

Test-beds for Molecular Electronics: Metal–Molecules–Metal Junctions Based on Hg Electrodes

Felice Carlo Simeone^a and Maria Anita Rampi^{ab*}

Abstract: Junctions based on mesoscopic Hg electrodes are used to characterize the electrical properties of the organic molecules organized in self-assembled monolayers (SAMs). The junctions M-SAM//SAM-Hg are formed by one electrode based on metals (M) such as Hg, Ag, Au, covered by a SAM, and by a second electrode always formed by a Hg drop carrying also a SAM. The electrodes, brought together by using a micromanipulator, sandwich SAMs of different nature at the contact area ($\approx 0.7 \mu\text{m}^2$). The high versatility of the system allows a series of both electrical and electrochemical junctions to be assembled and characterized: i) The compliant nature of the Hg electrodes allows incorporation into the junction and measurement of the electrical behavior of a large number of molecular systems and correlation of their electronic structure to the electrical behavior; ii) by functionalizing both electrodes with SAMs exposing different functional groups, X and Y, it is possible to compare the rate of electron transfer through different X–Y molecular interactions; iii) when the junction incorporates one of the electrode formed by a semitransparent film of Au, it allows electrical measurements under irradiation of the sandwiched SAMs. In this case the junction behaves as a photoswitch; iv) incorporation of redox centres with low lying, easily reachable energy levels, provides electron stations as indicated by the hopping mechanism dominating the current flow; v) electrochemical junctions incorporating redox centres by both covalent and electrostatic interactions permit control of the potential of the electrodes with respect to that of the redox state by means of an external reference electrode. Both these junctions show an electrical behavior similar to that of conventional diodes, even though the mechanism generating the current flow is different. These systems, demonstrating high mechanical stability and reproducibility, easy assembly, and a wide variety of produced results, are convenient test-beds for molecular electronics and represent a useful complement to physics-based experimental methods.

Keywords: Electron transfer · Hg electrodes · Molecular electronics · Molecular junction · Self-assembled monolayer



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1. Introduction

In 1971, Kuhn and Mann,^[1] by contrasting studies of electron-transfer carried out on supramolecular systems in solution, pioneered experimental molecular electronics by measuring electron transport through molecular layers sandwiched between metal electrodes in solid state.^[2] In 1974 Aviram and Ratner, in a theoretical paper, envisaged the use of molecules connected between two electrodes to make electronic devices.^[3] It was not until the late 90s that the combination of nanofabrication, scanning probe microscopies, and methods to form stable connections of molecules to metal surfaces in self-assembled monolayers (SAMs), triggered the fabrication of metal–molecule(s)–metal junctions, and opened the door to experimental ‘molecular electronics’.

In the last fifteen years, the number of works dedicated to the characterization of the electrical properties of several, a few, or individual molecules, sandwiched between two metal surfaces has increased exponentially. Among the large variety of molecular junctions proposed to the scientific community, we name only a selec-

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tion of the most popular ones: i) junctions based on fabrication of the second solid electrode on the organic layer by vapor deposition^[4] or nanotransfer printing,^[5] ii) crossed nanowire based junctions,^[6] iii) STM and conducting-AFM based junctions (c-AFM),^[7,8] iv) break junctions.^[9] Each one of these junctions shows both advantages and limitations, and the design of conceptually new molecular junctions able to give reproducible electrical measurements is still proceeding.

In parallel we observe that nowadays, on one side, the large number of advanced studies provides very detailed information, but on the other side, some fundamental factors influencing the electrical properties of metal–molecule(s)–metal junctions are still under debate and several questions remain open. For instance i) it has been shown in great detail how the molecular conductivity depends not only on the electronic structure, but also on the molecular conformation;^[10] and ii) the electrical characterization of complex systems highlights the idea of fabricating molecular devices that mimic the function of electronic components (conductors, transistors, rectifiers, logic gates).^[11–13] Nonetheless, at the same time, i) the value of the conductance of the single molecules is still elusive,^[14] ii) the contributions of interfacial processes in determining conductivities remain unclear,^[15] and iii) the effect of applying large bias on the mechanism of charge transfer is under discussion.^[16]

As far as the mechanisms of charge transport through organic molecules is concerned, ‘through-bond tunneling’ is the dominant mechanism in a large number of studies.^[17] It has been recently demonstrated that i) other mechanisms of charge transport – such as field effects – can contribute to the electrical behavior of molecular wires (MW),^[16,17] and ii) through a careful design of MWs, a hopping mechanism can become operative.^[8,18]

These observations indicate that molecular electronics would benefit from further efforts to gain the missing information and deeper insight.

First of all, in order to provide experimental data as a foundation for research in molecular electronics, the electrical measurements must be provided by junctions that are stable, reproducible, and broadly compatible with a range of organic structures. In addition, the comparison of results obtained by i) using different experimental approaches, ii) different anchoring-to-metal groups, and iii) different aggregation of molecules is mandatory. It worth observing that, while very informative results on the electrical properties of single or few molecules have been provided by STM and c-AFM based junctions and by break-junctions – as both have become more familiar

and more stable – the behavior of molecular films has been characterized by large area junctions in only a few cases.^[4b,12d,18]

Here we present a series of junctions of different geometry based on Hg electrodes and their electrical characterization. We show that these junctions are easy to assemble, mechanically stable, reproducible, and very versatile. Based on these characteristics, other authors have adopted Hg-based junctions on different substrates.^[19]

These systems take advantage of the properties of Hg. In particular, Hg-drop electrodes provide at least four advantages: i) Hg as a metal is highly conductive; ii) Hg forms well-ordered SAMs in a few seconds;^[20] iii) the Hg surface, as a liquid, is free of structural features – edges, steps, terraces, pits – that result in defects of adsorbed monolayers; and iv) the Hg drop conforms to the topography of solid surfaces, and forms a good conformal contact with the SAM-covered solid surface.

The versatility of these systems allows i) the incorporation and the electrical characterization of SAMs formed by a wide range of molecular systems of increasing

complexity; ii) irradiation of the photoactive SAMs sandwiched between the electrodes under applied potential; and iii) for measurements both in electrical or electrochemical mode

Fig. 1A and 1B show the two conceptually different types of Hg-based junctions: respectively the two-electrode electrical junction and the four-electrode electrochemical junction.

