

## STM study of Bias-Triggered molecular rectification and switching in Metal-ligand complex

In previous two chapters a small sized organic molecule, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone, from quinone family was studied theoretically as well as experimentally with VNL-ATK and STM systems respectively. It was observed and experimentally proved that single molecule induces bidirectional multiple negative differential resistance (BM-NDR) properties in a two terminal device configuration. However, the self-assembly of same molecule serves greater purpose in nanoelectronics as an asynchronous counter. In this study, we have for the first time observed the rectification as well as memory switching behavior of a newly synthesized polydentate Schiff's base ligand with the help of a Scanning tunneling microscope. The sample deposited on flat gold surface has been analyzed with the help of a tungsten tip mounted on Q-Plus sensor. Both rectification and memory switching characteristics of this ligand has been observed as a result of coordinate bonds breaking and forming interaction between tungsten tip and ligand molecules.

### 6.1 Introduction

Organic molecules have proven their importance in electronics components. The objective of touching down the atomic scale has been the dream of researchers from centuries. Langmuir-Blodgett system (Blodgett and Langmuir, 1937), whose design derived from the uniform spread of oleic acid on water, make it possible to deposit selective number of molecular layers of barium-copper stearate. However, the invention of scanning tunneling microscopy, which utilizes quartz piezo crystal to sense atomic roughness, by Gerd Binnig and Heinrich Rohrer in 1981 at IBM Zürich (Binnig and Rohrer, 1983) made it possible for researchers to dream of realization and characterization of variety of molecular electronics devices at atomic scale. Later on, several other techniques like molecular controlled break junction (MCBJ), atomic force microscopy (AFM) and transmission electron microscopy (TEM) along with deposition techniques like atomic layer deposition (ALD), molecular beam epitaxy (MBE) and e-beam lithography proved their worth to design a complex molecular electronics device structure. A single molecule three terminal device with back gate control on substrate is one among these electronics components which had been studied on 1,8-octanedithiol (ODT) and 1,4-benzenedithiol (BDT) (Song et al., 2009) with the help of mechanically controlled break junction (MCBJ) technique (Xiang et al., 2013b). Another similar attempt was made by additional e-beam lithography technique to study the side gate controlled electrical behavior of BDT molecule (Xiang et al., 2013a). These studies along with many others are step closer to complex designing of single molecule transistor devices (Hwang et al., 2009; Kubatkin et al., 2003; Liang et al., 2002; Xu et al., 2005). Chen et al. developed a solid state metal-insulator-molecule-metal (MIMM) device by depositing a thin insulating layer of HfO<sub>2</sub> on molecule with the help of Atomic layer Deposition (ALD) system between two metal electrodes (Chen et al., 2007b). A review study (Kumar, 2007) suggests the footprints to make use of molecular materials as Nano-insulator, Nano wires, resonance tunneling diodes (RTD) and more complex digital components like logic gates. In pursuit of the understanding of many such complex designs NDR behavior was studied on many organic molecules at atomic level (Garg et

al., 2015; Guisinger et al., 2004a; Guisinger et al., 2004b; Kang et al., 2010; Xue et al., 1999) which can be of great use in applications like multivibrator, oscillators and even as flip-flops for a well-controlled operating Q-point value. Organic materials can perform even better when they form super-structures or self-assembled structure. Some small sized molecules of Quinone family form super-molecular structure by atomic manipulation to work as 16-bit parallel processor (Bandyopadhyay and Acharya, 2008) while others form natural Self-Assembled Monolayer (SAM) to work as an unconventional asynchronous counter as discussed in chapter 5.

