in self assembled monolayers (SAM–R). In the second junction, Hg–SAM//R//SAM–Hg, the redox sites dissolved in solution are trapped by electrostatic interaction at the SAM formed at the electrodes. The current flowing through these junctions can be controlled by adjusting the potential applied at the electrodes with respect to the redox potential of the species by using an electrochemical system. The current flowing in these two junctions is mediated by the redox sites through different mechanisms. In particular, the current flowing through the Hg–SAM–R//R–SAM–Hg junction occurs through a self exchange mechanism between the redox sites organized at each electrode, while the current flowing through the Hg–SAM//R//SAM–Hg junction is dominated by a redox-cycling mechanism. The systems described here are easy to assemble, well-characterized, yield reproducible data and make it easy to modify the electrical properties of the junctions by changing the nature of the redox centres. For these characteristics they are well suited for collecting fundamental information relevant to the fabrication of molecular switches.

1. Introduction

In the last decade, the number of studies of electron transport through molecules by using metal–insulator–metal (MIM) junctions has been growing exponentially.¹ The most interesting results of these studies indicate that: (i) there is a correlation of electron transfer rate with the molecular structure,² similar to that widely investigated by using the molecular donor–bridge–acceptor (DBA system),³ (ii) the features of the I – V curves measured for some molecules show abrupt increases and decreases of the current. This phenomenon, called “negative differential resistance” (NDR) is of great interest in testing theories of electron transport and perhaps for electronic devices.^{4–14} Organic molecules are, in general, poor conductors of electrons, and “conduct” by tunnelling. However, when molecules have low-lying orbitals (usually the HOMO or LUMO), applying a potential across the electrodes of a metal–molecule–metal junction can cause the energy of the molecular orbital to fall between the Fermi levels of the electrodes (Fig. 1). Under these conditions, the current flowing through the molecule shows a large increase in current as a result of a change in the electron transport mechanism.^{15,16} In principle, molecules with well-defined and readily accessible redox states are, thus, attractive candidates to demonstrate that it is possible to obtain an NDR signal.

Here we show that, in junctions incorporating redox sites (Fig. 2) is possible to control the current flowing through a metal–molecules–metal junctions and to predict at which potential the junction will switch from an “off” to an “on” state. By placing the junctions, together with a Ag/AgCl reference electrode and a platinum counter electrode, in electrolyte solution, and by using a bipotentiostat, it is possible to control the potentials of the two electrodes independently with respect to the reference electrode (Figs. 3 and 4) and therefore to control the potential of the

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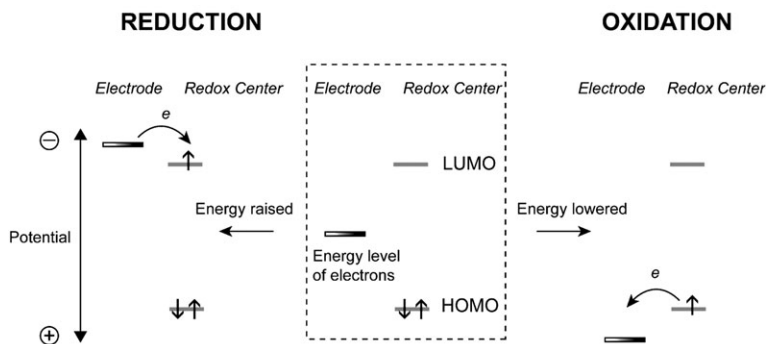


Fig. 1 Scheme of the electron transport mediated by molecules incorporating redox centers. The molecular orbitals HOMO (or LUMO) can donate (or accept) electrons as a function of the electrode Fermi levels under applied voltage.

electrodes with respect to the potential of the redox centre (E_0). We achieve this control over potential by carrying out two types of experiments. In one experiment (experiment A), we keep the potential of one electrode constant, and change that of the second electrode. In a second experiment (experiment B), the potentials of both electrodes are varied simultaneously, while maintaining a constant difference in potential between them.

We report a study of electron transfer by using two junctions that incorporate redox sites *via different kinds of interactions*. In the first junction Hg–SAM–R//R–SAM–Hg, the redox sites (R) are covalently linked to the electrodes being incorporated in self assembled monolayers (SAM–R) that cover the Hg-drop electrodes (Fig. 2a). The junction consists of two mercury drop electrodes, both of which are coated with a self-assembled monolayer (SAM) of the Ru-terminated thiol $\text{HS}(\text{CH}_2)_{10}\text{CONHCH}_2\text{pyRu}(\text{NH}_3)_5(\text{PF}_6)_2$ (henceforth abbreviated as HS–C₁₀–Ru).^{17,18} The thiol HS–C₁₀–Ru readily adsorbs from 1 mM acetonitrile solutions onto mercury electrodes and gives electroactive monolayers. After the formation of the SAMs on each electrode, the two Hg electrodes are brought in contact to form the junction Hg–SAM–R//R–SAM–Hg.