2. Electrical Junctions, M-SAM(2)//SAM(1)-Hg

The fabrication of these junctions is straightforward: in all cases, SAMs(1) and SAMs(2) are formed respectively on the Hg drop extruded from a syringe and on a solid metal surface (Fig. 1A). The Hg-SAM(1) electrode is brought into contact with M-SAM(2) by the use of a micromanipulator in an inert medium such as hexadecane: the presence of this liquid phase protects the mercury drop from vibration. Fig. 1A also shows the two contacting electrodes. A semitransparent solid surface

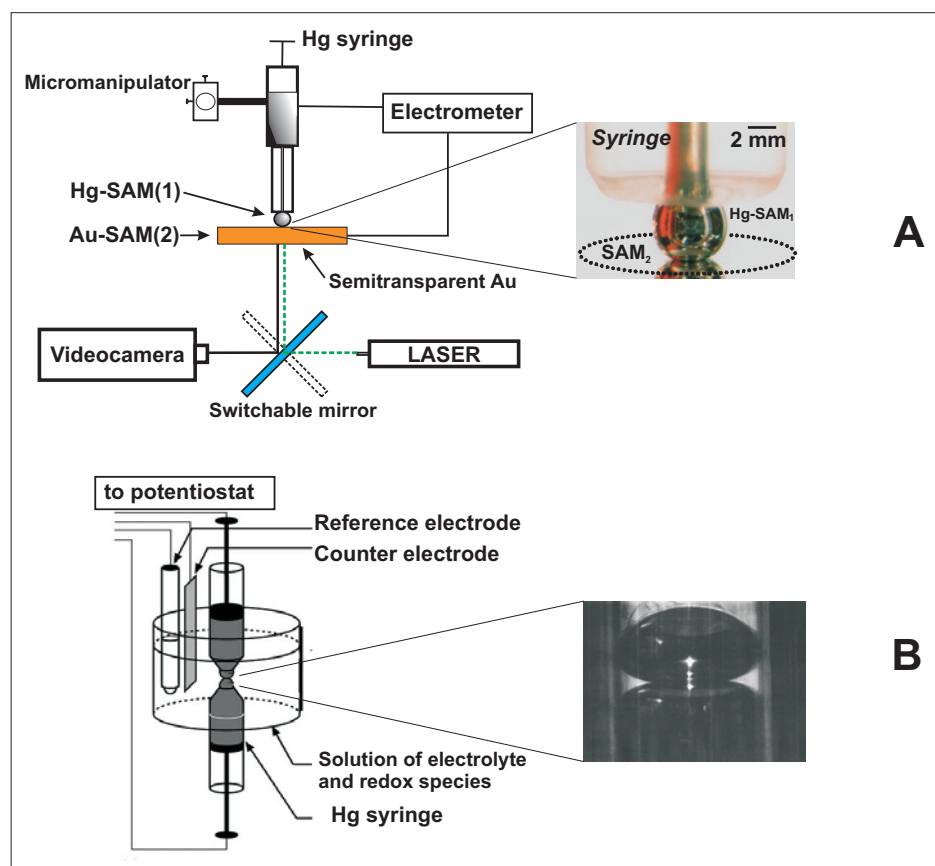


Fig. 1. A and B show respectively the scheme of the electrical and the electrochemical junctions based on Hg electrodes and the relative pictures of the contact area. A: the junction is formed by a Hg drop covered by SAM(1), usually formed from hexadecane thiol solutions, and a solid semitransparent metal surface (M= Au, Ag) covered by SAM(2). The two electrodes covered by the SAMs are brought into contact by a micromanipulator. The image of the contact area is collected by a mirror through the semitransparent gold surfaces. B: the electrochemical junction is formed by two Hg drops (electrodes) extruded from two micro syringes and covered by SAMs before being brought in contact. The Hg electrodes are electrically connected to reference and counter electrodes by an electrolyte solution.

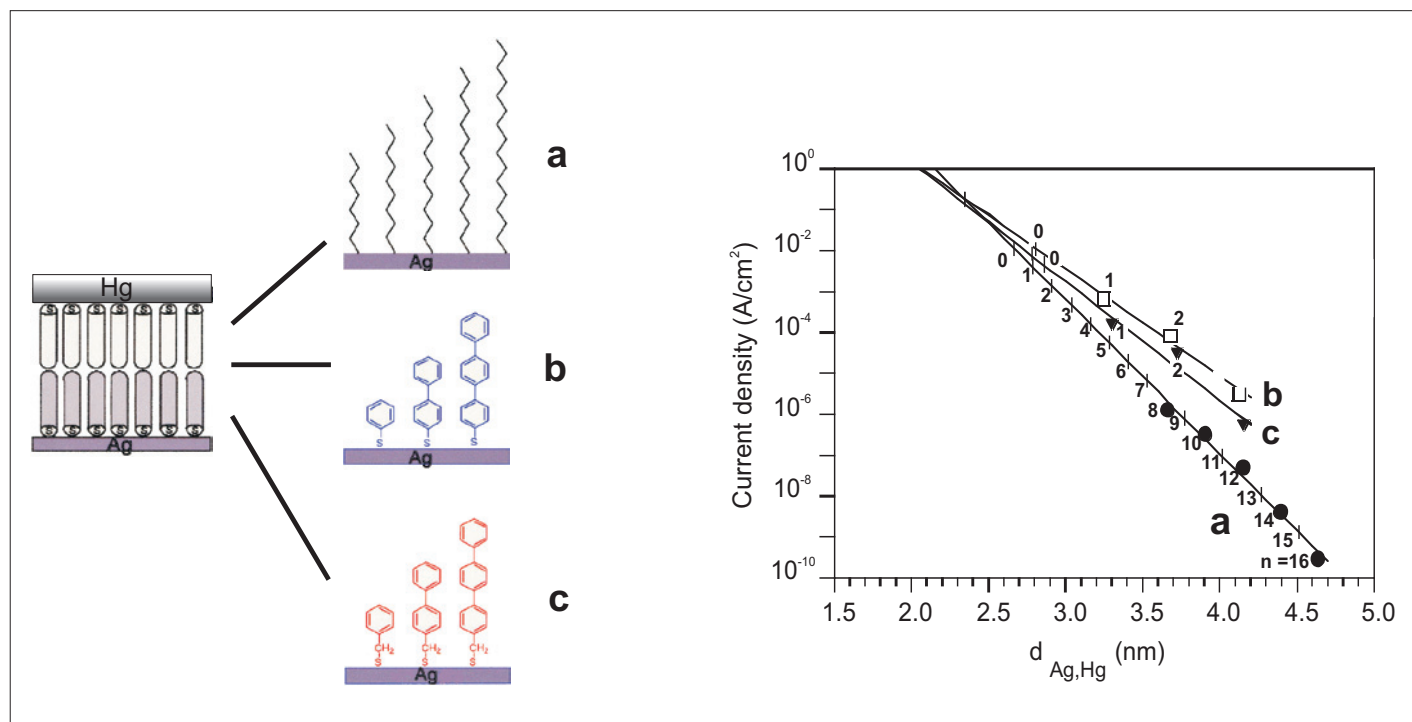


Fig. 2. Left: Schemes of the interface incorporating SAMs of organic molecules of different structure (a, b, c) on an Ag surface electrode. Right: Plot comparing the distance dependence of current density (values obtained at applied voltage $V = 0.5$) flowing through the a, b, c interfaces.

