

Do molecular rectifiers exist?

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1. Introduction

The semiconductor industries try to minimize their products by many scientific and technological innovations. In order to following this trend to provide faster and cheaper computers, the size of the microelectronics circuit components would be the scale of atoms and molecules in 15 years and require new device structure. As a result the concept of molecular electronics has aroused both in science fiction and among scientists. This field is currently a very active research field, and many fundamentals questions concerning both theory and experiments are left open. Simple molecular electronic devices usually consist of organic molecules sandwiched between conducting electrodes. One of the examples is the molecular rectifier which is a basic component in molecular electronics and has been explored in recent years. The size for the molecular diode is on the order of nanometers, more than a million times smaller than those presently available commercially.

Since more than three decades, after the theoretical work of Aviram and Ratner in 1974 [1] scientists design and synthesize molecular rectifiers made from a donor insulator acceptor molecule connected between two electrodes. In the D-B-A (Donor-Bridge-Acceptor) system, the electron donor should have low ionization energy which is separated from a high electron affinity acceptor by an alkyl chain. Under forward bias, the electrons can tunnel from the donor to the acceptor through the spacer. However, for the reverse bias conduction is not as easy. According to the seminal theoretical work in 1974, such a junction should give $I-V$ (current-voltage) characteristics similar to behavior of a p-n junction as in the solid-state physics; the rectifying behaviour is seen in the p-n junction or diode. The most basic property of this junction is conducting an electric current in one direction and block it in the reverse direction. This behaviour arises from the electric characteristics of the junctions. When the p-type region of the p-n junction is connected to the positive terminal of the battery, current will flow. The diode is said to be under forward bias. However, the current completely blocks when the battery terminals are reversed and it is called the reverse bias. So the current-voltage ($I-V$) curve for this junction, unlike the wires and resistors which are known as ohm's law, is nonlinear. Recently, this proposal for the rectification has been debated and other mechanisms are suggested. Some fundamental questions remain from different experiment and various observations. In the past decade rectification was measured on molecular layers formed by Langmuir Blodgett (LB) technique. A Langmuir-Blodgett film contains of one or more monolayers of an organic material, deposited from the surface of a liquid onto a solid by immersing the solid substrate into the liquid. A monolayer is added with each immersion step, thus films with very accurate thickness can be formed. An alternative technique of creating a single monolayer on a surface is that of self-assembled monolayer (SAM). Assembled monolayers are surfaces consisting of a single layer of molecules on a substrate. Assembled monolayer can be prepared simply by adding a solution of the desired molecule onto the substrate surface and washing off the excess. Also recent progress in nanotechnology and nanoscience has facilitated both experimental and theoretical study of molecular electronics. The development of the scanning tunnelling microscopy (STM) and the later the atomic force microscopy (AFM) have facilitated manipulation of single-molecule electronics. Understanding carrier motion in either single molecules or in assemblies of molecular subunits may help to design and construct molecular device like solid-sate devices.

In this paper we review different measurement techniques and various views about the molecular rectification.

2. Ingredients of the D-B-A system: Molecule

2.1 Electron delocalization

Electronic conduction in a material has two requirements: (1) a continuous system of a large number of strongly interacting atomic orbital leading to the formation of electronic band structure, and (2) the presence of an insufficient number of electrons to fill these bands. Electrons can be localized on certain atom(s) or delocalized between two or more atoms and type of the bond between two atoms depend on how much electron density is localized or delocalized among the atoms.

In molecules, two different chemical bonds can form. A molecule orbital that is symmetric along the axis connecting two atomic nuclei is called sigma bond. This bond formed from overlapping s or overlapping p orbital as depicted in the Figure 1. Pi bonds are formed when p orbitals overlap side by side. Figure 2. illustrate that the electrons density is concentrated in regions above and below the bonding axis.

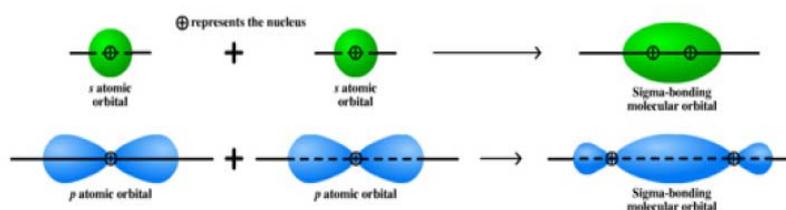


Figure 1. Schematic of sigma bond by s orbital and p orbital

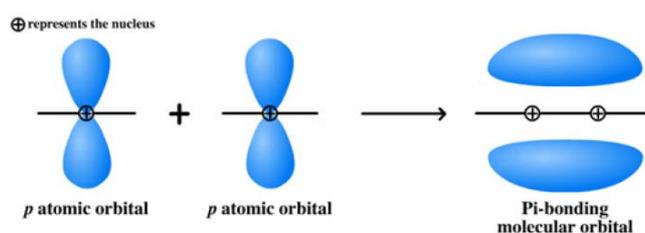


Figure 2. Schematic of Pi-bond by p orbital

Aliphatic molecules are singly bounded molecules like C-C or C-H that contain only sigma bonds. The positive charge of the nuclei prevents electron to travel along the axis of the molecule. Thus this structure can not easily transport electrons and they act as insulators and when they put in the middle of the conductive structure, they act as a resistor in a molecular circuits. Double bonds can be seen in the alkenes which contain double-carbon bonds, and referred to as unsaturated hydrocarbons. Ethene or ethylene is the simplest alkene, with the formula C_2H_4 . Carbons with double bond are sp^2 hybridized, with 3 sp type hybrids available to form sigma bonds, and 1 p orbital with 1 electron for bonding. Thus these two adjacent p orbitals can overlap to form a pi bond. (Figure 3.)

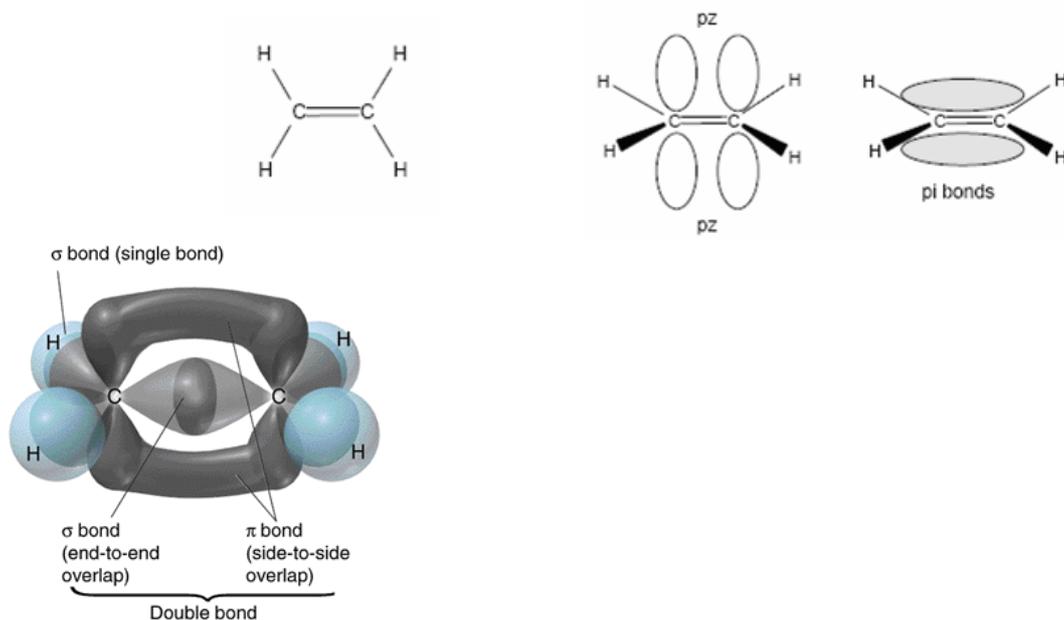


Figure 3. Pi bond in the Ethylene

In contrast with the aliphatic molecule, a conjugated molecule consists of alternating single and double bonds that link the subsequent atoms. There is an extended series of overlapping p orbital which make the pi bond. In conjugated oligomers electrons from pi are delocalize over entire molecule but sigma orbitals are not studied. Polyphenylene and polyphenylene-based molecules are good example of conjugated polymers. In the Figure 4. we can see delocalization, for instance in benzene(C_6H_6), each carbon atom has one p orbital, two adjacent p orbital share their electrons between more than two atom to form a delocalized pi bonds. The delocalization in benzene can be extended to other adjacent benzene ring.

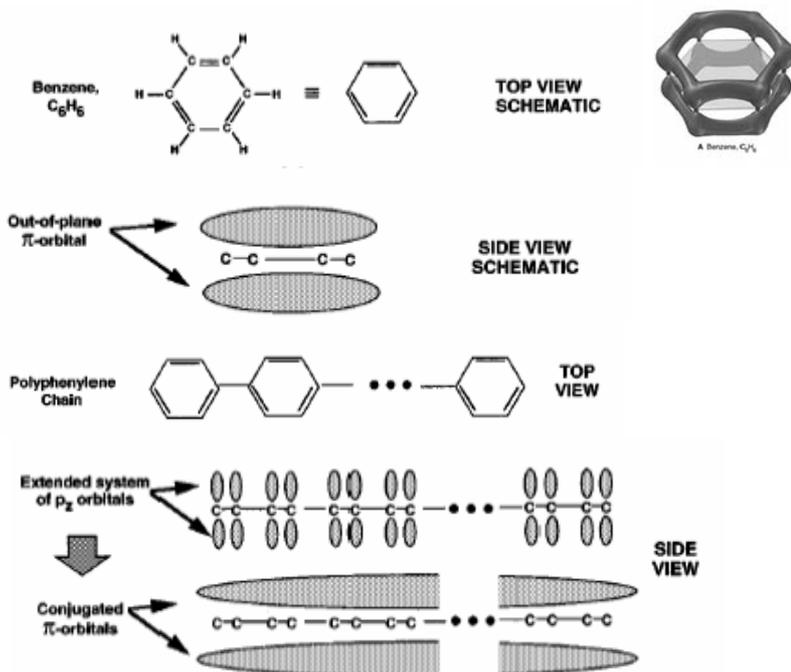


Figure 4. Schematic diagrams of the chemical structures and the molecular orbital structures for benzene and for polyphenylene molecules [5].

2.2 Conduction Mechanisms

Charge transport in molecular junction depends on both molecule and metal-molecule coupling. Transport through individual molecule is different from the bulk transport because of the inherently small size of molecule, also to understand conduction at the metal-molecule, the Fermi level matching (or mismatching) in metal and molecular orbital in the terminal molecule must be considered [11]. In general there is a contact barrier like a Schottky contact at interface because of mismatch between the Fermi energy of metal and HOMO or LUMO level of the molecule and transmission of the charges will be reduced. Applied bias can raise the energy of some molecular orbital and lower the energy of others. So the electronic structure of the molecules will change as a function of applied bias voltage. (Figure 5.)

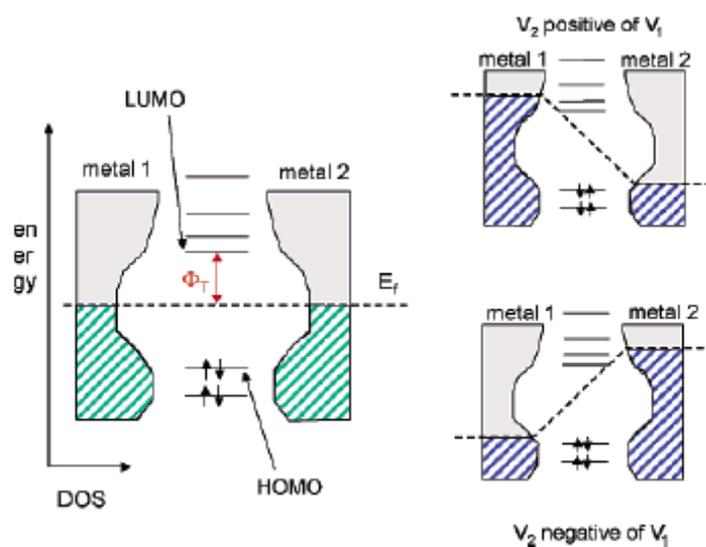


Figure 5. Schematic energy levels of a metal/molecule/metal molecular junction at zero bias (left) and with an imposed voltage (right). The curved positioned of the metal contacts represents the density of electronic states in the metal and E_f is the Fermi level. The green hashed region represents the filled orbitals when $V=0$, and blue regions are filled orbitals when a bias is applied. The dashed lines in the right drawing represent the imposed electric field, and Φ_T is the tunnelling barrier at zero bias [11].