The very first organic molecular electronics device in the form of a diode was introduced by Aviram and Ratner (Aviram and Ratner, 1974) with the concept of acceptor-donor pair of molecule which replicated p-n junction of silicon based technology. Ever since several other organic molecules have been identified to rectify in either directions of applied biasing (Elbing et al., 2005; Jäckel et al., 2004; Martin et al., 1993; Perrin et al., 2016; Roth et al., 1998). Some of these rectifiers have been tested with applied AC biasing to observe half wave rectification (Mohanta and Pal, 2009; Nijhuis et al., 2011). Various organic materials are also seen as alternate in memory switching applications. The most common switching phenomenon observed in metal-oxide based memory devices is filament formation which involve penetration of metal ions from one electrode to another through oxygen vacancies in oxide layers (Lee et al., 2015). However, these types of memory devices shows very good cyclic endurance, high device yield and sufficient on-off current ratio, but due to ion migration these devices failed to show tremendous retention property. This problem can be solved by organic molecules based memory devices as the switching mechanism observed in organic materials based memory devices is mainly focused on redox reaction in donor-acceptor type big molecules or conformational change in the electronic states in the small molecules having pi-pi / sigma-pi conjugation (Gao et al., 2019).

In the continuous search for new switching and conduction mechanisms in organic molecules we had synthesized and characterized a new ligand and investigated its physical and electrical properties with the help of a tungsten mounted Q+ sensor as well as Platinum-Iridium (Pt-Ir) tip. The detailed synthesis and characterization of Schiff's ligand has already been reported previously, however in order to better understand the structure, we have again provided the facile synthetic route adopted for this cost-efficient ligand. Q+ sensor has two quartz prongs. One prong is kept fixed for real time referencing purpose while another prong is flexible which can act as a cantilever. The tungsten tip is attached to the flexible prong which ultimately scanned the surface and did the electrical characterization. On the other hand, Pt-Ir tip was used directly without cantilever. The role of W-tip is even important as it is a group VI element which can accommodate 3 lone pair of electrons to form dative bonds with two oxygen atoms and one nitrogen atom in the ligand molecule. A comparative study of observed IV characteristic has been discussed for both tungsten and Pt-Ir Tip.

## 6.2 Experimental

### 6.2.1 Synthesis of Ligand

For the synthesis of ligand, a three-step process has been followed. In the first step, nitration of 3,3'-Dinitrobiphenyl-4,4'-diol has been performed with the help of addition of nitric acid to a solution of glacial acetic acid. Further the precipitates were washed with the help of distilled water and ethanol. For the second step, the compound obtained from the previous step was subjected for the process of reduction with the help of hydrazine monohydrate and Pd/C in around bottom flask. After 24 hours, the addition of N,N-DMAc was continued till dark grey precipitates of the solution gets dissolved. Following this, the white precipitates so obtained were washed with solvents and dried in oven. In the final step, the Schiff's base condensation process has been adopted to synthesize the ditopic ligand, by refluxing equimolar ratio of product obtained from the last step and 2-hydroxy-1-naphthaldehyde in dry ethanol, and tetraethyl orthosilicate under N<sub>2</sub> atmosphere, for a period of 6 hours. Then the purification of this step yields final ligand, which is pale-yellow in color. The structure of the ligand is shown in Fig. 6.1.

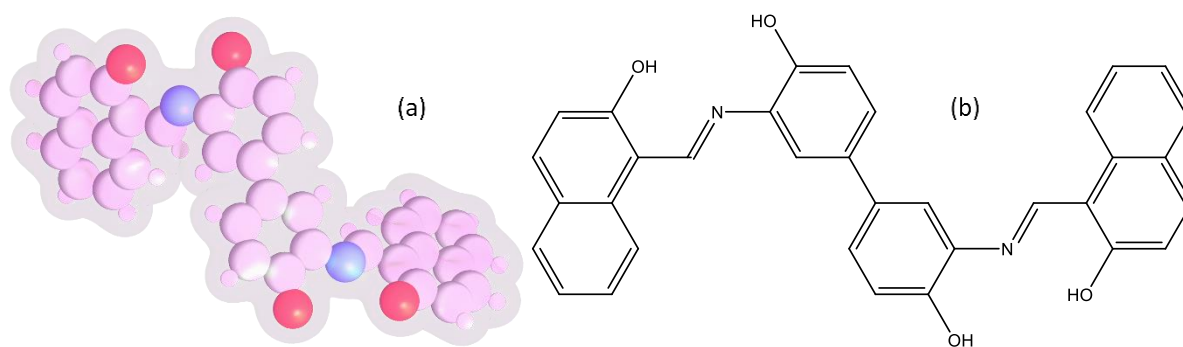


Fig 6.1. (a) Energy relaxed structure of Ligand molecule. The molecular modal of ligand having carbon (C) atoms in pink (big size), hydrogen (H) atoms in pink (small size), oxygen (O) atoms in red and nitrogen (N) atoms in blue colors. The transparent cloud corresponds to electron density of molecule. (b) Stick diagram of Ligand molecule.