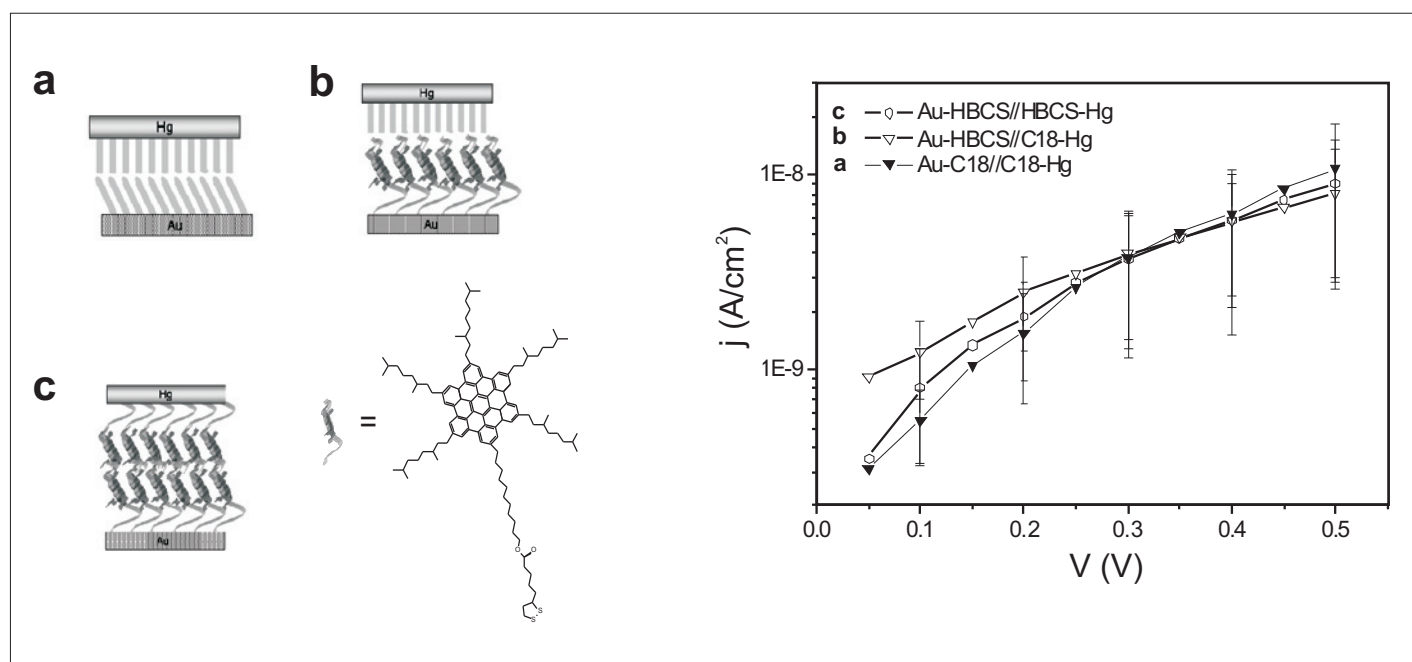


Fig. 3. Left: Scheme of the interface of the assembled junctions: a: SAMs of octadecane thiols (C18) on both electrodes; b: SAMs of C18 on the Hg electrode and of HBCS on an Au electrode; c: SAMs of HBCS on both electrodes. Right: i - V curves measured for the three junctions a, b, c.

(Au or Ag) allows the image of the contact area to be collected by a mirror and sent to a magnifying video camera.

Significantly this junction can sustain high electrical fields (6 MV cm^{-1}) without electrical breakdown when it incorporates SAM(2) formed by molecules with very different structures (alkanes, polyphenylene, derivatives of anthracene and cholesterol) on different metals (Ag, Au, Hg, Au/Hg alloy).^[21]

The geometrical characteristics of the electrical junction and the use of a semi-transparent solid metal surface enable a number of different studies of charge transport, as described below.

2.1 Correlation between Electrical Properties and Chemical Structure

Our first study focused on the comparison of electron transfer rates through molecules of different electronic structure.^[22,23]

We assembled three series of junctions, as shown in Fig. 2a, b, and c, where SAM(2) is respectively formed by alkanethiols, $\text{HS}(\text{CH}_2)_{n-1}\text{CH}_3$ ($n = 8, 10, 12, 14, 16$), oligophenylene thiols, $\text{HS}(\text{Ph})_k\text{H}$ ($k = 1, 2, 3$), and by benzylic homologs of the oligophenylene thiols $\text{HSCH}_2(\text{Ph})_m\text{H}$ ($m = 1, 2, 3$). The i - V curve was measured for each junction – where SAM(1) was formed by hexadecanethiol and SAM(2) by molecules of the same length and structure. Fig. 2 (right) shows the