In the second junction Hg–SAM//R//SAM–Hg, the redox sites are incorporated between the electrodes by trapping them from a solution *via* electrostatic interaction with the SAMs formed on each electrode (Fig. 2b). The junction is formed by using two mercury drop electrodes, whose surfaces are covered by SAMs carrying charged terminating groups so that oppositely charged redox centres in solution to be trapped between the two electrodes by electrostatic interaction. We used self-assembled monolayers of alkanethiols terminated with carboxylic acid groups (11-mercaptodecanoic acid, henceforth abbreviated as HSC₁₀COOH) for two reasons. Carboxylic acid groups of this SAM on gold can be ionized at $\text{pH} > 4$, and the COO^- groups allow positively charged $\text{Ru}(\text{NH}_3)_6^{3+}$ ions in solution to be trapped between the two electrodes and to access the electrode surfaces *via* defect sites. This feature allows redox centres to be incorporated into metal–SAM//SAM–metal junctions without involvement of chemical synthesis and would be highly attractive for its simplicity and versatility.

By measuring the current flowing through the junctions by standard electrochemical techniques we demonstrate that these junctions become conductive when the electrode potentials are adjusted

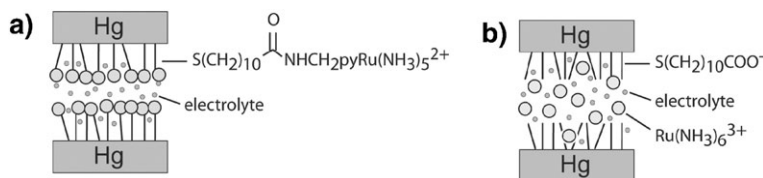


Fig. 2 Schematic representations of interfaces of (a) the junction Hg–SAM–R//R–SAM–Hg and (b) the junction Hg–SAM//R//SAM–Hg.

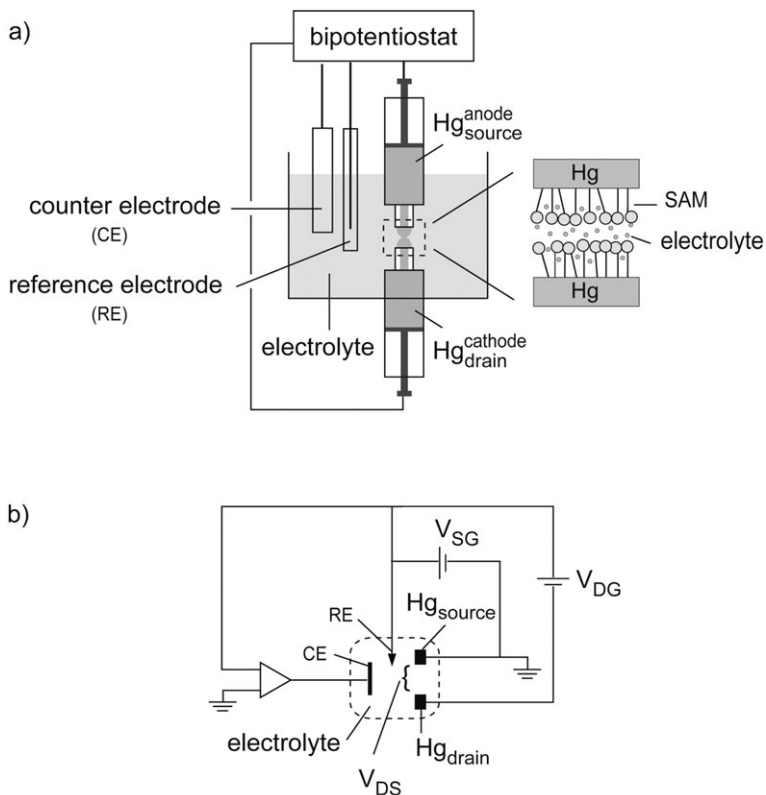


Fig. 3 Scheme of (a) the electrochemical system used to characterize the Hg-SAM-R//R-SAM-Hg junction and (b) the electrical circuit for the experimental setup. V_{SG} and V_{DG} are the potentials of the source and drain electrodes with respect to the reference electrode, respectively. The electrolyte is the gate whose potential is established by the voltage applied to the reference electrode relative to ground. I_D and I_S are the currents at the drain and source electrodes, respectively.

to the formal potential of the redox centres, and that they show diode like characteristics analogous to those of solid-state devices. We also show that the current flowing through the two junctions are dominated by two different electron transfer mechanisms.