### 6.2.2 Deposition of Gold on mica substrate

Atomically flat gold layer has been deposited on mica surface by already optimized technique (Chidsey et al., 1988). First, a mica substrate was split into two parts with a very sharp blade. The cleaved side of mica is supposed to form big atomically flat plateaus because two layers of muscovite mica are bonded with each other with weak van der Waals forces. To remove any residual or impurity mica substrates were heated at 200°C in a vacuum oven for 12 hours. The substrates were then transferred to thermal deposition system for gold deposition under  $10^{-6}$  mbar pressure and 300°C temperature. Gold deposition rate was kept constant at 0.1nm/s till a gold layer of 150nm thick was deposited. After deposition the substrate was cooled down with a very minimal rate. The gold deposited mica substrates were further processed in preparation chamber of STM system to achieve gold 111 formation.

### 6.2.3 Deposition of ligand on Au/mica substrate

0.9mg of Polydentate Schiff's base ligand was used with 2ml of methanol to prepare an orange color solution. The solution was then diluted 10 times in methanol to achieve around 1µmol/ltr concentration. Due to such a low concentration the solution turned transparent from orange color. A drop of solution was then dropped on Au/mica substrate inside load lock chamber of STM system. To evaporate the methanol, sample was kept inside the load lock for few hours. The sample was then transferred directly for scanning but big lumps of ligands were visible all over the surface. The sample was then heated up to 300°C temperature using PBN heater in preparation chamber of STM system to degas the residual impurities and bind solvent with substrate.

## 6.3 Results and Discussions

### 6.3.1 Physical properties of ligand

The sample prepared by depositing Ligand on top of Au 111 surface was scanned at -1V between the tip and substrate which is grounded under Ultra-High Vacuum (UHV) conditions. Surprisingly ligand molecules interact with each-others in such a way as if they have formed polymer structure.

In the previous report, the ligand has been used in conjugation with Fe (II) ions to form metal-organic hybrid Polymer. The NDR and switching behavior have also been observed in Fe (II)-Poly devices where polymer undergoes redox reaction and induces change in its conformation under applied bias (Oberoi et al., 2018). In that study a thin film of Fe (II)-poly was sandwiched between two metal electrodes.