The transport in molecular junctions is dominated by electrons or holes depending on the height of their barriers, the barrier thickness and the presence of the defects in such a contact. Table 1. is depicted different mechanisms like electron tunneling, thermally induced hopping, transmission through Schottky barriers, and other process [11, 14]

1. *Schottky emission*: known as thermionic emission is important to show the electron transfer at interface.

2. *Frankel-Pool Conduction*: This tunnelling is related to hopping, and developed to explain the effect of traps in the semiconductors or molecules. A trap means a “columbic” site whose potential well depth varies in an electric field. It is varies exponentially with the square root of the electric field, but the energy barriers for Pool-Frankel conduction are within the molecule rather than at the molecule/contact interface.

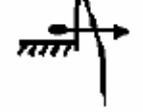
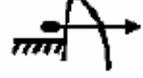
Conduction Mechanism	Characteristic Behavior	Temperature Dependence	Voltage Dependence	Schematic Band Diagram
Schottky Emission	$I \sim T^2 \text{Exp}\left(-q \frac{F - \sqrt{\frac{qV}{4\pi\epsilon d}}}{kT}\right)$	$\ln\left(\frac{I}{T^2}\right) \sim \frac{1}{T}$	$\ln(I) \sim V^{1/2}$	
Frankel - Pool Conduction	$I \sim VT^2 \text{Exp}\left(-q \frac{F - 2\sqrt{\frac{qV}{\pi\epsilon d}}}{2kT}\right)$	$\ln\left(\frac{I}{T^2}\right) \sim \frac{1}{T}$	$\ln\left(\frac{I}{V}\right) \sim V^{1/2}$	
Hopping Conduction	$I \sim V \text{Exp}\left(-\frac{\Delta E}{kT}\right)$	$\ln\left(\frac{I}{V}\right) \sim \frac{1}{T}$	$I \sim V$	
Fowler-Nordheim Tunneling	$I \sim V^2 \text{Exp}\left(-\frac{4d\sqrt{2m}}{3qhV}(qF)^{1.5}\right)$	—	$\ln\left(\frac{I}{V^2}\right) \sim \frac{1}{V}$	
Direct Tunneling	$I \sim V \text{Exp}\left(-\frac{4\pi d}{h}\sqrt{2mF}\right)$	—	$I \sim V$	

Table 1. Possible conduction mechanisms [14].

3. *Hopping Conduction*: This term is related to thermally activated electron transfer that follows a classical relation: $k_{ET} = k_{ET} \exp(-E_a / kT)$ where k_{ET} is the electron transfer rate, E_a is an activation barrier, and k is the boltzman constant. Hopping involve electron motion over the barrier, while tunnelling involves electron transfer through the barrier. Hopping will be changed like d^{-1} with distance not exponential. For large d , the electron can not propagate by tunnelling, thus hopping is dominant. Also it depends on the temperature.

4. *Fowler-Nordheim Tunnelling*: Also called “field emission”, this tunnelling occurs in the high electric fields. “High” means that applied voltage is higher than barrier height. It is independent from temperature, but decrease exponentially with distance. Also it occurs at interface of the system.

5. *Electron Tunnelling*: In quantum mechanical objects exhibit wave-like behavior unlike the classical objects. When the potential energy, U , is greater than the total classical energy, E , the barrier or forbidden region is made. An electron of energy E impinging on the potential barrier from left in Figure 6. has an exponentially damped. If U and E are both large (several electron volts) and d is very small (of the order of 1 nm), there is a finite probability of the incident electron emerging into the classically allowed region III. Quantum mechanics predicts that the transmission probability will be proportional to $\exp[-Ad\sqrt{U - E}]$. Thus, Electron tunnelling is defined as motion of electrons from one classically allowed region to another through a region where the electron is classically forbidden to exist.

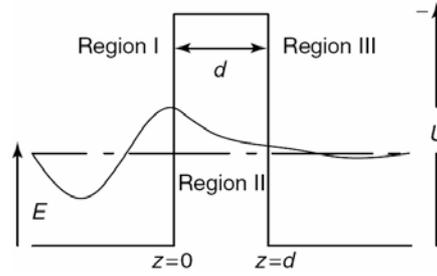


Figure 6. Schematic representation of the elastic tunnelling process [15].

5.1 Elastic and Inelastic Tunnelling: If the energy of the incident and emerging electron are the same, we have elastic tunnelling which is known as non-resonant – coherent or direct tunnelling. This normal elastic tunnelling can occur through a large potential barrier. Barrier is often a very wide band gap insulator. When the energy between the incident and emerging electron due to loss of energy is different an inelastic- incoherent or resonant tunnelling will occur. Impurities or trap in insulator, vibrational coupling (inelastic collisions) can be some reasons for losing the energy. Resonant tunnelling can happen in the semiconductor when transport energy level, HOMO and/or LUMO in the barrier (or quantum well) are closely situated to the electron potential energy (or Fermi levels for metals).

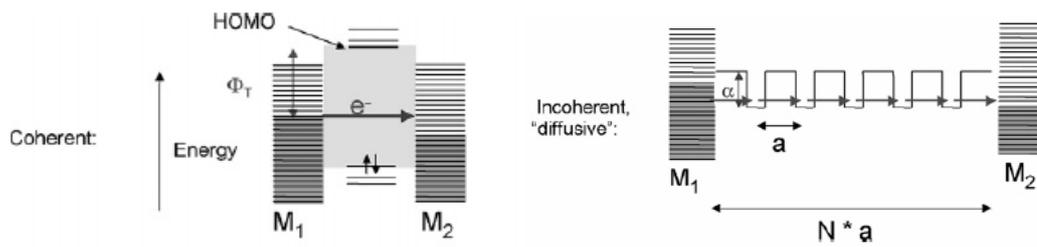


Figure 7. Schematic energy level diagrams for coherent and incoherent tunnelling. Φ_T is the barrier for coherent tunnelling, α is the potential well depth of N sites spaced apart by a distance a . M_1 and M_2 are metallic contact [11].

Figure 8. shows a typical tunnel junction such as an Al-Al₂O₃- anthracene – Pb diode and both elastic and inelastic tunnelling is depicted [15]. The HOMO and LUMO of anthracene are also shown in this Figure, with some schematic ground vibrational levels. The weak interaction between the top metal and anthracene causes a shift in anthracene’s energy levels but does not produce significant changes in its level spacing. This is not true for every molecule/metal combination, but recent studies indicate that it is usually true. In the realistic model, each metal have its own work function, Φ_M . As two metals and an insulator are brought together, electrons flow by tunnelling until the Fermi levels are matched. When the Fermi energy is matched, no current flows.

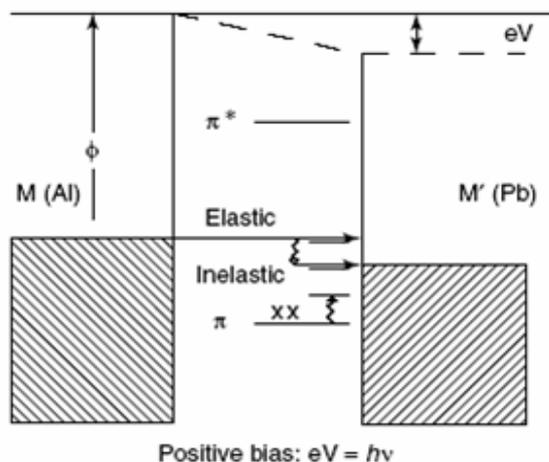


Figure 8. Energy diagram for an Al–Al₂O₃–anthracene–Pb tunnel diode showing elastic and inelastic tunneling processes. (a) The hatched region represents the filled states of the top and bottom metal electrodes. The area in the center represents the anthracene coated alumina. The HOMO (π) and LUMO (π^*) orbital energies and a few vibrational levels are indicated. The case shown is where the bias energy (eV) is just sufficient to allow inelastic tunneling with excitation of the first vibrational level, $eV = hv$. Energy loss (equilibration) for the tunneling electron occurs through a cascade process in the M' electrode [15].

2.3 Aviram and Ratner model

Based on the model proposed by Aviram and Ratner [1,5], the molecular rectifier consists of three parts, a donor, an acceptor and a bridge which separates the donor and acceptor by sigma bonds. This molecular system should show the properties of the p-n junction. By using substituents on the aromatic system; we can modify the pi electron density of the organic molecule. Electron donating substituents which increase the pi-electron density make the molecule electron rich like the n-type oppositely; the electron withdrawing substituents decrease the electron density on the organic molecule and modify the molecule to act like a p-type. Because the system of donor and acceptor can interact strongly with one another, we should separate them by the use of a sigma-electron system.

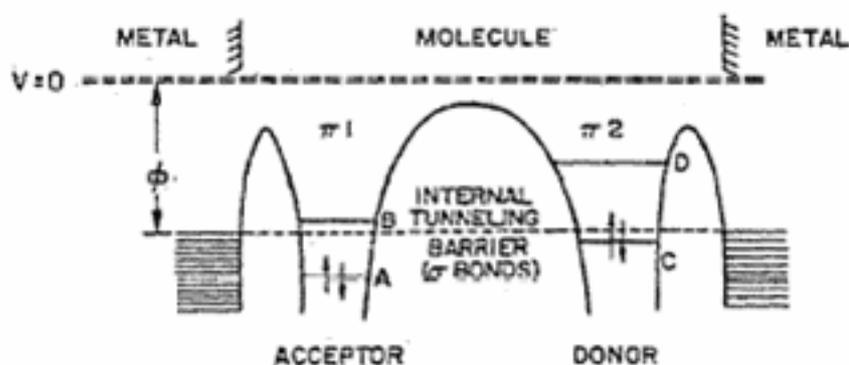


Figure 9. Energy versus distance of the device. B and D the affinity levels and A and C the highest occupied levels, of acceptor and donor, respectively [1].

Making a good electron donor happens by lowering the ionization potential which increases the pi-electron density and creating a good electron acceptor is done by raising the electron affinity which decreases the pi electron density. Electron affinity is the empty orbital which accepts electrons from the cathode. The electron affinity will be of the order 1-3.5 Volts. The electron affinity level of the acceptor should be empty and lie at or slightly above the Fermi level of electrodes in a good rectifier. The ionization potential of the donor will be of order of 5-9 Volts. In this model electrons can transfer from a cathode to the acceptor and from the donor to an anode.