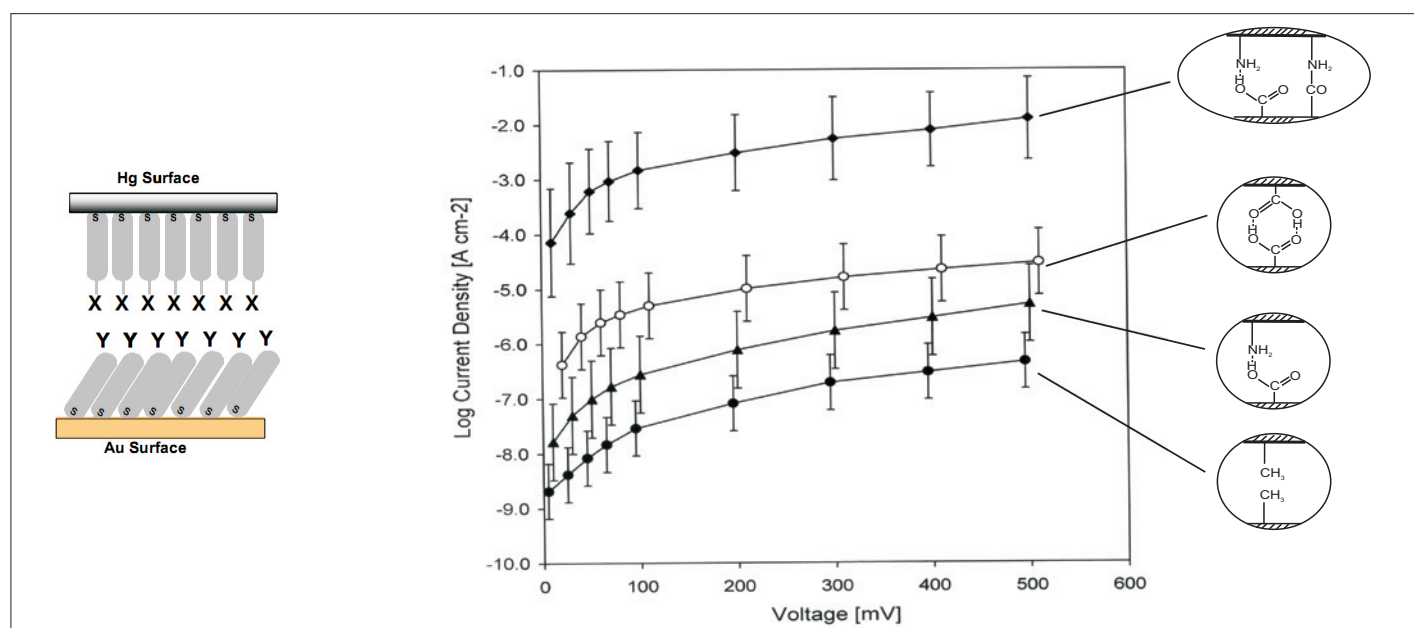


Fig. 4. Left: Scheme of the interface of junctions incorporating SAM with different X and Y terminal groups. Right: i-V curves for junctions incorporating the schematized interactions.

log of J at 0.7 V, plotted versus the distance separating the electrodes ($d_{\text{Ag,Hg}}$) for each homolog series of molecules. The linearity of the plot indicates that the current values follow the relation $I = I_0 e^{-\beta d_{\text{Ag,Hg}}}$, a relationship that holds for charge transport dominated by a tunneling mechanism.^[17] From the results, we have extracted the values of β as $0.87 \pm 0.10 \text{ \AA}^{-1}$ for alkanethiols, $0.61 \pm 0.10 \text{ \AA}^{-1}$ for oligophenylene thiols, and $0.66 \pm 0.10 \text{ \AA}^{-1}$ for the benzylic derivatives of oligophenylene thiols.

Significantly the values of β are in good agreement with those extracted from electrical measurements performed by c-AFM,^[24] and with those measured by transient spectroscopy on supramolecular systems.^[1]

These results indicate that the mechanism of electron transport in these molecular junctions is dominated by tunneling and that there is a correlation, represented by the β factor, between the electrical properties of molecules (MWs) and their electronic structure.

2.2 Electrical and Mechanical Characteristics of Organic SAMs

On the basis of the above-mentioned results we focused on a member of the nanographene family, hexa-*peri*-hexabenzocoronene (HBC), a highly conjugated molecular structure very popular for its outstanding electronic properties.^[25] HBC functionalized by a C19 alkane-thiol (HBCS) (Fig. 3b) forms SAMs on gold surfaces with a well-defined up-right orientation as indicated by SPX and NEX-FAS.^[26] We aimed to measure the conductance along the graphite-like core of the HBC compound by comparing the current flowing through the interfaces schematized in Fig. 3 (left): i) junction formed by

SAMs of octadecane thiols (C18) on both electrodes (Fig. 3a), ii) junction formed by SAMs of C18 on the Hg electrode and of HBCS on the Au electrode (Fig. 3b), and iii) junction formed by SAMs of HBCS on both electrodes (Fig. 3c). Fig. 3 (right) reports the values of the current density of the three junctions and importantly shows that the current densities are very similar.

These results indicate that the 30 Å thick SAM formed by HBCS can be considered as effectively composed of two parts: a 'highly conductive' HBC layer with a thickness of 10 Å and an 'low conductive' aliphatic part with a thickness of 20 Å.^[26] The aliphatic chains are mostly responsible for the total barrier to electron transport of the monolayer, whereas the HBC cores are comparably 'transparent'.

These data are the first quantitative and comparative measurements of the i-V curves for the current flowing across the plane of the HBC aromatic core. Both high mechanical stability and high electric 'conductivity' of the HBC unit qualify this material as a promising building block for molecular and organic electronics.

2.3 Electron Transfer through Different Molecular Interactions

The way to assemble the junction – by using a micromanipulator for approaching and contacting the Hg and Au electrodes covered by SAMs – suggests a simple solution to measure and compare rates of electron flowing through different molecular interactions. By functionalizing each electrode with SAMs carrying different functional groups, X and Y, as schematized in Fig. 4 (left), it is straightforward to incorporate a variety of interactions into the junction. By using terminal func-

tional groups such as $-\text{CH}_3$, $-\text{COOH}$, and $-\text{NH}_2$ for X and Y (see Fig. 4, right), we aimed to compare electron transfer rates through molecular interactions present in folded proteins, such as van der Waals interactions and hydrogen or hydrogen/ionic bonds. It was also possible to bridge two SAMs covalently by reaction of a SAM terminated with anhydride groups on gold with a second SAM terminated in amine groups on mercury.^[27] This reaction generates amide $\text{C}(\text{O})-\text{NH}$ groups covalently bridging the two electrodes. The electron transfer rate for each of these interactions can be considered as single contributions to the overall electron transfer process occurring through the 'tunneling pathway' so extensively studied in engineered proteins.^[28] Theoretical models that fit experimental rates of electron transfer in proteins^[28] inferred the following orders of rates of tunneling: covalent > noncovalent bonds, and hydrogen bonds > van der Waals contacts.^[29,30]

Fig. 4 (right) shows the i-V curves obtained for each type of junction and indicates how they depend on the nature of the X...Y interaction. By using as reference the junction having van der Waals interactions at the interface, the ratio of the currents flowing through the different interactions were $I(-\text{CO}_2\text{H}\cdots\text{NH}_2)/I(-\text{CH}_3/\text{H}_3\text{C}) \approx 9$; $I(-\text{CO}_2\text{H}\cdots\text{HO}_2\text{C})/I(-\text{CH}_3/\text{H}_3\text{C}) \approx 40$; and $I(-\text{C}(\text{O})\text{NH}/-\text{CO}_2\text{H}\cdots\text{NH}_2)/I(\text{CH}_3/\text{H}_3\text{C}) \approx 104$.