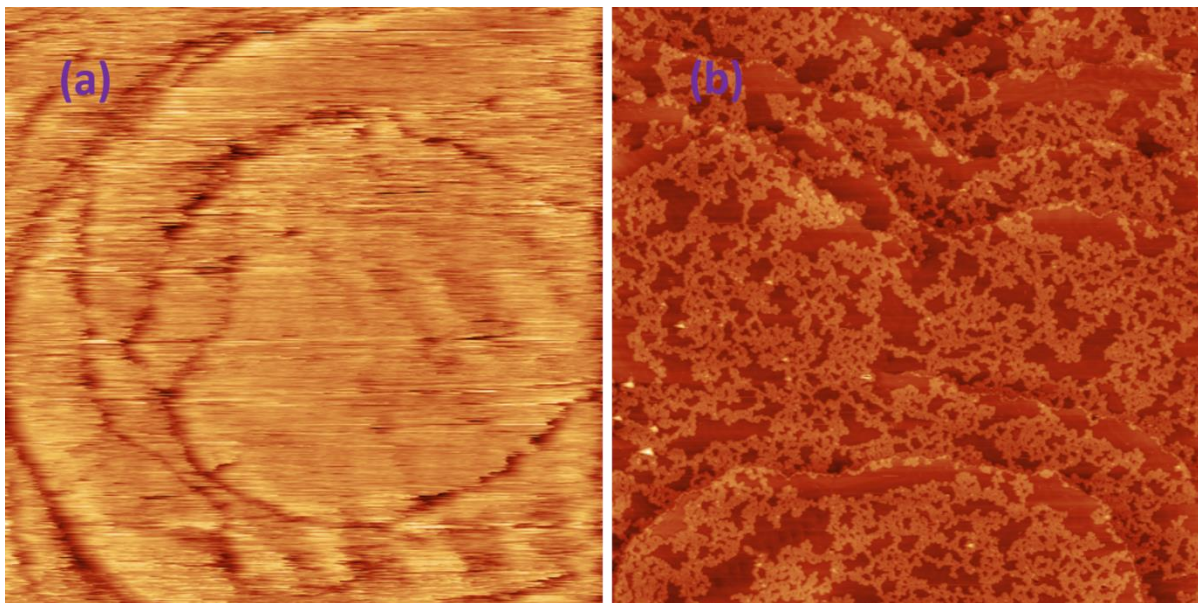


Fig 6.2. Change in the sample surface after treating the surface at high temperature. (a) Shows the 300nm x 300nm area scanned without heating while (b) with 244nm x 244nm area, formed monolayer polymerization on gold surface.

But in current study we are characterizing at molecular scale. The deposition of the ligand on the gold surface was carried out by drop-casting method. Substrate was scanned right after drop casting of ligand. Fig 6.2(a) shows the dense spread of ligand on gold substrate in 300nm x 300nm area. The processing of sample requires post deposition heating to evaporate residual impurities and monolayer formation of ligand on gold surface. Under UHV condition and high heating temperatures the ligand starts forming polymer like structure as shown in fig 6.2(b).