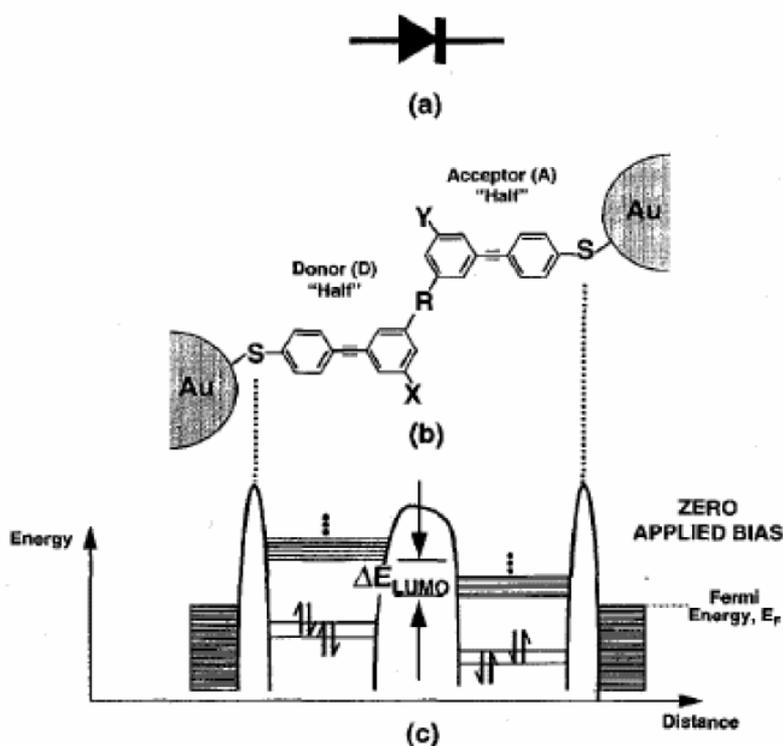


Figure 10. Molecular structure and schematic of electron orbital energy levels for a proposed polyphenylene-based molecular rectifying diode switch [5].

Figure 10. depicts the molecular structure and the energy level of polyphenylene-based rectifier according to the Aviram & Ratner proposal.[5] The electron donating group and electron withdrawing moiety are incorporated into a single molecule. The X and Y groups are known as “intermolecular dopants”, because they act like a dopant in the solid state to transfer the electronic properties. In this Figure R is the semi-insulating group. As depicted in the Figure 9(c) in the energy diagram, the bridge creates a tunnel barrier. Also there is a barrier between the gold surface and the molecule due to thiol linkage. But this barrier is not high enough to prevent electron tunnelling. For group R, most obvious candidates are aliphatic groups like methylene($R = -CH_2-$) or dimethylene groups ($R = -CH_2CH_2-$). The electron donating substituents X are $-NH_2$, $-OH_2$, $-CH_3$, $-CH_2CH_3$, etc. the electron donating which are bound to the aromatic ring and create more electron density in the ring so the repulsion increases among the electrons in the molecular orbitals of ring. Thus, these repulsive interactions raise the total energy (Figure 10(c)). The common electron withdrawing groups Y are $-NO_2$, $-CN$, $-CHO$, $-COR$, etc. where the R is an

aliphatic chain. These groups reduce the electron density in the aromatic ring thus the repulsive interaction between the electrons decreases and total energy will be reduced.

2.3.1 Forward Bias

As shown in Figure 10(c) there is a difference between the pi orbital energy levels of the acceptor and donor made by the substituents unit (dopant). By applying a voltage in the forward bias, with higher voltage on the left-hand gold contact and the lower voltage on the right-hand side, energy levels of the electrons will shifted to the higher energies on the right-hand contact and the and to the lower energies on the left-hand contact depicted in the Figure 11(c), the difference in the energy induced the electron to flow from right to left through the molecule to reach the lower energy level.

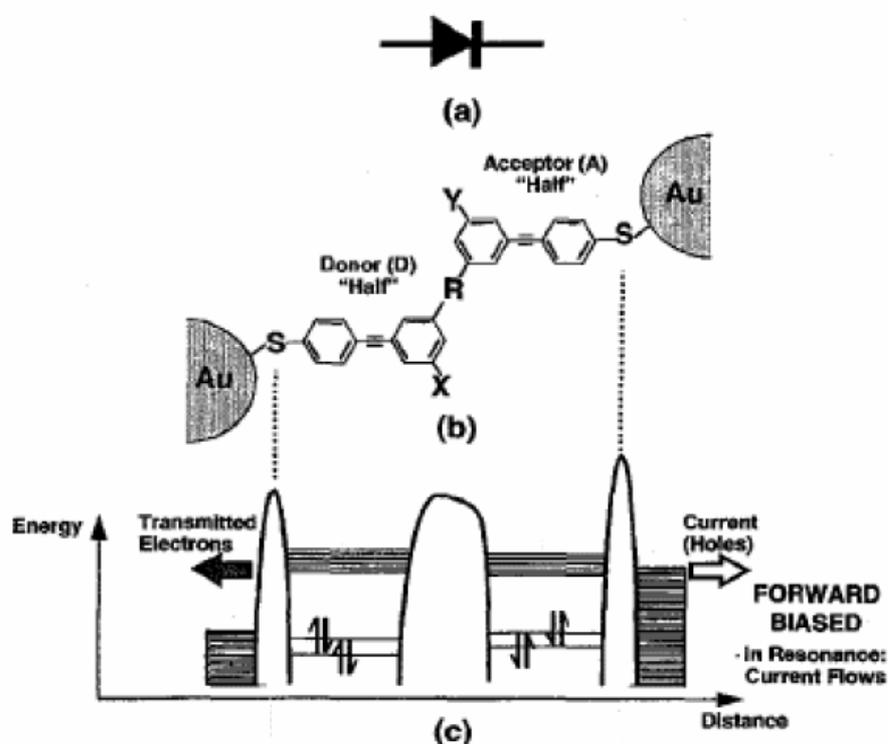


Figure 11. Schematic describing operation of a proposed polyphenylene-based molecular rectifying diode switch under forward bias [5].

The closely spaced horizontal line at the far left and far right of Figure 10 and 11 represent occupied levels in the valence band. Fermi level is the highest of these occupied levels, which is known as Fermi energy in the metal contact. Unoccupied levels above these occupied levels are so close but they are not depicted in the Figure 10 and 11. The voltage bias must be sufficient to increase the Fermi energy of the electrons in the occupied levels of the gold on the right at least as high as the energy level of the LUMO of pi-orbital in the acceptor segment. Then, the electrons can tunnel from the right gold contact into the empty LUMO of acceptor. As the LUMO on the left part align with those on the right hand side of the molecule therefore electrons again can tunnel into the insulating barrier to the unoccupied level in the donor segment. Finally resonant transmission into the left-hand contact happens,

because the unoccupied level of the metal is very dense. In the forward bias only a relatively small voltage bias is required to raise the Fermi energy of the right contact exceeds the acceptor's LUMO, because total energy of the acceptor have been lowered by the presence of the dopant group Y.

2.3.2 Reverse bias

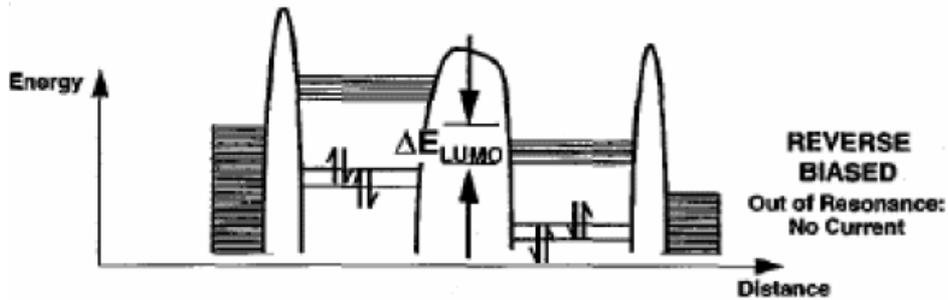


Figure 12. Operation of a proposed polyphenylene-based rectifying diode under reverse bias [5].

In contrast, if we applied the reverse field to the system with the higher voltage on the right-hand contact and the lower voltage on the left gold contact, the Fermi energy on the left raised and on the right side decreased as depicted in Figure 12. In this situation for electrons to tunnel from the left contact to the right the voltage must be sufficient to raise the Fermi level of the gold contact at least as high as the energy of the LUMO of the donor. However in the reverse bias, the threshold voltage should be relatively high compare to forward bias because the total energy of the donor unit is raised by dopant group X. This is the true rectification because a rectifier has a threshold voltage for conduction in one direction that is larger than in the other direction. Thus, the rectifier characterization is nonlinear like depicted in Figure 13.

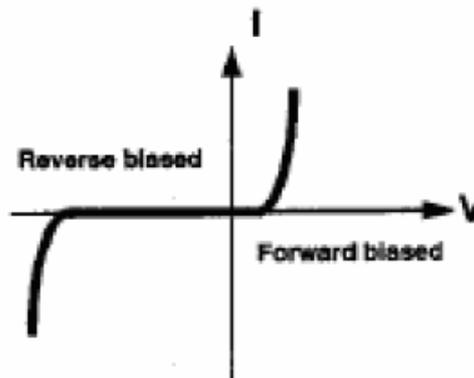


Figure 13. *I-V* Characterization

2.4 Examples of molecular rectifiers

The hemiquinone molecule shown in Figure 14. is a molecule introduced by Aviram and Ratner as a molecular rectifier. The quinone groups on the left decrease the pi density and increase the electron affinity, but the methoxy groups (- OCH₃) on the right side increase pi density and lower ionization potential. Thus, the molecule with high electron affinity on the donor side and low ionization potential on the acceptor segment can show the rectification [1].

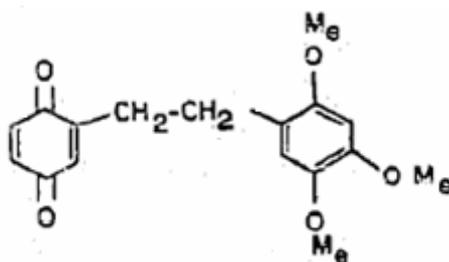


Figure 14. Example of molecular rectifier [1].

Also the molecule depicted in Figure 13 is an example of molecular rectifier, tetracyanoquinodimethane (TCNQ) as an acceptor and the donor tetrathiofulvalene (TTF) segment which separate by triple methylene (-CH₂-) bridge to ensure molecular rigidity [1].

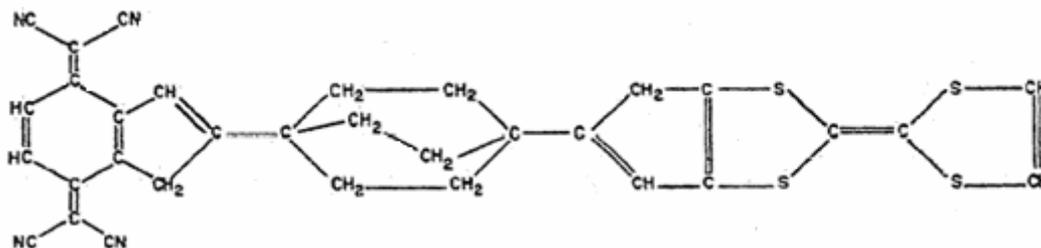


Figure 15. Example of molecular rectifier [1].

2.5 Fabrication

Investigation the electronic properties and transport in the individual molecule by fabricating a single molecule device is usually difficult, therefore scientists attempt to understand this behavior by using synthetic chemistry. For macroscopic connections, two techniques are used (1) the Langmuir-Blodgett (LB) film and (2) Covalent “self assembly” which connect the molecule to the electrode interface. These techniques are simple and rapid to fabricate and analyze.