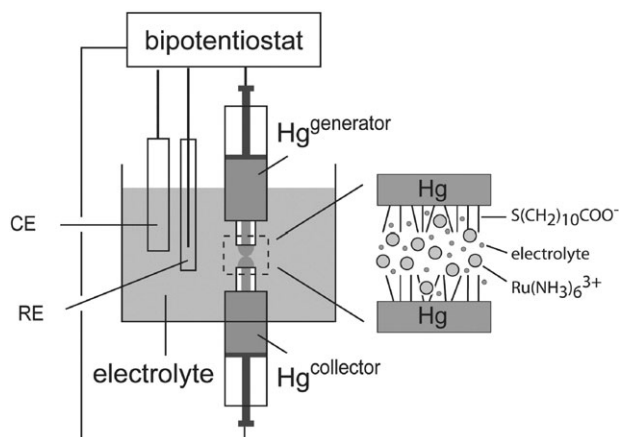


Fig. 4 Scheme of the electrochemical system used to characterize the junction Hg-SAM//R//SAM-Hg.

2. Results and discussion

Junction Hg–SAM-R//R–SAM–Hg

To test the organization of monolayers of HS-C₁₀-Ru on Hg drops, we run cyclic voltammograms of a monolayer of HS-C₁₀-Ru in contact with a 0.2 M aqueous Na₂SO₄ electrolyte (pH 4). The results show a stable redox wave corresponding to the Ru(II) \rightleftharpoons Ru(III) interconversion at $E^{\circ} = -0.04$ V vs. Ag/AgCl, a value that is close to that of an analogous dissolved compound in the same medium ($E_{\text{solu}}^{\circ} = +0.04$ V vs. SCE). In addition, the oxidation and reduction peaks are symmetrical, with a < 10 mV difference between the peak maxima, and an ideal full width at half maximum of 90 mV. These observations indicate that the monolayer is well-ordered and that the pyRu(NH₃)₅²⁺ moieties are homogeneous in their redox behaviour; we infer that they are located at the external surface of the monolayer and are solvated by the electrolyte.

To assemble the junction, we aligned two microsyringes on a vertical line, in opposite directions (Fig. 3a). Two Hg drops were extruded inside a solution of a thiol HS-C₁₀-Ru 1 mM acetonitrile solutions. After the formation of the SAMs on each electrode, the thiol solution was removed and replaced with an electrolyte solution of Na₂SO₄. The two Hg–SAM-R electrodes are brought into contact and placed together with the reference and the counter electrodes into the electrolyte solution, then we run experiments A and B. In the experiment A, the potentials of the mercury electrodes were controlled such that one (cathode) acted as the electron donor and the other (anode) as the electron acceptor. We designated the cathode and anode as the drain and source electrodes (Fig. 3b), respectively, by analogy to the convention used in semiconductor devices, where current is considered to flow from a more positive region to a more negative region.¹⁹ We measured the conductance through the junction as a function of the potentials of the drain and source electrodes with respect to the reference electrode (*i.e.*, V_{DG} and V_{SG} , respectively) and as a function of the potential between the source and drain (V_{DS}), using the electrolyte solution as a gate. We controlled the potential of the gate by controlling the potential applied to the reference electrode relative to ground. Since the source electrode is at ground, this voltage is V_{SG} . Fig. 5a shows the drain/source currents when V_{DG} is fixed at -0.20 V, where the attached ruthenium is in its +2 oxidation state, and V_{SG} is varied. For $V_{\text{SG}} \leq V_{\text{DG}}$, the currents are negligible and the junction is non-conducting. Increasing V_{SG} to values more positive than -0.14 V results in an anodic current flow corresponding to the oxidation of Ru^{II} to Ru^{III} at the source and a cathodic current flow corresponding to the reduction of Ru^{III} to Ru^{II} at the drain. 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° , of the Ru^{II/III} couple. Based on these observations, we propose that charge transport through the junction occurs as a result of oxidation of Ru^{II} to Ru^{III} at the source, electron exchange between Ru^{III} at the source and Ru^{II} at the drain, and reduction of Ru^{III} at the drain back to Ru^{II} as key steps. In the experiment B, the conductance of the Hg–SAM//SAM–Hg junction was measured operating at fixed drain-source potentials. Fig. 5b shows that at fixed $V_{\text{DS}} = +0.10$ V, the drain current is negligible for V_{SG} less than -0.25 V and greater than $+0.15$ V. Upon scanning V_{SG} from -0.25 to $+0.15$ V, the current increases from zero to a maximum value near the E° of the redox couple and then decreases again to zero. Charge therefore passes from one electrode to another only when V_{SG} is at or close to the Ru^{II/III} redox potential.²⁰

The junction shows electrical behaviour similar to that of a solid-state transistor when the electrolyte is used as the gate. The channel length in this case is defined essentially by the thickness of the SAMs between the two mercury electrodes, that is a few nanometers.