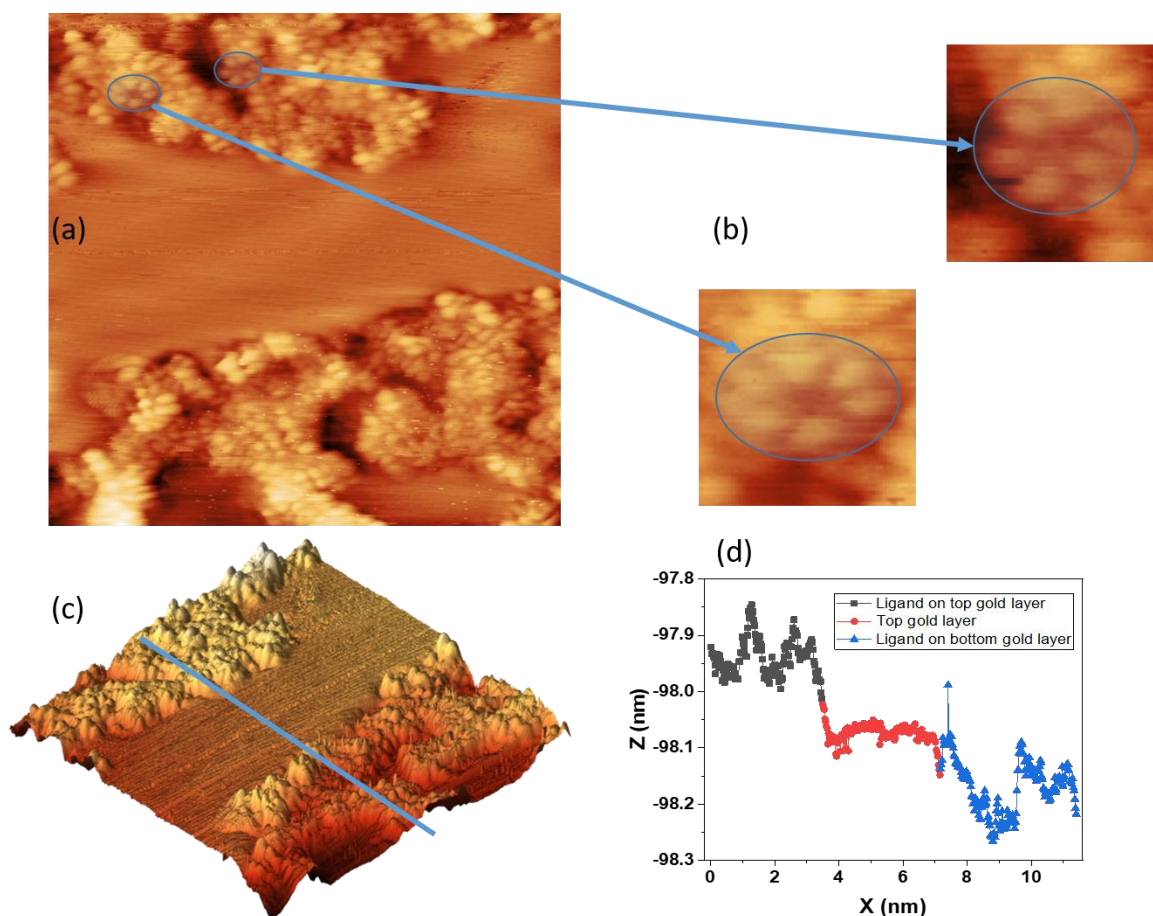




Fig 6.3. (a) 11.4nm x 11.4nm image scanned with -1V between the tip and the substrate and current set-point of 1nA with a Q+ tip. (b) Selective portion of (a) at which benzene rings can be spotted aligning with the scanning plane. (c) 3D hologram image of (a). (d) Roughness measurement plot of (c) along the line. The black dotted data corresponds to the roughness of ligands deposited on top layered gold surface and red dotted data is for top gold layer while the blue colored data depicts the morphology of ligands on bottom layered gold surface.

High temperature helps in binding ligand with substrate and evaporates residual or loosely bonded particles. The sample prepared by depositing Ligand on top of Au 111 surface was scanned at -1V between the tip and substrate grounded under Ultra-High Vacuum (UHV) conditions. Surprisingly ligand molecules interact with each other in such a way as if they form polymer structure. The roughness difference between pre-annealing and post-annealing is also significant as the roughness of substrate before annealing was of the order of few nanometers while the same after annealing reduced to few angstroms.

To capture the closer look of the spread of ligands on gold surface a Q-plus sensor was used to scan 11.4nm x 11.4nm area with a Q-factor of 1480 at room temperature. Fig. 6.3 (a) shows the spread of ligand on the gold surface. Individual atoms can easily be identified in the image. The blue circles show the presence of benzene rings which are aligning parallel to scanning plane. As the ligand is not planer hence it is difficult to identify the exact position of individual atoms of the molecule. Moreover, the ligand molecules seem to be bonded with one another randomly to form a polymer like structure. The hilly area in fig. 6.3 (c) corresponds to the ligand while the flat region is gold surface. The depression region also corresponds to ligand but on lower flakes of gold surface. Fig. 6.3 (d) shows the change in surface morphology along the blue line in fig. 6.3 (c). All the three colors correspond to different roughness levels. The black dotted region is showing presence of the ligand molecules on the topmost gold surface. The red dotted region is comparatively smooth and this is because of the presence of the flat gold atoms. While the blue dotted region is again comparatively rough but under depression because these are same ligand molecules but not on topmost gold substrate but rather on lower flakes.