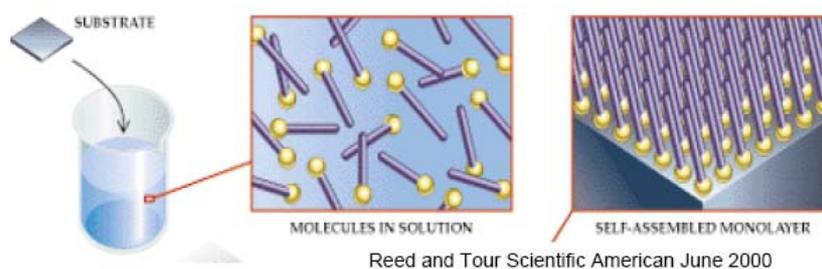


Figure 16. Self assembled monolayer process

Self assembly is a phenomenon in which atoms, molecules, or groups of molecules arrange themselves in a regular pattern spontaneously without outside intervention. As depicted in the Figure 16. The self-assemble monolayer (SAM) can be formed by putting the solid surface for certain time to an environment which contains active surfactant. The order monolayer is energetically favorable. A common and simplest example is an alkanethiolates on gold surface. Sulphur has particular affinity for gold and an alkane with a thiol head group will stick to the gold surface. Thus SAMs are chemically specific which means that thiol will absorb on an Au, but not on the Si. In self-assembly two forces participate: first, strong covalent bond between the metal substrate (Au) and the linking group (S) and the second force is van der Waals interaction between adjacent hydrocarbon tails. These interactions form a well-ordered layer on the substrate [7]. The electronic properties of a SAM are dependent on the metal substrate on which the SAM forms (Au, Ag, Cu, Pd, Pt, Hg, GaAs), the chemical structure of the chain (alkane, aromatic), and the linking group that binds covalently to the metal like S, Se, and Te and this linking group is known as “alligator clips”

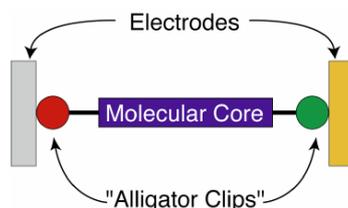


Figure 17. Drawing of electrons, molecule and alligator clips [13].

In the past decade, researchers also used the Langmuir-Blodgett (LB) technique to prepare the $D\sigma A$ diodes. By this technique monolayers or multilayer films can prepare. The LB technique is similar to the self-assembly, except that a force from outside is present and it does not need thiols or Au surfaces. They used an aliphatic chain attached to one end of the molecule. This chain will form a tunnel barrier and make a strong coupling between the molecule and two electrodes. The asymmetric coupling because of the aliphatic chain can lead to rectification behaviour itself. Thus, based on some experiment the observed rectification could be due to the aliphatic chain in the LB technique rather than the $D\sigma A$ bridge. In order to get some information before doing experiments, scientist attempt to predict the result by some theories and calculations. Recently some new method based on the density functional theory is used to model the behaviour of the molecular device coupled to electrodes with different work functions. Two phenylene-ethynylene segments are connected by

a dimethylene bridge and coupled to the gold electrodes by thiolate bonds. An amino and nitro side group are attached on the D and A respectively.

Based on this new method, it is investigated that the electronic structure of the D σ A depends on the bias. It means that electronic states are localized either in the donor part or in the acceptor part of the molecule, except for certain voltage at which the states are delocalized entire the molecule. In this voltage, the current increase suddenly and rectification will appear. However, for the above-mentioned molecule rectification was not found. To obtain a better diode characteristics, the gap between the HOMO of the D part and the LUMO of the A part should be decrease, so the resonant conditions can be obtained for a smaller bias. To achieve smaller gap, other electroactive substituents should be used. Stokbro and co-workers [8] by using this new method of calculation density functional theory conclude that the Aviram-Ratner diode can be an effective rectifier. And they can use this method to predict experimental result in advance.

3. Ingredients of the D-B-A system: Junctions

3.1 Molecular-Metal contact

In the previous parts, rectification was explained based on the D-B-A system. Under forward bias in that system the electrons can tunnel from the donor to the acceptor through the spacer but not in the reverse bias. However it is difficult to realize rectifier behaviour just by this principle. Observation of the rectification is easy but nontrivial to observe true molecular rectification, because the current can be rectified in many parts of the device. Indeed the rectifier behavior also depends on the structure of the bridging molecules and the way of connection to metal surface, the details of how the molecular diode made is important, the way how molecules assemble across the junction, whether the molecules are bound covalently or noncovalently and what materials use in the electrodes.

3.2 Rectification of Schottky barrier at interface

In the solid state physics, the contact of the metal-semiconductor is most common form of junction which is used in circuits. At the interface of this junction, a barrier can be made known as Schottky barrier Φ_b , as shown in Figure 18. However, not all metal-semiconductor junctions are Schottky barriers. It depends on the metal's work function (work function is defined as the energy to remove the electron from the Fermi level to vacuum state), the band gap of the intrinsic semiconductor, and the type and concentration of dopants in the semiconductor.

Various models try to explain how these barriers are determined. However the structure, impurity, defects, etc, at the interface is not known. If the work function of the metal is larger than work function of the semiconductor, electron start to flow from the semiconductor in to the metal until the Fermi energy of both solids is equal. Thus a depletion region of width W is formed in the semiconductor and a negative layer in the surface of metal.

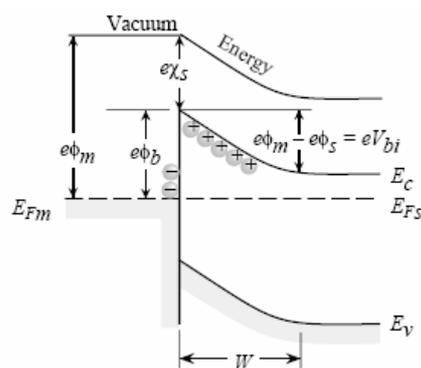


Figure 18. Metal-Semiconductor (n-type) junction at equilibrium.

Schottky contact has a rectification capability, with large current in the forward bias and very low in the reverse bias and suitable for use as a diode. The I - V curve for Schottky junction in metal-semiconductor connection is depicted in the Figure 19. compare to the ohmic contact. As we can see the nonlinear I - V curve is similar to the I - V curve in molecular diode.

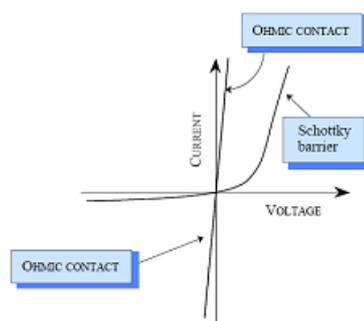


Figure 19. I - V characterization for Ohmic contact and Schottky contact.

The same barrier can occur at the interface of the molecule and metal, because of the mismatch in the work function of metal and orbitals in the molecule. Therefore, the rectification behaviour in the molecular diode can correspond to this barrier not to the properties of the molecule. Now, this can be also regarded as a molecular rectifier and the following question arises:

Does the junction rectify because of the molecule or because of the Schottky barrier?

Ashwell and co-workers [2] tried to answer this question by showing rectification in the metal/organic-multilayer/metal for a special molecule, zwitterionic, $C_{16}H_{33} - \gamma Q3CNQ$ (Figure 20.). This molecule again consists of three parts, an electron donor, an electron acceptor, and a bridge segment. In this experiment, they used passive organic barriers between the active molecule and metal layers to investigate the Schottky barrier effects. The Langmuir-Blodgett film of the zwitterionic molecule, between platinum and magnesium electrodes is prepared as a sample. For the first time a passive organic spacer, ω -tricosenoic acid layers is used to separate the active molecule and electrodes, because this barrier prevents Schottky barrier effects.

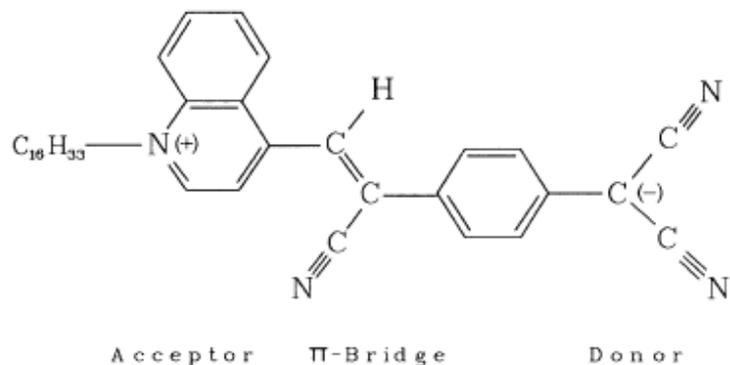


Figure 20. Chemical composition of $C_{16}H_{33} - \gamma Q3CNQ$ [2].

First, the metal/Langmuir-Blodgett multilayer/metal (M/LB/M) was fabricated. Then the voltage, typically less than 2 V, was applied to this system. Rectifier characteristics have been observed in lower thickness junctions of the M/ $C_{16}H_{33} - \gamma Q3CNQ$ /M. However, because of the high noise levels, the thicker monolayer junctions (> 5 monolayer) are used. Figure 21 depicts the $J-V$ curve for the 7 monolayers of $C_{16}H_{33} - \gamma Q3CNQ$. However, there is not a good theory to explain this $J-V$ characteristic.

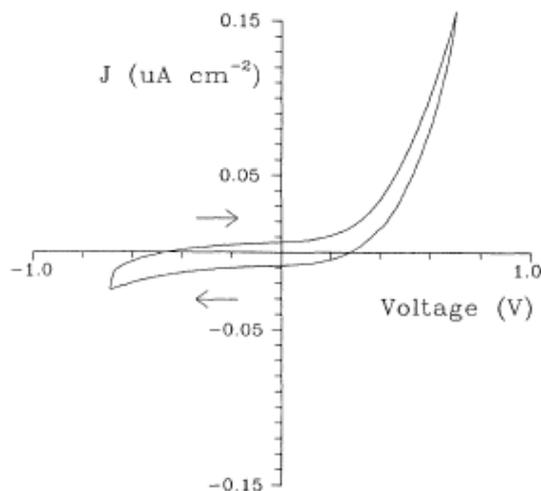


Figure 21. Current density-voltage curve from a Ag/7 monolayers of $C_{16}H_{33} - \gamma Q3CNQ$ /Mg junction [2].

The second structure investigated is the Ag/22TA/ $C_{16}H_{33} - \gamma Q3CNQ$ /22TA/Mg/Ag where 22TA represents a ω -tricosenoic acid LB film. Figure 22. is a typical $J-V$ curve for a bilayer ω -tricosenoic acid / trilayer of $C_{16}H_{33} - \gamma Q3CNQ$ film/ bilayer ω -tricosenoic acid film. Data for the forward and also for the reverse bias again follow same function, just the maximum of the current reduced compare to the previous experiment and the dependence are the same as for single-component $C_{16}H_{33} - \gamma Q3CNQ$ junctions.

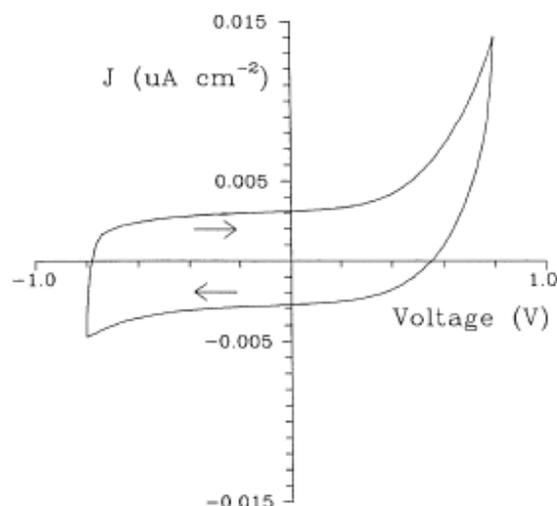


Figure 22. Current density-voltage curve from a Ag/22TA/ C₁₆H₃₃- γ Q3CNQ /22TA/Mg junction with bilayers of ω -tricosenoic acid and 3 monolayers of C₁₆H₃₃- γ Q3CNQ [2].

Therefore, the first rectifying characterization is shown for the active molecule between electrodes and the same type of rectifying behaviour is demonstrated in the second experiments in which the active molecule is separated from the electrodes by a passive layer.

The experiment for the zwitterionic molecule has demonstrated that Schottky barriers at the interface do not cause the rectifying behaviour of the M/ C₁₆H₃₃ - γ Q3CNQ /M junctions and the experiments clearly proof that the rectifier characterization is associated with the molecular structure and it depends on the spatial asymmetry during the deposition of the zwitterionic Langmuir-Blodgett film.