The agreement of our results with the limited experimental and theoretical data of electron transfer in proteins^[29,30] suggests that the junctions described here are systems highly qualified for quantifying electron transfer rates relative to molecular interactions.

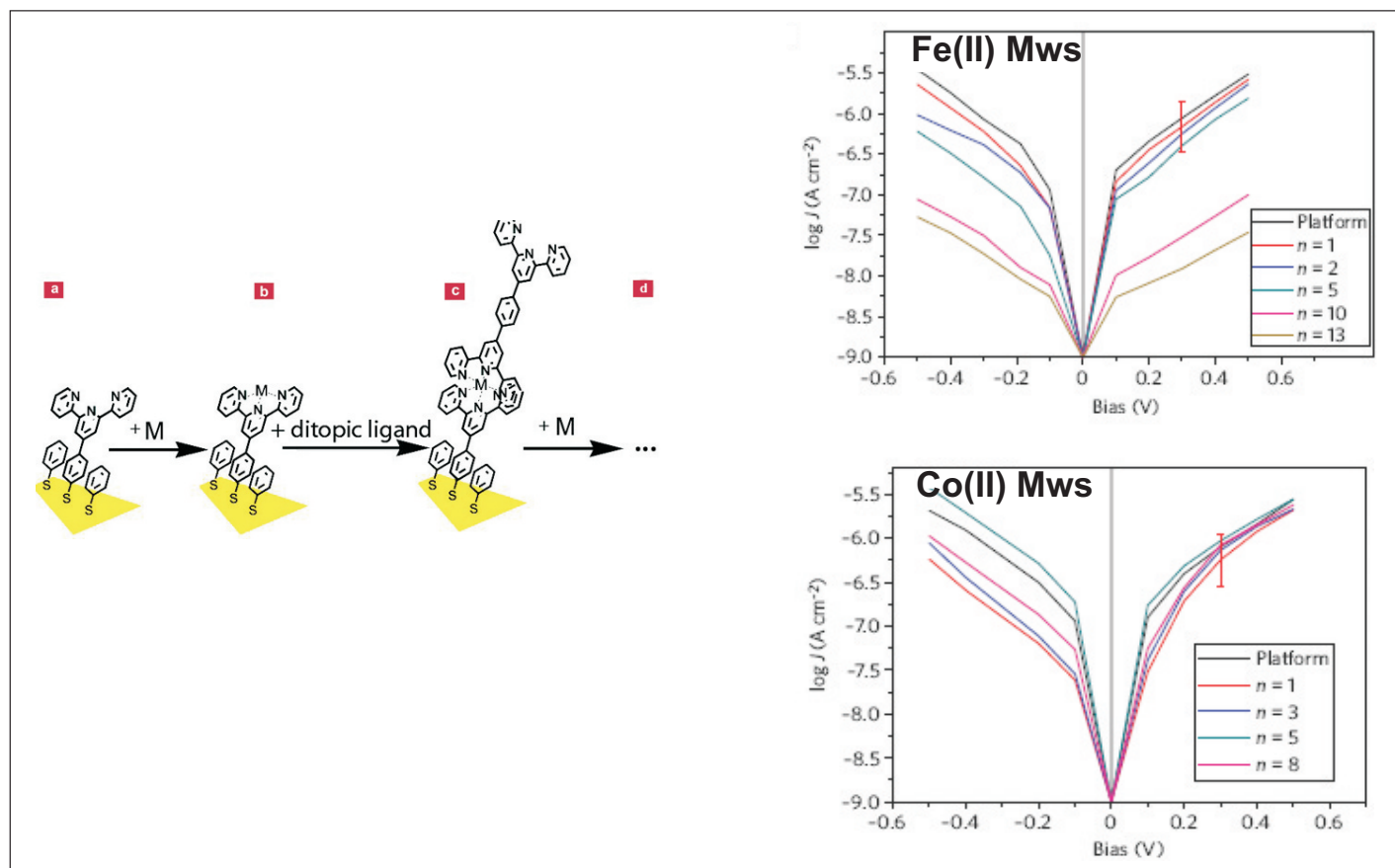


Fig. 5. Left: Scheme of the stepwise assembly (a-d) of the molecular wires (MWs) based on metal centres, M. Right: i-V curves measured for junction incorporating the MPTP “platform” SAM, and Fe(II) and Co(II) based MWs, with different numbers, n, of metal centres, Ms.

2.4 Junctions Incorporating Extralong Highly Conductive Molecular Wires

In molecular electronics, the possibility to connect large gap electrodes with highly conductive, extralong molecular wires (MWs) is a long sought goal. Improving charge transfer rate by incorporating redox sites as electron stations into molecular systems is a tantalizing idea.^[31]

With the aim to attain both highly conductive and extralong MWs, we have adopted the strategy to assemble directly on the metal surface a large number of redox centres (MCs) by coordination to a rigid organic backbone in a stepwise sequential mode, as schematized in Fig. 5 (left). As MCs we selected Fe(II) and Co(II) ions because they provide both low lying energy states and easy coordination reaction to terpy-based ligands. We used i) a 4'-(4-mercaptophenyl)-2-2':6'2''-terpyridine (MPTP) to anchor ‘*in situ*’ on metal surfaces redox active species^[32] and ii) a symmetric hexadentate ligand, 1,4-di(2,2',6',2''-terpyridine-4'-yl)benzene (TPT), for the stepwise complexation of the MCs. The MWs assembled ‘*in situ*’ on Au surfaces show a tightly packed organization.^[33] The values of current density flowing through the MPTP layers and through the Fe(II) and Co(II) based MWs of different number of metal centres, n, are

reported in Fig. 5 (right). The results indicate that current values measured for junctions incorporating MCMWs of different length i) decrease by half order of magnitude for 14 nm long Co(II) based MWs, and ii) decrease to one and half order of magnitude for 20 nm long Fe(II) based MWs. The current values at 0.5 V, plotted according to equation $I = I_0 e^{-\beta d}$,^[17] yields β values which are extremely low with respect to other organic molecular wires: $\beta_{\text{Fe}} = 0.028$ and $\beta_{\text{Co}} = 0.001 \text{ \AA}^{-1}$ respectively for Fe(II) and Co(II) based MWs. On this basis, a tunnelling mechanism is inadequate to model the charge transfer process occurring across these MWs:^[34] a multistep electron/hole hopping mechanism between redox sites is suggested to be operative.^[18]

The outstanding electrical and mechanical characteristics of these easy-to-assemble molecular systems open the door to a new generation of MWs, able to bridge large gap electrodes, and to form robust films for organic electronics.