### 6.3.2 Electrical Properties of Ligand

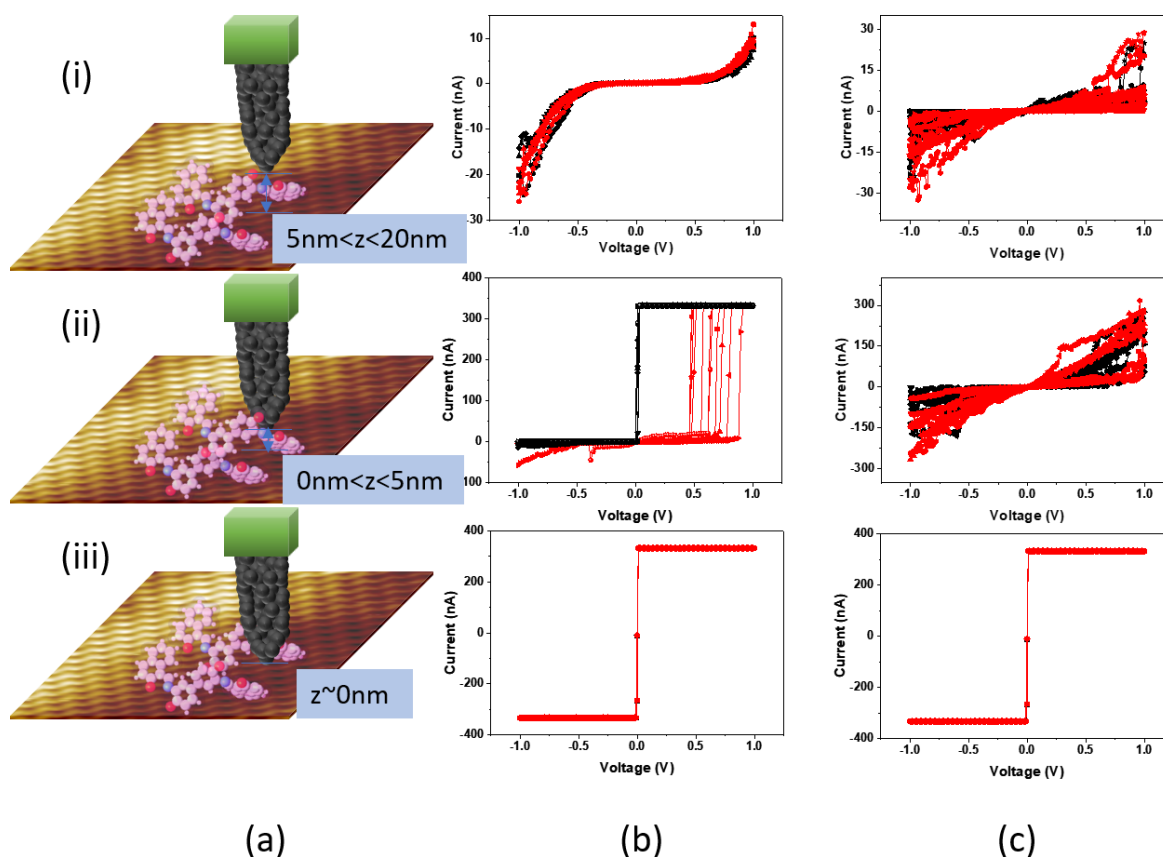


Fig 6.4. (a) Schematic representation of relative separation between tip and substrate. From (i) to (iii) the tip is approaching towards substrate, whereby, (i) and (ii) respectively are low and high tunneling regime, (iii) Tip touching the substrate. (b) and (c) are IV characteristics for Tungsten and Pt-Ir tip respectively corresponding to the tip location.

The ligand also shows interesting electrical properties as well. The ligand shows both rectification as well as switching behavior when operated in tunneling region. In Fig. 6.4 (b),  $z$  represents the normalized distance between tip and substrate. Keeping that in mind, the tip was brought near to substrate while keeping potential at tip to  $-1V$ . There was no change in current when move from normalized  $z$  value of  $-149$  nm to  $-174$  nm which shows that tip is not interacting with substrate because it is too far from it. But after  $-174$  nm the current starts rising which is basically due to tunneling phenomenon. Though the magnitude of current is small at early tunneling tip-substrate distances but it is still significant to show the presence of ligand on the substrate. The switching behavior of the ligand was only observed when the tunneling distance is reduced to few nanometers. At such short distance between the substrate and the tip, it is expected that the tip strongly interacts with ligand molecule and forms break junction (Beall et al., 2015).

Many IV data were recorded to study the statistical behavior of electrical characteristics. In fig 6.5 (b) 250 I-V data were taken along the blue line out of which for 4.8% there was no useful interaction between tip and substrate. For 7.6% a little interaction was observed and semiconducting behavior can be seen. But the most dominating among all was rectification behavior and it was observed 57.2%. The second dominating IV characteristic behavior was rectification cum switching with narrow threshold voltage window. This covers 25.2% of sample space. A threshold voltage less than  $+0.5$  V is considered narrow here. While remaining 5.2% shows rectification as well as switching with wide threshold voltage window greater than  $0.5$  V. This pattern was observed when tungsten tip was used for characterization. While there was no rectification or memory switching observed when characterized with Pt-Ir Tip. The reason behind this is that tungsten has  $+6$  oxidation states which coincide with 3 lone pairs of electrons of ligand molecule. Moreover, platinum and iridium are more noble elements as compared to tungsten.