3.3 OPEs Systems

In contrast with previous experiments some research groups still pay attention to metal-molecule contacts, since they believe that this contact play a key role in determining the current-voltage characteristics of a molecular junction. Also some experiments support their ideas. From this view metal/ molecule/metal junction can be divided in three parts: the molecular core and two metal- molecule contacts, one on each side. It is claimed that the metal-molecule contacts are as important as the molecule core in defining the I - V characterization. Many groups investigated metal-molecule contacts by chemically bond at one side while keeping the other interface constant. Controlling the metal-molecule contact at one side should provide a means for controlling rectification. [12, 13]

Oligo(phenylene ethynylene) (OPE) system is one of the molecular electronic system which received a lot of attention. Researcher can fabricate these kinds of molecules in the well-ordered monolayer. Also investigations of the properties of the molecule-metal interface by the simple structure of these molecules are easy. Also OPE molecules can make well-ordered monolayer.

Kushmerick and his colleagues [12] synthesized and measured four different OPE s to explore the effect of metal-molecule contacts on the I - V characteristics. SAMs are used to fabricate OPEs on the electrode surfaces by using some alligator clips namely, O, N, H, S. These four molecules indicated in the table 2.

Compound	Chemical structure	Length (Å)
1		13.5
2		11.5
3		19.5
4		20.2

Table 2. Chemical structures and lengths of compounds. The lengths are determined from molecular models and are defined as the distance from the S atom to the opposite terminal atom (O, N, H or S respectively) [12].

Figure 23. shows the I - V curve for a junction containing a monolayer of component **1** from table 2. between two Au electrodes. The I - V curve here is the absolute current versus the absolute value of the bias voltage (the negative bias is mirror imaged onto the positive bias axis). In this Figure, we can see that the curve is not symmetric. Open symbols for positive bias correspond to electron injection at the Au-nitro or Au-pyridine interface. Maximum amount of rectification is observed for the Au/**1**/Au with current at +1 V almost two times higher than the current in the -1 V.

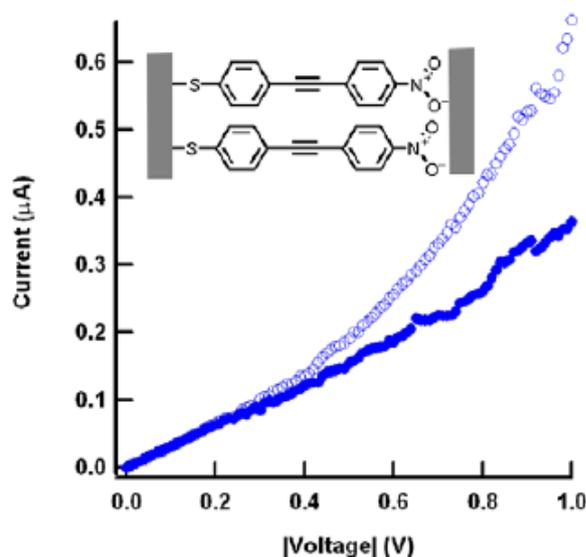


Figure 23. Transport characteristics of a Au/**1**/Au junction. The open symbols correspond to electron injection at the Au-nitro interface [12].

However, in the Figure 24. the I - V curve of the Au/**2**/Au is almost symmetric with respect to the bias voltage polarity.

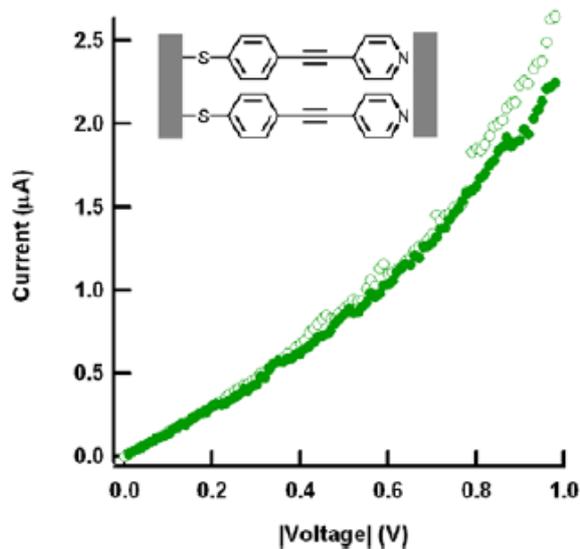


Figure 24. Transport characteristics of a Au/2/Au junction. The open symbols correspond to electron injection at the Au-pyridine interface [12].

The rectification ratio for these four molecules illustrated in the Figure 25. In an Au/3/Au junction we can find strong rectification, while for the Au/4/Au the I - V curve is completely symmetric.

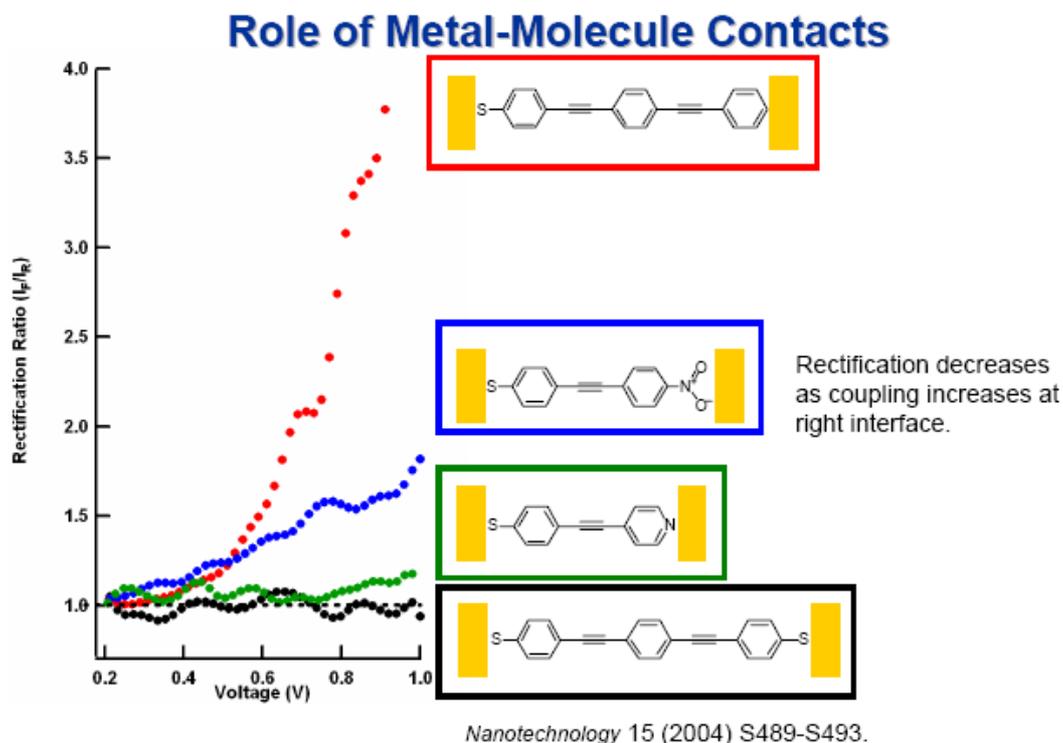


Figure 25. Rectification ratio as a function of applied voltage for Au/molecule/Au junctions formed the four compounds shown. The rectification ratio is the forward current divided by the reverse current.

This observation [13] show that the rectification is somehow dependent on the interface, because the difference between these molecules is just at the interface of

metal-molecules, indeed the rectification can be associated with the coupling at the one interface Au-S which is not held constant. The observed current rectification can be related to the amount of electronic coupling at the metal-molecule contact. Estimating how strong the coupling will be at the two metal-molecule contacts can be shown by the difference between the Au/1/Au and Au/2/Au junctions. Kushmerick and his colleague argue that rectification or voltage drop at a metal-molecule interface happens because of the poor contact. A large voltage drop occurs at the phenyl-Au interface due to poor metal-molecule mixing, leading to the rectification behaviour. To understand how strong the contact at the interface is, charge density of occupied and unoccupied orbital for **1** and **2** bound to three Au atoms can be calculated [12] by density functional theory (DFT).(Figure 26.)

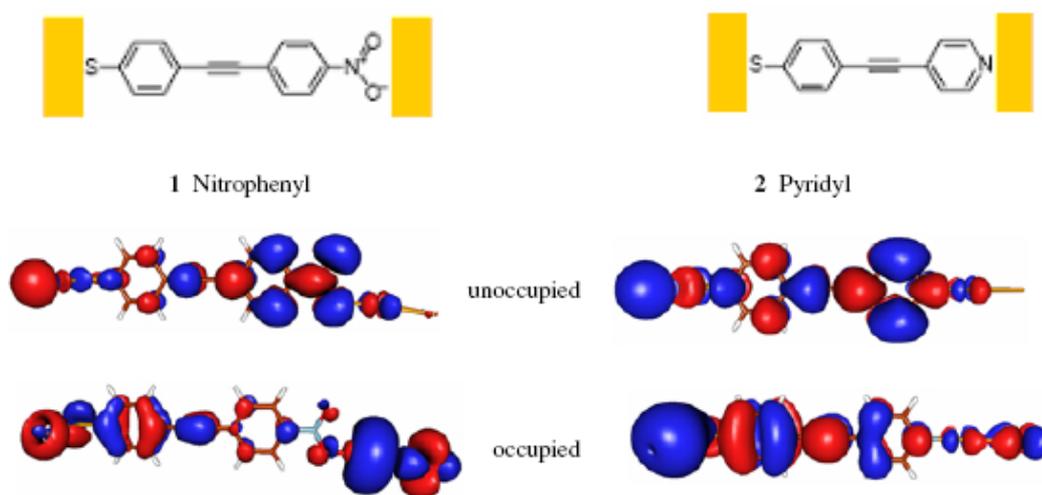


Figure 26. DFT based orbital diagrams for compounds **1** and **2** [12].

Delocalized orbitals that span the entire molecule and are positioned near to the Fermi level facilitate charge transport. However the orbitals that are not spanning from the contact to contact will not be important in the conduction. Comparing the topology of the occupied and unoccupied orbital, it will be clear that for **2** that the density of the orbital (occupied and unoccupied) is distributed across the length of the molecule, but that in **1** the unoccupied orbital is pointed toward the nitro phenyl terminus and that for **2** the occupied orbital is biased toward the thiol terminus. So the nitro group which not have an orbital density on the occupied orbital and acts as a spacer. In **2** the charge density is the same from two terminals so the charge injection is much more symmetric.

From density functional theory molecular orbital calculations it is clear that the interface of the Au-nitro is more weakly coupled than the pyridine-Au interface and this prediction is proven by the experimental result from the I - V curve.

For the molecule **3**, the rectification is higher because the Au- phenyl interface has the weakest coupling. The orbital density for this system is depicted in the Figure 27. DFT calculation show the symmetry in the density of the orbital of the molecule **4** is the delocalized over the entire system. The situation for the symmetric system shows no current rectification

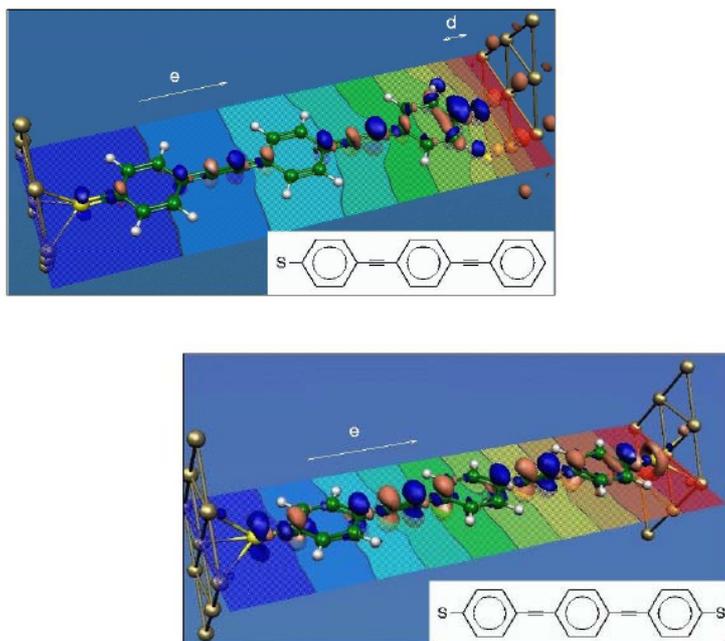


Figure 27. DFT based orbital diagrams for compounds **3** and **4**.