Junction Hg–SAM//R//SAM–Hg

The junction was assembled as follows. SAMs were formed separately on the two Hg electrodes from a solution of 1 mM of HSC₁₀COOH in ethanol. The two electrodes covered by the SAMs, were immersed in a solution containing 1 mM Ru(NH₃)₆³⁺ in 0.1 M electrolyte at pH 9 and brought in contact by a micromanipulator. By placing the reference and counter electrodes to create an electrochemical cell, we run experiment A. In experiment A, the potentials of the mercury electrodes were controlled such that one acts as an electron donor to Ru(NH₃)₆³⁺ and the other acts as an electron acceptor from Ru(NH₃)₆²⁺ (Fig. 4). It is well known that electroactive species confined

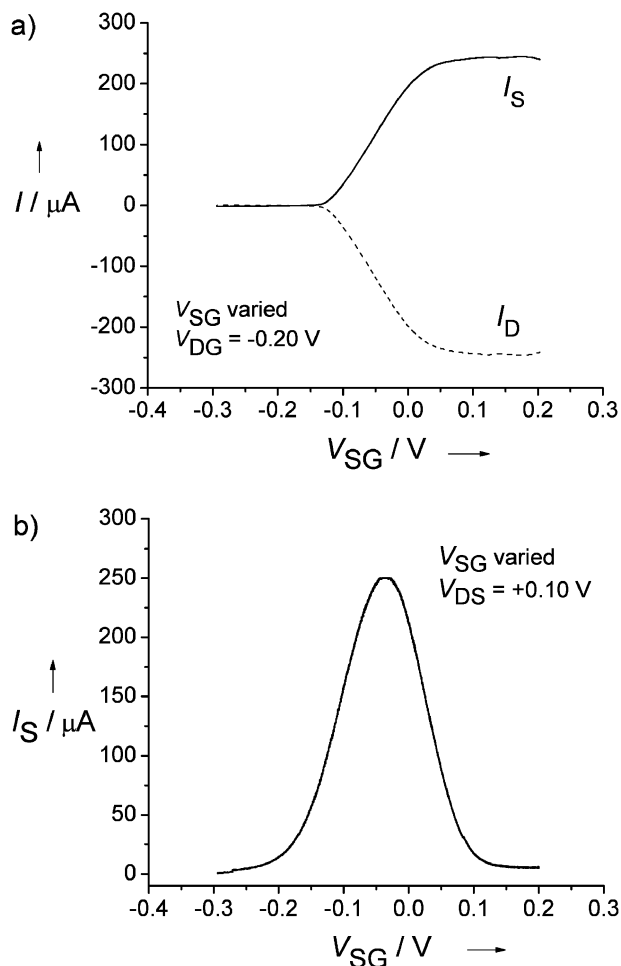


Fig. 5 Current–voltage characteristics of the Hg–SAM–R//R–SAM–Hg junction showing diode like behaviour. All experiments were carried out in 0.2 M aqueous Na₂SO₄ at pH 4. (a) I_D and I_S as a function of V_{SG} . V_{DG} was fixed at -0.20 V and the scan rate was 50 mV s⁻¹. (b) I_S as a function of V_{SG} for the same junction as in (a). V_{DS} was fixed at $+0.10$ V.

between two electrodes closely spaced, generate a current when the potentials of the electrodes are controlled such that one donates electrons and the other accepts them.^{21–24} The species generated at one electrode (the “generator” electrode) can diffuse to the second electrode (the “collector”)^{21,22} and generate current *via* a mechanism called redox cycling.²³ The potential of the collector electrode was held at $+0.10$ V vs. Ag/AgCl, while the generator electrode was swept towards negative potentials past E^o (-0.21 V) for the $\text{Ru}(\text{NH}_3)_6^{3+} \rightarrow \text{Ru}(\text{NH}_3)_6^{2+}$ reaction and back again (Fig. 6). Fig. 6 show a typical I – V curve measured after cycling the potential across the junction. The current–voltage curves show that at the generator and at the collector the current initially increases slowly, and then typically becomes sigmoidal and increases rapidly until a steady-state current–voltage curve (*i.e.* the currents of the forward and reverse scans are about the same). This result indicates that (i) ruthenium hexaamine is trapped inside the junction, and (ii) that the two mercury electrodes are close enough to one another for redox cycling to occur.