2.5 Junctions Incorporating Photoactive Molecules: A Photoswitch

The possibility to couple the electrical response of molecular junctions to an external signal represents a crucial step for mimicking electronic devices. With the aim of using light as external signal, we

have designed and assembled a junction based on a transparent metal surface as the support of a SAM(2) (Fig. 1A). This setup allows SAM(2), formed by photoactive units through the transparent support, to be irradiated and to measure the changes of current flow under irradiation.

Azobenzenes-based compounds have been extensively studied for their unique photoisomerization:^[35] the transition from the thermodynamically more stable *trans* to the *cis* conformation can be induced by irradiation with UV light and reversed upon heating or irradiation with visible light.

Several authors have observed that when azobenzenes units are anchored to metal surfaces by flexible chains to form SAMs, the photoconversion yield is quite poor.^[36] We have recently demonstrated that rigid and fully conjugated mercaptoazobenzene compounds (AZO), in spite of forming densely packed SAMs on Au surfaces,^[37] show an unexpected high yield of photoconversion.^[38]

Both the *trans* and the *cis* form of these AZO SAMs (SAM_{AZO}) have been incorporated into the electrical junction, as schematized in Fig. 6a and 6b.^[39] Fig. 6c shows that the i-V curves measured across these interfaces differ by more than one order of magnitude. The same electrical properties of the AZO *trans* and *cis* isomers have been observed also by c-AFM.^[40]

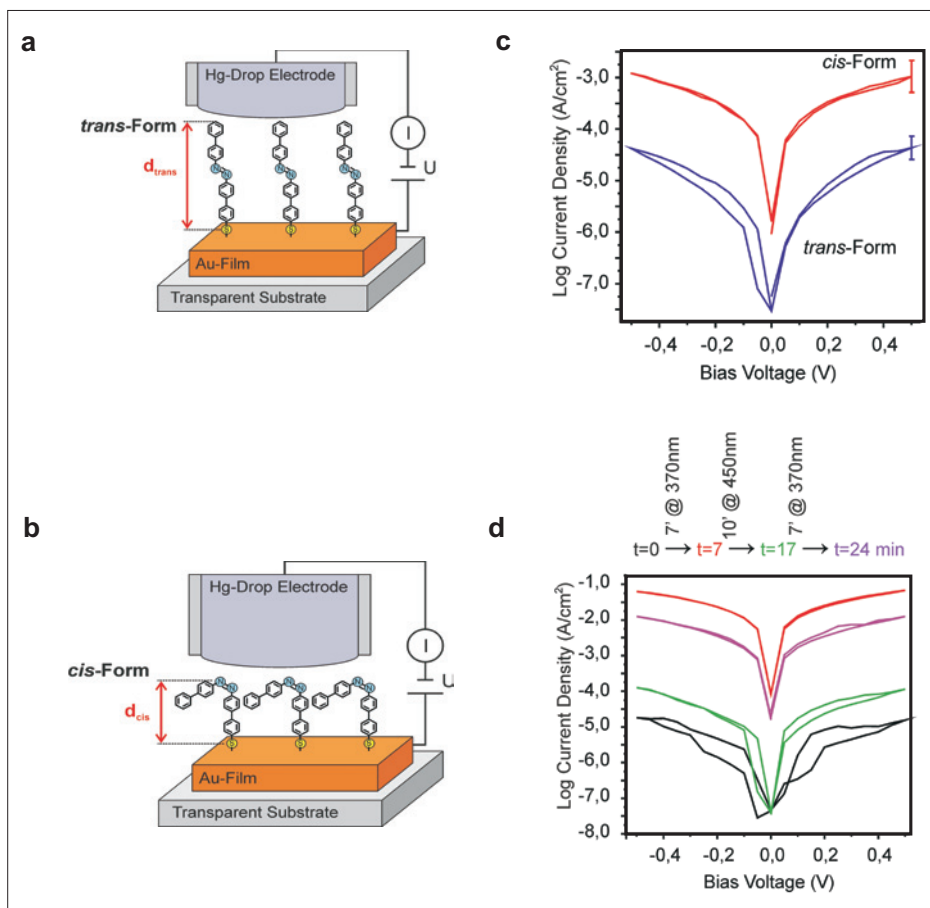


Fig. 6. Left: Schemes of the junction incorporating the SAM_{AZO} in the *trans* (a) and the *cis* form (b). Right: c. i-V curves for junctions a and b; d. i-V curves measured under ‘*in situ*’ alternating irradiation at $\lambda = 370$ nm and $\lambda = 450$ nm.

The most significant results were obtained by measuring the i-V curves upon alternating irradiation ‘*in situ*’ through the transparent Au surface of the SAM_{AZO} sandwiched between the two electrodes. Starting from the SAM_{AZO}-junction in its *trans* conformation, the i-V curves show that the current density increases and decreases reversibly over one order of magnitude upon alternating irradiation ‘*in situ*’ at $\lambda = 370$ nm and $\lambda = 450$ nm, as shown in Fig. 6d. Importantly, similar differences in current were obtained upon *in situ* (Fig. 6b) and *ex situ* (Fig. 6a) irradiation.

These data demonstrate that the SAM_{AZO} is able to keep the electrical contact with the upper C₁₂-SAM-stabilized Hg electrode upon repeated cycles. In fact a loss of electrical contact would result in a lower current for the *cis* with respect to the *trans* isomer, while the results show the opposite. To keep such a contact, the *cis* form of the SAM_{AZO} must be able to lift the Hg drop when returning to the *trans* form, under irradiation at $\lambda = 450$ nm. We explained the switching behavior in terms of the SAM_{AZO} reversibly lifting and lowering the Hg drop on top of the SAM_{AZO}. On the basis of detailed calculations, the force exerted by the Hg drop on a single AZO molecule is estimated to be $F = 2.6 \cdot 10^{-14}$

N. Comparison of this value with the one determined by Gaub and coworkers,^[41] who reported 10^{-12} N, indicates that in the present performances, the system is still far from exploiting its full potential.