The charge transfer from metal to molecule (Au-S) is very complicated from theoretical point of view. But experimentally, these different contacts can be evaluated through the synthesis of the molecules with oligo (phenylene ethynylene) structure. As a result, choosing the metal electrode and chemical functionality or alligator clip which connect the molecular core to the electrodes will control the nature of the contacts. Indeed, the amount of mixing between the discrete molecular orbitals and the metal band structure will control the contact.

3.4 Various methods

As mentioned many molecules such as oligo(phenylene-ethynylene) molecules or other π -conjugated molecules, in ensemble or single-molecule can be used in the devices. One of the limiting parameter to probe a two-terminal molecule is associated with fabricating a structure that can connect to both ends of a molecule. Various techniques [7] can probe single molecules or molecules in self-assembled monolayers (SAMs), using break junctions, nanopores, conducting atomic force microscopy, scanning tunnelling microscopy, crossed wires, and other techniques. By these techniques we can make molecular devices and investigate the I - V characterization. Some of methods in Figure 28. will describe by more detail.

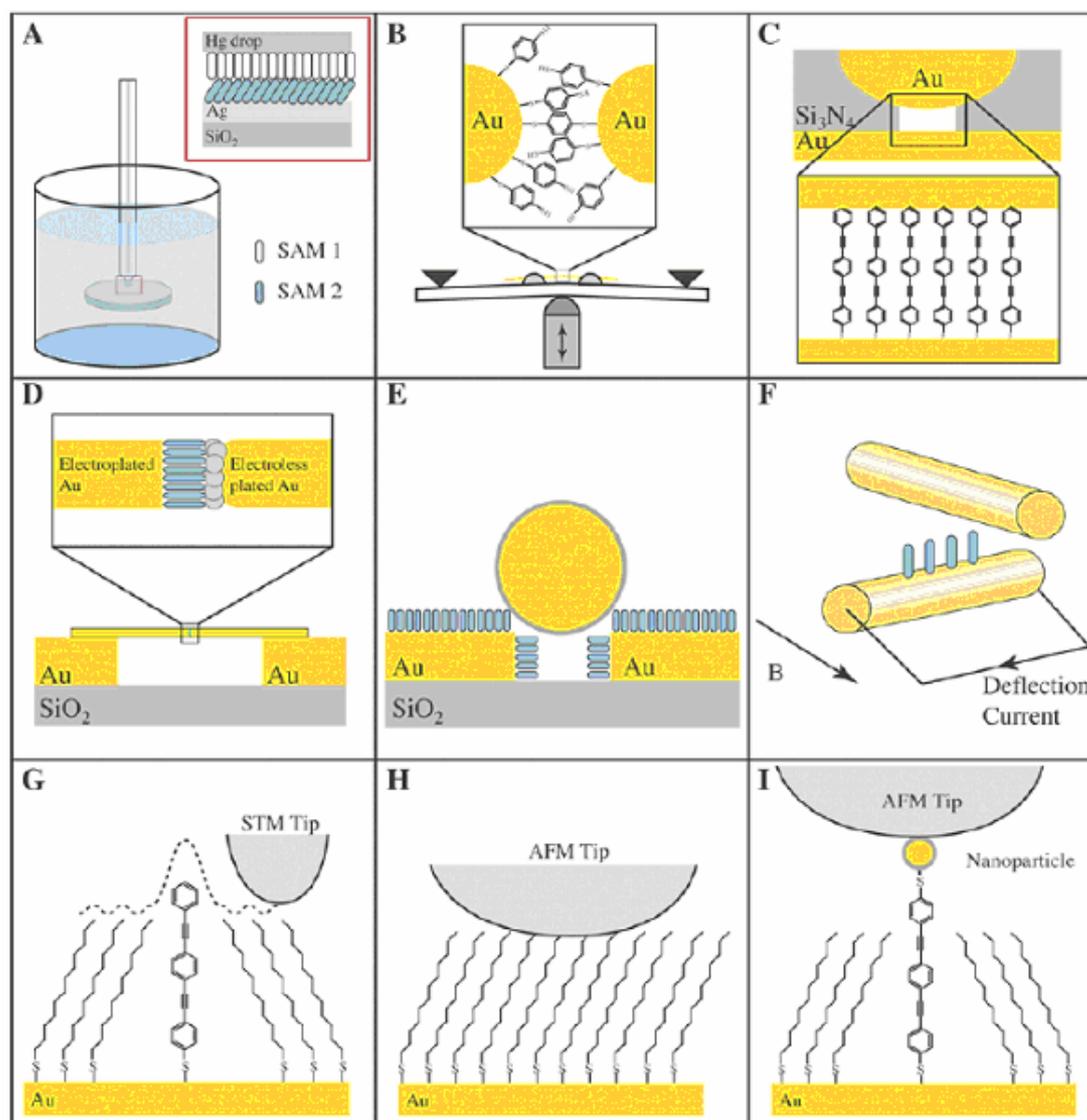


Figure 28. The various techniques used to measure electronic properties of molecules. Note that images are not to scale. (A) Hg drop junction. (B) Mechanically controlled break junctions. (C) Nanopore. (D) Nanowire. (E) Nanoparticle Bridge. (F) Crossed Wires. (G) STM. (H) Contact CP-AFM. (I) Nanoparticle coupled CP-AFM [7].

3.4.1 Mercury drop junction

Mercury drop can use as one of the electrodes in the metal/molecule/metal junction. Similar to gold, mercury can form thiol-based SAMs. This junction can produce easy and quick. The laboratories of Rampi and Whitesides reported molecular junctions made between two mercury drops or between mercury and a solid metal (Ag, Au, and Cu). In both cases the junction was formed by putting the Hg drop(s) inside the SAM solution as depicted in Figure 29. Because of the opposing SAMs on the two contacts surface the $I-V$ curve will be asymmetric for Hg/SAM₁/SAM₂/metal.[11]

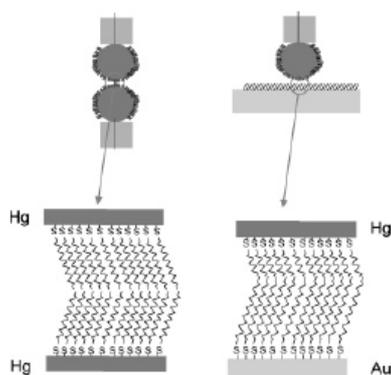


Figure 29. Schematic drawing of Hg/SAM/Hg and Hg/SAM/Au junctions. In both cases, the Hg drops are macroscopic (about 1 mm diameter), and the drawing are not to scale. For the Hg/SAM/Hg junction, the two Hg drops are brought together in a solution of an alkanethiol. For the flat Au substrate on the right, the Hg drop is lowered through the thiol solution onto the performed SAM on Au [11].

3.4.2 Break junctions

Break junction is a technique to produce a gap between two electrodes mechanically by a few atoms distance. Metal wire is bent a piezoelectric crystal. The bending causes the metal wire to break in a controlled way. First time electronic transport in the single molecule was proved by this technique.

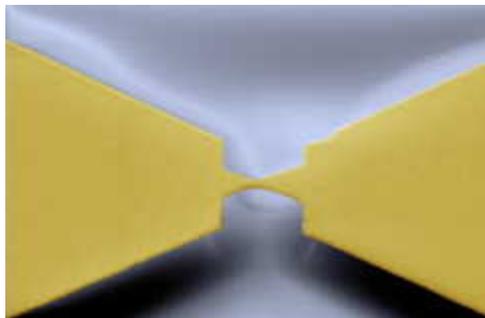


Figure 30. Mechanically controlled break junction for single molecule experiments [6].

In order to investigate the principle and mechanism of current flow through single molecules they must first be contacted. For this purpose a 50 nm thick gold should bend carefully until separate to make a gap about 0.01nm. This process is controlled by measurement of the current flow across the metal. When the metal is broken, we can see a high resistance. If two ends of the electrode bring together, the current flow can be observed, allows the precise positioning of the electrodes.

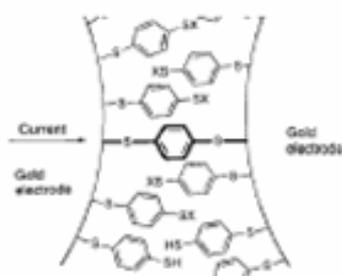


Figure 31. Schematic of break junction consisting of a break in a Au wire spanned by one or more phenyl-1,4-dithiol molecules.

Rigid rod like molecules in solution with end groups which easily bond to gold electrodes can be used in the break junction. Thiol groups are particularly suitable with sulphur containing end groups. By using the electrical field the molecules align themselves with the direction of the field. When the first molecule bonds to the electrodes, an increase in current is detected. If a symmetrical molecule is measured the current characteristic is independent of the current direction. The presence of an additional group making the molecule asymmetric and shows a dependence on the direction of the current. This method has several advantages. It is clean, because the junctions can be made in a high vacuum and also it is fast, thus enables a lot of independent measurement in a few hours.

3.4.2.1 Single organic molecules

Reichert and his colleagues did some interesting experiments [6]. They investigated the current through single organic molecules. For such an experiment two types of organic molecules specifically were designed. These two molecules are very similar to each other. In the central part of molecule they have rigid rod like section and at the end both have additional thiol functions to form a covalent bond to gold electrodes. As a result comparable electronic properties are expected. However, they have different in their spatial symmetry. The first one is symmetric molecule with the symmetry plane perpendicular to the molecule's sulphur to sulphur axis, but in second one the symmetry plane is absent. The length of both molecules is about 2 nm. (Figure 32.)

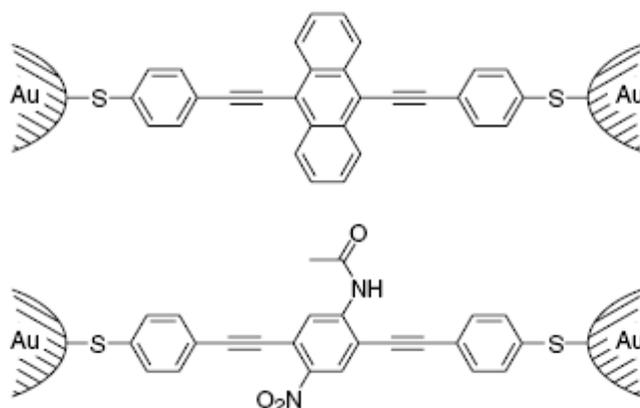


Figure 32. Scheme of the experimental setup: a spatially symmetric [9, 10-Bis ((2'-para-mercaptophenyl)-ethynyl) - anthracene] and an asymmetric molecules [1, 4- Bis ((2'-para-mercaptophenyl) -ethynyl) - 2- acetyl-amino-5-nitro-benzene] in between two gold electrodes [6].

To obtain a contact to a single molecule from both electrodes, the mechanically controlled break junction is used to provide an electrode pair with tunable distance. To prepare the experiment, the substrate bend to elongate the bridge and finally it breaks. Then a droplet of the molecule put on top of the opened break junction. When the molecules approach the surface of any gold electrodes, the chemical bond between the sulphur atom and the gold surface is established. When electrodes are approaching each other from a large distance, the current will increase exponentially with distance, as expected for tunnelling. The conductance is highly unstable, until system will go to the stable configuration. For the symmetry molecule the $I-V$ curves may be expected to be symmetric but for the asymmetric molecule they may not be symmetric respect to voltage inversion.

Figure 33 shows nine dashed lines in the $I-V$ graphs of asymmetry molecule for the stable configuration. They are clearly nonlinear as expected. As long as the junction remains stable, data can be reproduced. If the electrode gap change slightly then another configuration can be established. Conductance is highly unstable at higher bias voltage ($U > 0.2$). In Figure 33(a) the differential conductance dI/dU is depicted (solid lines). This data also is clearly asymmetric.