We also observe a negative shift of the half-wave (half-maximum) potential $E_{1/2}$ relative to E^o for the $\text{Ru}(\text{NH}_3)_6^{3+} \rightleftharpoons \text{Ru}(\text{NH}_3)_6^{2+}$ reaction. The value of $E_{1/2}$ corresponds to the formal potential for reduction of $\text{Ru}(\text{NH}_3)_6^{3+}$ trapped inside the junction. The negative shift in $E_{1/2}$ is indicative of the

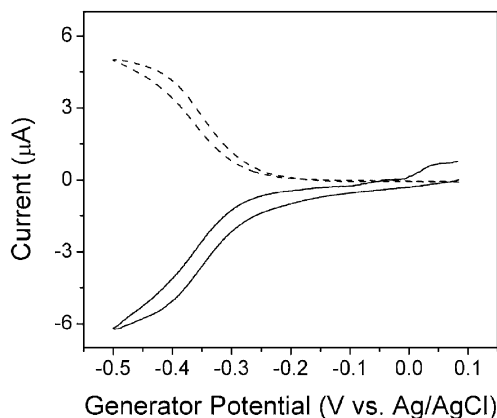


Fig. 6 Generation–collection voltammogram of 1 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ in a Hg–SAM//R//SAM–Hg junction at pH 9. The collector potential was held at +0.10 V, and the generator potential was cycled between +0.1 and –0.5 V at a scan rate of 50 mV s^{-1} . The areas of the junctions were *ca.* 0.20 mm^2 .

generation of a more polar environment inside the junction. We propose that under applied voltage scans across the junction, a tilting/compression of the SAMs can occur^{25,26} with a consequent expulsion of the electrolyte. Such a process would cause the two SAM-covered electrodes to approach one another and allow the interaction between the surface-immobilized COO^- groups and the $\text{Ru}(\text{NH}_3)_6^{3+}$ couple to increase. Also this junction switches from “off” to “on” by varying the potential applied at the generator: when the potential of the generator approaches the formal potential $E_{1/2}$, the junction became conductive.

3. Conclusions

The results of this study show that redox sites can be incorporated at the interface of the junction by different interactions: in the junction Hg–SAM–R//R–SAM–Hg, the redox sites are immobilized at the surface of the electrodes by a covalent bond in a SAM, while in the junction Hg–SAM//R//SAM–Hg the redox sites trapped between the two electrodes are free to diffuse inside the interelectrode nanometer gap. The current flowing through both these junctions can be controlled by controlling the potential of the electrodes by conventional electrochemical measurements: the current flows only when the potential of the electrodes are controlled so that one can oxidize the redox species and the other can reduce it. Significantly, the current flow is generated in these two junctions by a different mechanism. The junction Hg–SAM–R//R–SAM–Hg switches from *off* to *on* when the electronic states of the redox centres on the two monolayers falls between the Fermi levels of the electrodes. The intensity of the current depends on the rates of (i) electron tunnelling between the mercury electrodes and the surface-bound $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ centres and (ii) electron hopping between adjacent Ru^{II} and Ru^{III} centres.

In the junction Hg–SAM//R//SAM–Hg the current flows through the junction only when the electrode potentials are adjusted so that one donates electrons and the other accepts them. Under these conditions, the current is dominated by a mechanism of redox cycling. The intensity of the current depends on the distance between the electrodes. It is important to stress that, in such a confined space, electron hopping between adjacent species in different oxidation states, could become operative. In both systems, the current flowing through the junction depends on the number of redox centres trapped in the area in which the two compliant mercury electrodes are in contact. The systems described here are easy to assemble and make it easy to modify both the area and electrical properties of the metal–metal junctions. The area can be modified by changing the pressure applied to the mercury electrodes, while tuning of the electrical properties may be achieved by changing the nature of the redox centre. Because these junctions are well-characterized and yield reproducible data, they are well suited for collecting fundamental information relevant to the fabrication of molecular switches.

Acknowledgements

This work is supported by NSEC (award no. NSF-PHY-0117795), NSF (award no. CHE-0101432), and NSERC (in the form of a postdoctoral fellowship to E.T.), by the EU: Project Contract GRD1-2001-40772 (MWFM) and Project Contract IST-2001-35503 (LIMM).

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