The junction incorporating azo-based SAMs behaves as a switch, where light is used as an external trigger. The reversible switch is based on the force exerted by the SAM_{AZO} in lifting the Hg drop electrode.

3. Electrochemical Junctions, M-SAM/R/SAM-Hg (Fig. 1B)

The Hg-based junctions enable redox species (R) to be sandwiched between the Hg-SAM electrodes and the potential applied to the two Hg electrodes to be controlled with respect to the potential of R. This control can be achieved only in an electrochemical four-electrode junction, where the potential applied to each electrode is adjusted relatively to the redox potential of the electroactive species, R, by an external potentiostat.

Fig. 1B schematizes the electrochemical junction based on Hg electrodes and shows the picture of the interface. The junction is assembled directly inside the electrolyte solution, by bringing in contact the two

Hg-drops extruded from the micro-syringes covered by SAMs. The electrochemical connection of the Hg electrodes to the reference electrode *via* a potentiostat allows independent control of the potentials applied to the Hg electrodes so that one can act as electron acceptor (drain) and the other as electron donor (source) to the redox center.

We have used two different approaches to trap the electroactive species in-between the electrodes.

3.1 Redox Centres Covalently Linked to the Electrodes

Redox centers have been incorporated inside the junction by forming at each Hg electrode a SAM of HS(CH₂)₁₀CONHCH₂pyRu(NH₃)₅(PF₆)₂ (abbreviated as HS-C₁₀-Ru), as schematically shown in Fig. 7a. Fig. 7b shows the current flowing through the junction when the potential of the drain (V_D) is swept across the formal potential of the Ru^{III/II} couple, $E^{\circ}_{\text{Ru(III)/Ru(II)}} = -0.04$ V, while the ruthenium species attached at the source electrode are kept in the +2 oxidation state by holding the potential at -0.2 V. For potential of the drain electrode negative of $E^{\circ}_{\text{Ru(III)/Ru(II)}}$ the current flowing through the junction is negligible. When the drain electrode are given potentials positive of $E^{\circ}_{\text{Ru(III)/Ru(II)}}$, both the anodic and cathodic currents increase to reach a plateau with a half-wave (half-maximum) at potential $V_D = -0.04$ V, and a value of $I_{\text{lim}} = 250$ μ A.^[42–44] The charge transport through the junction occurs as a result of the key steps schematized in Fig. 7c: i) oxidation of Ru^{II} to Ru^{III} at the drain, ii) electron exchange between Ru^{III} and Ru^{II} at the interface, and iii) reduction of Ru^{III} at the source back to Ru^{II}.

The electrochemical junctions behave as a switch (or a diode), where the current flow is switched from ‘off’ to ‘on’ by an external signal controlled through the reference electrode.

3.2 Redox Centres Electrostatically Trapped between the Electrodes

Redox centres have been incorporated into an electrochemical junction by using electrostatic interactions as shown schematically in Fig. 8. SAMs were formed separately on the two Hg electrodes from a solution of HSC₁₀COOH, and immersed in an electrolyte pH = 9 solution containing Ru(NH₃)₆³⁺. The negatively charged -COO⁻ exposed by the SAMs in this experimental conditions, have the role to electrostatically attract the positively charged Ru(III) complex and to keep the complex in the gap, when the two electrodes are brought in contact by the micromanipulator (Fig. 8c).^[45]

The potentials of the Hg electrodes were set so that one electrode acted as an

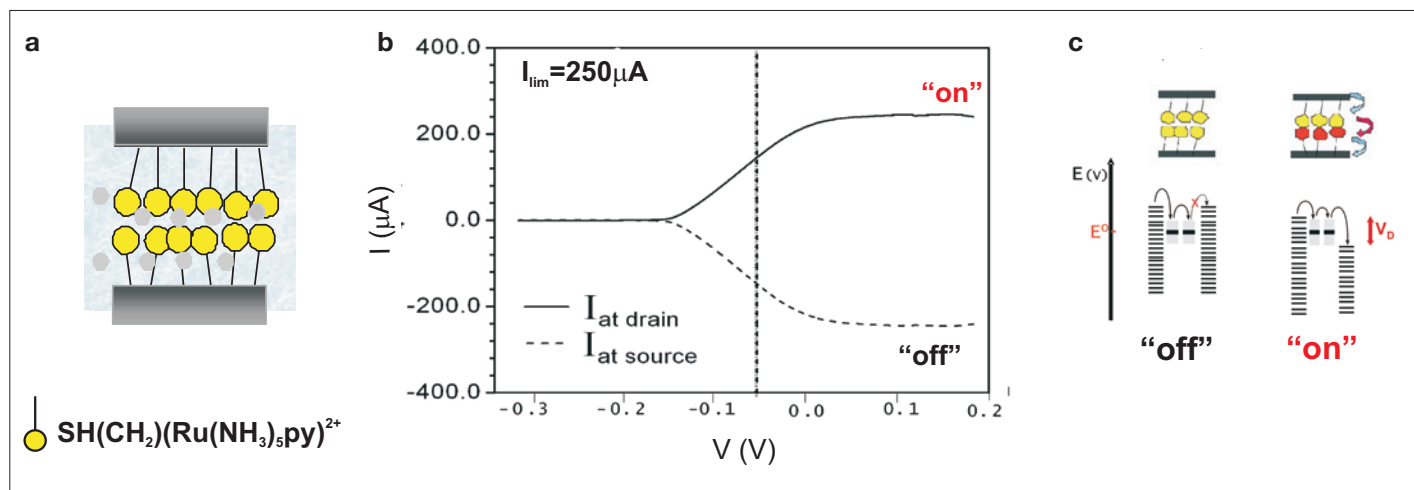


Fig. 7. a: Scheme of the interface of junctions incorporating covalently linked Ru(II) based redox sites. b: i-V curves showing the diode-like behaviour, and c: the operating self-exchange mechanism.