This configuration is stable for about 1 to 100 min; the system will go to the higher or lower conductance. If the electrodes gap change a little then the system again will go through another stable configuration. In Figure 33(b) the same system in unstable situation is illustrated. The main difference between the stable and unstable graph is the structure of the contact region between molecule and electrode, which is different from junction to junction and this influence the $I-V$ curve strongly. This experiment again shows the effect of the molecule and electrode junction on the $I-V$ curve. And the conductance is very sensitive to contact variations.

There is an important question, do we really measure individual molecule or not?

Experimentally, because the overall conductance does not change vary by large amounts, therefore, the same numbers of molecules are observed. This group believe that because of different contact configuration, the effect of the environment on the transport properties of a single molecule can observe.

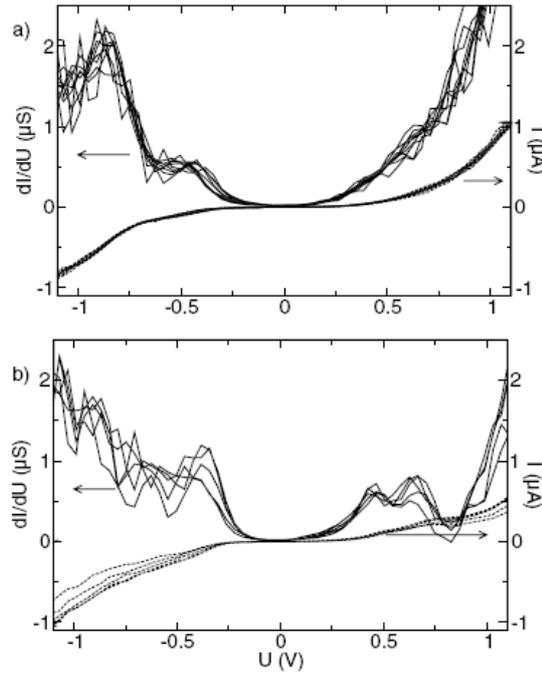


Figure 33. Transport data of the asymmetric molecule. (a) Current- voltage (I - V) raw data (dashed lines) on a stable junction and the numerically differentiated data dI/dU (solid lines) from the above I - V . (b) Data from a subsequent junction [6].

Data for the symmetric molecule is illustrated in the Figure 34(a) and (b). The experimental process is the same like the asymmetric molecule. The maximum current is about $0.6 \mu\text{A}$ at $U=1 \text{ V}$, which is similar to the asymmetric molecule. More than 50% of the stable I - V s of the symmetric molecule were highly symmetric, while all of the I - V s for the asymmetric molecule were clearly asymmetric. This result shows that the sample molecule was measured and not adsorbates or anything else. The observed I - V s reflect an intrinsic property of the sample molecule and the spatial symmetry of the molecule.

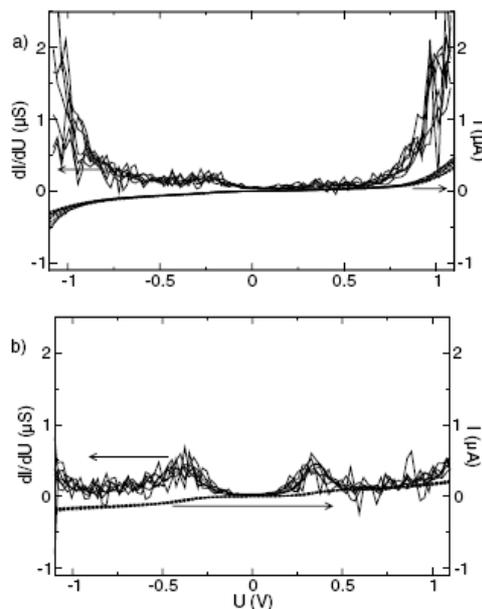


Figure 34. Current I (dashed lines) and dI/dU (solid lines) as a function of the bias voltage U from two subsequent junctions with the symmetric molecule [6].

However, the authors also illustrated nicely that part of the experiment shows asymmetric I - V s for symmetric molecule. Reichert and co-workers thought that symmetry can be broken by additional molecules, different electrode surface, etc. They manipulated a junction by slightly adjusting the electrode distance several times. Figure 35(a-c) shows the sequence of stable I - V s. The symmetric I - V s which is not shown here is first situation. After that they increase the electrode distance, the I - V characterization is changed to asymmetric in the Figure 35(a). Obviously, one of the molecule-metal contacts was changed. Again after future manipulations, the symmetric situation was recovered (Figure 35(b)). The third image which is mirror of the first image shows that the molecule in this process was not lost. Hence from this image they apparently manipulated the contacts of only one molecule.

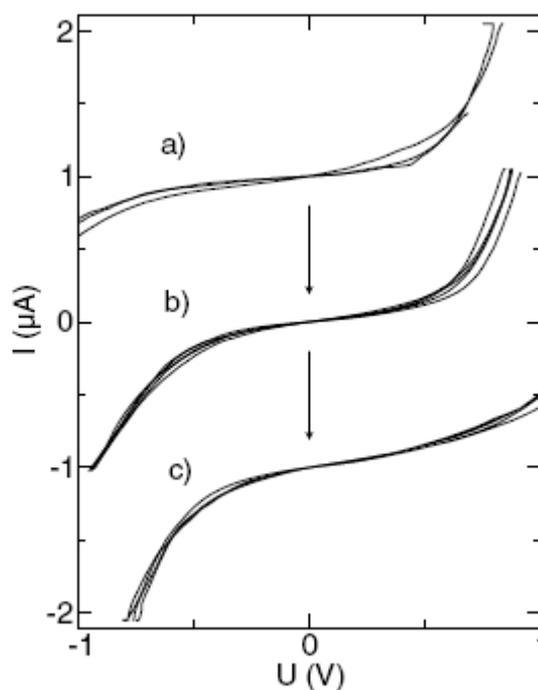


Figure 35. Three subsequent stable I - V s with the symmetric molecule. Observed during skillful manipulation of the electrodes (a) An asymmetry was mechanically induced. After an intermediate symmetric regime (b), the IV appears inverted with respect to bias voltage (c). Note that the junction was not lost during this procedure [6].

Asymmetries in the I - V s demonstrate that microscope details in the contact have important effect on the I - V characterization. Although all contacts were chemically stable, for individual molecule different I - V s can be observed.

3.4.3 Nanopore

The group of Reed at Yale [4] fabricated nanopores to measure the conduction directly through a small number (about thousands) of organic molecules. The nanopore consists of a SAM of conjugated molecules sandwiched between two electrodes. An Au contact is evaporated on top of the aperture and device is putting in a solution of the molecule to form a SAM. After deposition, the bottom electrode is formed by evaporating 200 nm of Au onto the sample in low temperature (77K) to

minimize damage of the SAM. They used this device to measure the conductance properties of one organic molecule. This molecule show strong rectifying behaviour because of the asymmetry in the molecule. Two sources of asymmetry in this molecule can be observed (Figure 36.). First, only one side of the molecule has a thiol for covalent bonding to the Au electrode. Second, for this special experiment, a Ti adhesion layer was evaporated on the phenyl end group of the SAM before the Au layer was evaporated. This Ti layer presents a different metal-molecule interface than the Au-S barrier (the work function of Au>Ti) and, thus, allowed electrons to flow only from the Au/Ti electrode to the S-Au surface. Rectifying behaviour is observed, the current at 1_V is about 500 times higher than the current at -1_V. This group argued that the different contact barriers made this asymmetry somehow like Schottky barriers.

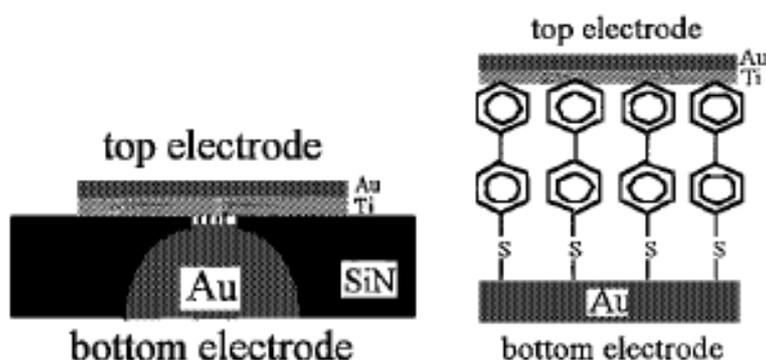


Figure 36. Nanopores: Au-Ti top/SAM/ Au bottom structure and specific SAM (4-thioacetyl biphenyl) [4].

3.4.4 Nanowires

A wire with dimension of the order of a nanometer is a nanowire. It is also known as “quantum wire” because at these scales the quantum mechanical effects are important. Nanowires could be used as a component electrical circuit, to create an extremely small circuit. This device can be grown with nanometer-scale diameters but micrometers in length which allows the nanowires to connect to the outside of the world. Rather than sandwich the molecule in a vertical structure, Mallouk and co-workers [7] used nanowire to prepare molecular junctions. Using electrodeposition in 100 Å diameter pores in polycarbonate. A first metallic contact was electrodeposited in a large collection of pores, then a dithiol was allowed to adsorb to the contact surface. After a second metallic contact was deposited, the polycarbonate was dissolved in methylene chloride to achieve a large number of nanowire junctions. The *I-V* curve generally is symmetric, with a strong dependence of current on molecular structure.

3.4.5 Bridging Nanoparticles

A nanoparticle is a microscopic particle whose size is measured in nanometres (nm). Nanoparticles are interesting because, they can connect bulk material and atomic or molecular structures like a bridge. Metallic nanoparticles have used to

bridge the gap between two electrodes. By assembly Au electrode grows with a gap of 40-100 nm if a SAM is formed on the Au electrodes before the nanoparticle is trapped, a metal-molecule-nanoparticle-molecule-metal is formed. The $I-V$ curve for this device predicts to be symmetric respect to the voltage.

3.4.6 Crossed wires

Crossed-wire tunnel junctions are formed by placing two wires, one of which is prepared with a SAM, in a crossed geometry where one of the wires is perpendicular to an applied magnetic field. This method has the advantage of forming a metal-molecule-metal contact without using an evaporated layer to form the second metal-molecule contact, decreasing the chance of damaging the organic layer.

Kushmerick [7], by using this technique, has shown the influence of symmetry in the metal-molecule junction. The symmetry is determined by the functionality of the “head” and “tail” groups on the molecule. It was found that for a symmetric molecule when the Au-molecule-Au contact is established, the $I-V$ curve is symmetric and for an asymmetric molecule the $I-V$ curve is asymmetric. The rectification in the system is because of the chemical contact of one of the metal-molecule junctions. The voltage is dropped at the junctions, so the rectification observed for the asymmetric system.

3.4.7 Scanning Tunneling Microscopy (STM)

The scanning tunneling microscope (STM) is a microscope to scan a surface to detect a weak electric current flowing between the tip and the surface. The STM allows detecting the region of high electron density and indicating the position of atoms and molecules on the surface. STM uses principles of quantum mechanics. The electron cloud for metal atoms at a surface extends a very small distance above the surface. When a very sharp tip approaches the surface, a strong interaction is made between the electron on the surface and the tip atom and an electric tunneling flow when a small voltage is applied. The tunneling current rapidly increases as the distance between the tip and the surface decreases.

STM is a very good technique to measure electron transfer through single molecules. The molecules are bound to one electrode and the STM tip acts as the second electrode. The $I-V$ characterization caused by STM is asymmetric as tunneling feedback forms a metal-molecule-gap-tip junction. [7]

3.4.8 Contact conductive probe AFM

When the tip is approached to the surface, the Van der Waals force between the tip and the sample makes the cantilever deflect according to Hooke's law (Figure 37.). The deflection is measured by a laser spot reflected to the detector. In the contact-mode, the force between the tip and the surface is kept constant during scanning by keeping a constant deflection. In the non-contact mode, the tip is oscillated at or close to its resonance frequency. The oscillation is modified by tip-sample interaction forces; these changes in oscillation with respect to the external reference oscillation provide information about the sample's characteristics.

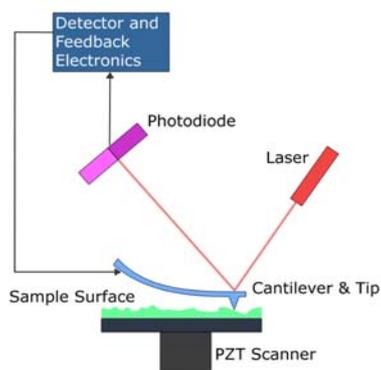


Figure 37. Atomic Force Microscope.

CP-AFM also has been used to measure electron transport in metal-molecule system. CP-AFM, a metal-coated AFM tip is directly in contact with the SAM. By this technique, we can not probe the I - V curve across single molecules, but interpretation of the curve is easier because the probe is in direct and controllable contact with the SAM. The I - V curve is like STM should be asymmetric, because of asymmetry in the connection SAM to electrodes; one electrode has chemical contact and the other physical.

4. Conformational molecular rectifier

Most current experiments in molecular electronics use the rigid molecules. However, conformational motions caused by the electric field might also lead a molecular junction with rectifier behaviour. Here two simple example of conformational molecular rectifiers present [10]. The design is based on the building blocks of organic chemistry, thus providing flexibility synthesis. Conformational molecular rectifier (CMR) has two parts; one connected to the electrode and the other part like C-F or C-CN bonds which is mobile and has a strong dipole. Several groups are preparing materials based on mobile dipolar segment. A simpler molecular dipole is made by the cyanomethyl ($-\text{CH}_2\text{CN}$) connected to a rigid group like phenyl and connecting the dipolar unit with acetylene also permit rotation around the triple bond with little or no barrier. These different conformations are very close in energy otherwise; molecule will go to the lowest energy conformation and to change this conformation, a lot of energy needed. Finally, to have a rectifier, it is necessary that different conformations induced by the external field have large difference in conductance. The metal-molecule interaction or the intramolecular interactions can make different in the conductance of various conformations.

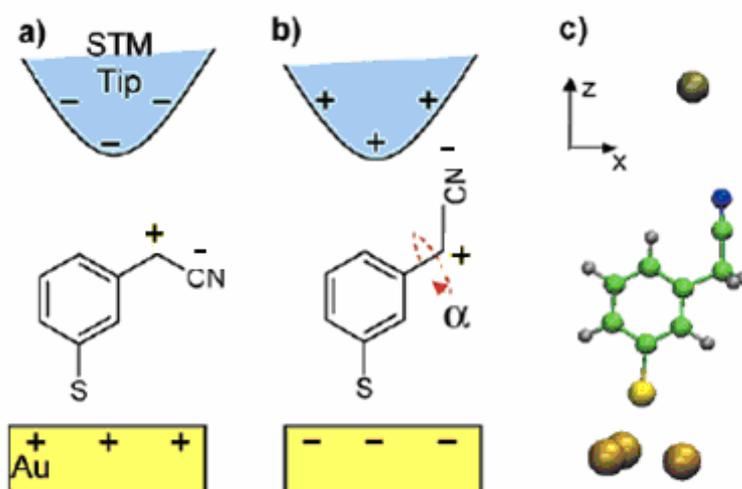


Figure 38. (a,b) Schematic of the contact modulated CMR. The conformation of the polar CH_2CN group is influenced by the applied potential. (c) The atoms included in the calculation of the relative conductance [10].

Figure 38(a,b). show a simple contact modulated system that show conformational rectification. The benzenethiol meta-substituted with the cyanomethyl group chemically absorb on the gold surface. Benzenethiol here links as the “alligator clip”. The asymmetry of the junction is through the chemical bond between the molecules and least one electrode.

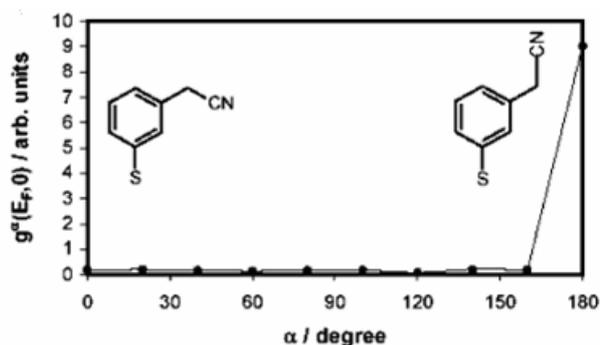


Figure 39. Relative conductance as a function of the dihedral angle α [10].

In this molecule the cyanomethyl group makes the dipole and this dipole can rotate by the applied field as shown in the Figure 38. The relative conductance as a function of the angle α is shown in the Figure 39. When the CN group points toward the tip the conductance is much higher. Because the atomic orbital of CN group is much more near to the tip, so the electrons can transport between the tip and molecule. The conductance will decrease when the CN group is pointing away from the contact. This behaviour show the rectification in the I - V curve, one situation has high conductance and by changing the voltage polarity the other has lower conductance.

Temperature plays an important rule in this experiment, because by increasing the temperature the dipole segment of the molecule can rotate easily, as a result all the conformations become populated. Rectification at room temperature is reduced because all the possible conformations at this temperature can be populated. As illustrated in Figure 40, the rectification behaviour is more pronounced when the temperature is lowered. At 50 K and $V > 0.5$ V only the high conductance conformation, α about 180° , is populated but for $V < -0.5$ V the population shifts toward the low conductance, α about 0° , conformation.

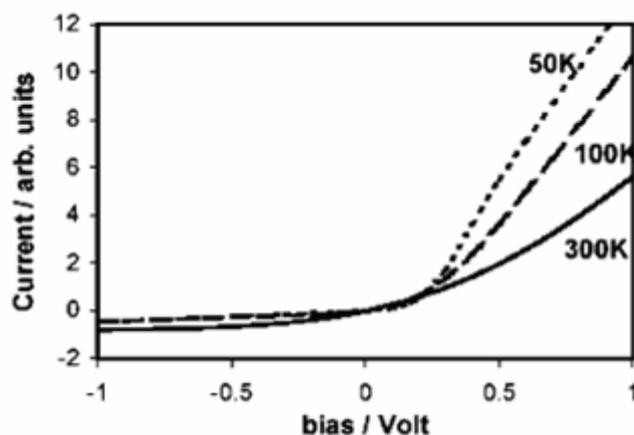


Figure 40. Simulated I / V curve at different temperatures [10].

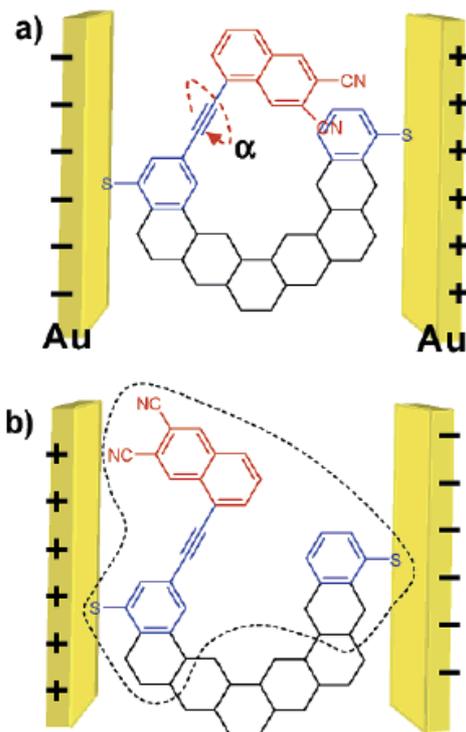


Figure 41. Schematic of the bridge-modulated CMR. The preferred conformation of the polar dicyanonaphthalene group depends on the applied potential. The conductance in (a) is much larger than in (b) [10].

Figure 41 shows another example for the CMR, this molecule is sandwiched between two gold electrodes. The rigid part of the molecule made of cyclohexanes which separates two benzenethiol units connected to the metal electrodes.

A dicyanonaphthalene unit is connected to the molecule by the acetylene spacer. When the left electrode is negative, conductive conformation is made. Figure 41(a) shows the larger conductance, because in this configuration the bridge part rotates to overlap well with the orbitals in the opposite benzenethiol.

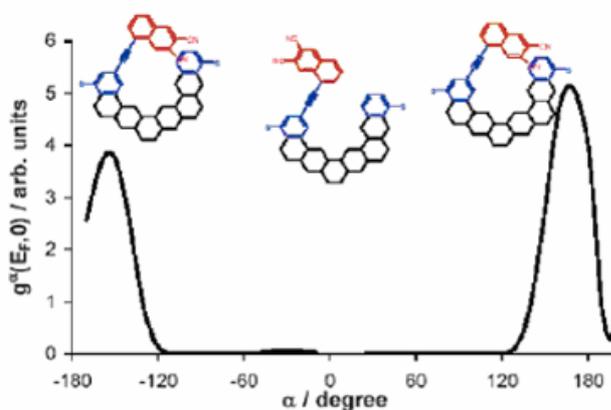


Figure 42. Relative conductance as a function of the dihedral angle [10].

The rectifying behaviour for this system at room temperature shows remarkable rectification (Figure 43.). Here the rectifying is determined by the molecule, because

the metal-molecule contact is invariant so just by changing the position of the bridge part in the molecule, the rectifier is observed.

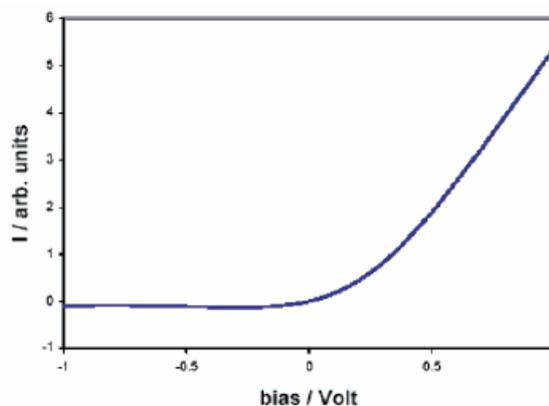


Figure 43. Stimulated I - V curve at 300 K [10].

From these two examples, it is clear that one condition to observe CMRs is the possibility to control the molecule orientation at the interface. Another condition is that the conductive and nonconductive conformation must be close in energy otherwise if the less conductive conformation was the most stable, then the rectification is not observed.

5. Conclusion

Based on the discussions in this paper, there is rectifying behaviour when the molecule is connected between two metal electrodes. The first model predicts that the rectification in the I - V curve happens because of the molecule itself. The structure of the molecule creates a p - n diode and the fundamental explanation is similar to the classical p - n junction. However, recent experiments show that the geometry in the system is the reason for the rectification in the I - V characteristics. The metal-electrode contacts have an effect to drop the voltage across the contact barrier. As a result of these two points of view, scientists debate on which one is correct or more important. This question is still remaining more than three decades: “Do molecular rectifier exists?” Or does the nature of the metal-molecule contact induce this behaviour.

In my conclusion recent measurements which show the effect of the molecule-metal contact in the rectifier behaviour are more convincing. In science each theory should be proved experimentally. The Aviram and Ratner proposal was the basic idea for diode behaviour in the molecules, after that research groups attempt to make this junction. From 1970s, lots of new devices and strong techniques are invented that can be used to measure molecular properties. Most of these recent experiments show the effect of the metal-molecule contact junction. However, these methods still need to improve. For instance, in this paper we demonstrated that one group used passive organic layer and proved that the rectification is due to the molecule and not the Schottky barrier. However, other groups believe that this is because of the barrier at the interface. Or in the single organic molecules measurement by the break junction method, the symmetric molecule shows the asymmetric curve by changing the distance of the break gap. These results are in contrast with each other; show that more accurate measurement and device need to solve this mystery, although making better and better device has some limitation at end.

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7. References

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