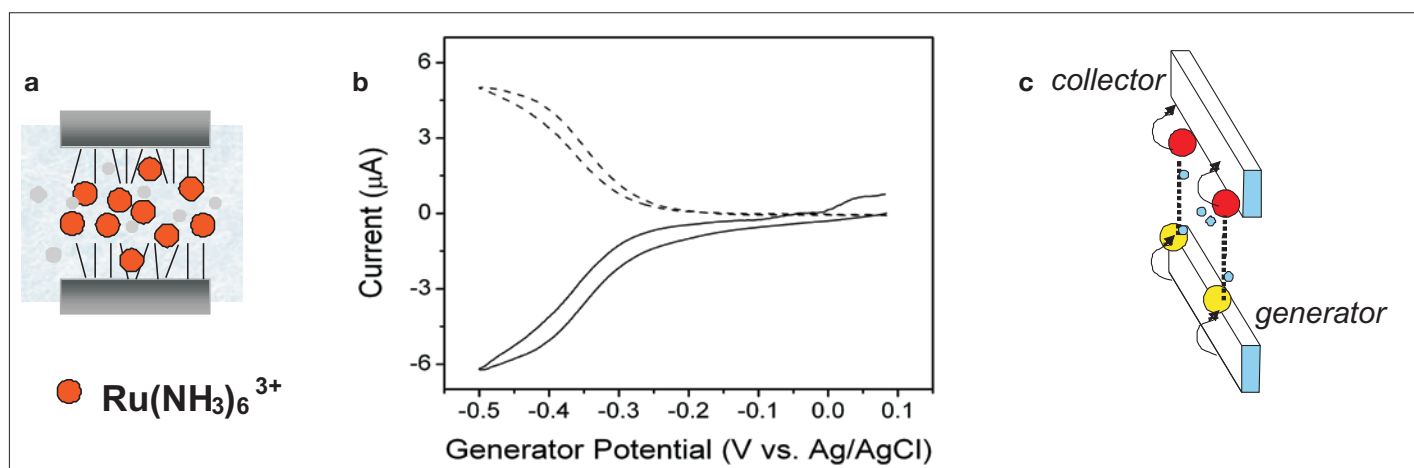


Fig. 8. a: Scheme of the interface of junctions where Ru(III) based redox sites are electrostatically trapped between the electrodes. b: i-V curves showing the diode-like behaviour, and c: the operating redox cycling mechanism.

electron donor (generator) to $\text{Ru}(\text{NH}_3)_6^{3+}$, and the other as an electron acceptor (collector). The electrical measurements were performed by i) cycling the potential of the source electrode (generator) between +0.10 and -0.50 V across the formal potential E^0 (-0.21 V) for the $\text{Ru}(\text{NH}_3)_6^{3+} \rightarrow \text{Ru}(\text{NH}_3)_6^{2+}$, and ii) fixing the potential of the drain (collector) at a value of +0.10 V, keeping the ruthenium in the Ru(III) form. As shown in Fig. 7, the current flows through the junction only when the potential of the electrodes is controlled in such a way that one is able to reduce and the other to oxidize the ruthenium species.

It is well known that electroactive species, confined between two closely spaced electrodes, held at potentials such that one donates electrons and the other accepts them, can generate a current by a redox cycling mechanism.^[46] In the present case, the Ru species confined in a nanometer-wide gap, transport the current through the junction by diffusing back and forth between the collector and at the generator where they are respectively oxidized

and reduced, as depicted in Fig. 7c. This very easy-to-assemble electrochemical junction traps free to move redox centres and behaves as a switch where the current flow, generated by a redox cycling mechanism, is controlled by an external signal.

4. Conclusions

The Hg-based junctions can be considered horse power test-beds for organic electronics on the basis of the results reported above and of a series of major advantages. The major advantages are: i) the easy, inexpensive method used for the assembly, ii) the mechanical stability (only 20% of the junctions short or show anomalous conductivity) and reproducibility,^[47] iii) the variety of conceptually different designs, and iv) the ability to incorporate a range of organic structures of increasing complexity.

When used in electrical mode, they show a clear correlation between the electrical properties of organic molecules with their electronic structure. Signifi-

cantly, we have observed a good agreement between the values of β extracted from electrical measurements performed by the Hg-based junctions, and by c-AFM, with those obtained by transient spectroscopy on supramolecular systems in solution. β remains therefore the parameter that gives fundamental information on the electrical properties of the core of organic molecules, independent of the still problematic interactions between molecule and metal.

A number of electrical and electrochemical Hg-based junctions exhibit the function of solid state electronic devices as switches. In junctions incorporating SAMs formed by photoactive azo compounds on a semi-transparent Au electrode, the current flow is controlled by light: the AZO unit is the core engine powered by light of a molecular-cargo-lifter resulting in an electrical switch. In electrochemical junctions incorporating R at the interface redox sites, either by covalent or electrostatic interactions, the current switches from 'off' to 'on' signal in dependence of the potentials applied to the electrodes respect to that of

the redox site. It is interesting to observe that, even though both electrochemical junctions show diode-like characteristics, the currents are generated by two different electron transport regimes, that is respectively by a hopping and a redox cycling mechanism. We observe that in these easily fabricated devices, the electrodes, being spaced by two SAMs, are separated by just a few nm.

The results species obtained by incorporating electroactive species both in the electrical and the electrochemical junctions, underlay the role of redox centres in molecular electronics: they can provide well defined, easily reachable energy levels which are available stations for the electrons to hop. In fact, we have shown that by incorporating a number of redox centres in a rigid organic backbone, it is possible to obtain MWs which exhibit an ohmic electrical behaviour via a hopping mechanism.

In this case, by increasing the number of redox centres, the MWs, longer than 50 nm, remain highly conductive and they are excellent candidates for connecting electrically larger gaps as easier to fabricate electrodes.

The Hg-based junctions present also some disadvantages with respect to physics-based experimental methods: i) they do not have the molecular-level resolution that makes measurements using scanning tunneling microscopy (STM) and break junctions so informative; ii) they are not compatible with measurements over a range of temperatures; iii) they cannot be developed into practically useful microelectronic components because of the unfriendly nature of Hg. Recently, the Hg drop electrode has been replaced by with a liquid In/Ga alloy drop,^[48] or alternatively, a conductive polymer was spin-coated on the SAM in order to avoid electrical shorts with the Hg-drop.^[49]

These junctions measure the collective electrical behavior of a large number of molecules ($\sim 10^{13}$) sandwiched between the electrodes at the contact area. In this respect they represent a useful complement to physics-based experimental methods (STM, c-AFM).

Whether single molecules will ever be used as active elements in electronics is still a questionable issue; certainly SAMs of organic molecules are closer than single molecules to application in organic molecular electronics.

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