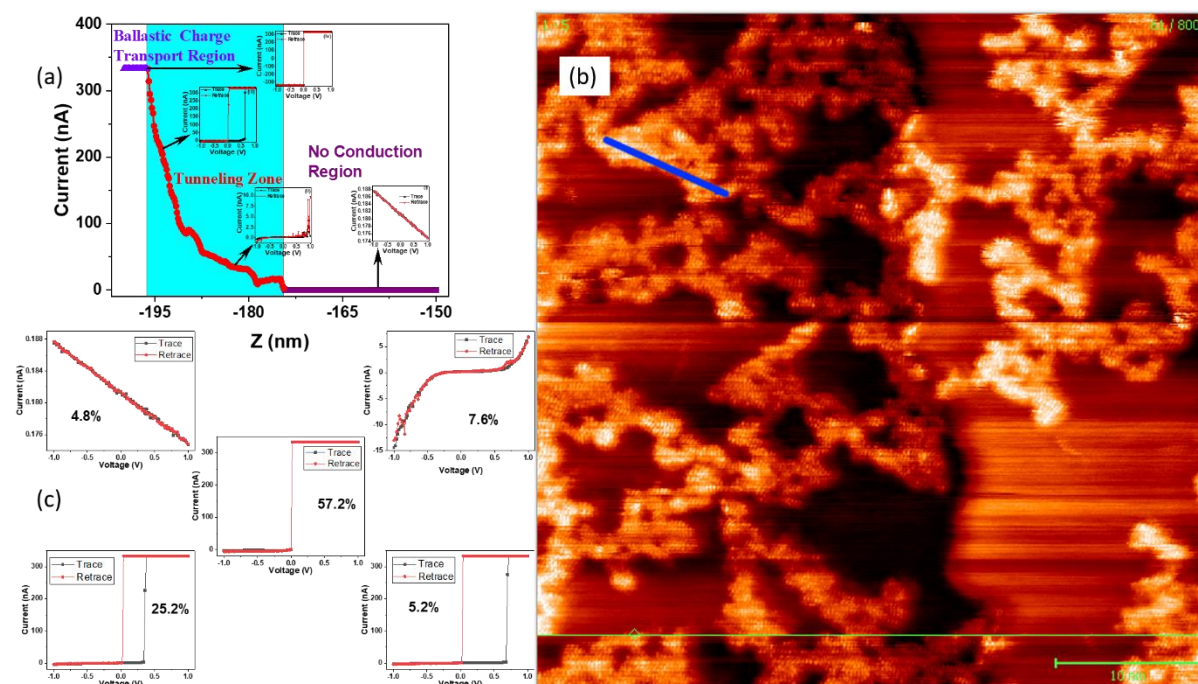


Fig 6.5. (a) Depiction of difference in distance between tip and substrate. Inset (i) to (iv) corresponds to current-voltage plots when tip-substrate distance is high to low (b)  $46.3 \text{ nm} \times 46.3 \text{ nm}$  region scanned with Q+ tip with  $-1V$  gap voltage. Several IV's were taken along the blue line. (c) Statistical distribution of different I-V Plots along the blue line is shown in (b).

To understand the difference in the I-V characteristics as observed by W-tip and Pt-Ir tip, polydentate behavior and elemental composition of ligand was explored. The ligand forms dative bonds with transit metals and p-n junction at the metal-ligand interface. Because of this p-n junction, the single molecule device shows rectification behavior in negative biasing conditions. While in positive biasing condition, the ligand shows memory switching behavior. And this is because of change in the conformation of the ligand under high electric field between tip and substrate which momentarily drag ligand towards tungsten atoms at the tip. At the moment when ligand and tip forms dative bond electrons found a conductive path in p-n junction at positive biasing on tip. But as soon as this positive bias been removed, the dative bond will dissociate because nitrogen and oxygen atoms no longer agree to share their lone pair of electrons with tungsten atoms at the tip which ultimately leads to the junction breakdown. This kind of dissociation of dative bonds is very common in Lewis acid base complexes (Lewis and Jolly, 1923). This formation and deformation of metal-ligand junction leads to rectification while change in molecular conformation in positive biasing will bring memory switching property of the complex. It is hard to do all these analysis on single ligand molecule because of strong aromaticity.

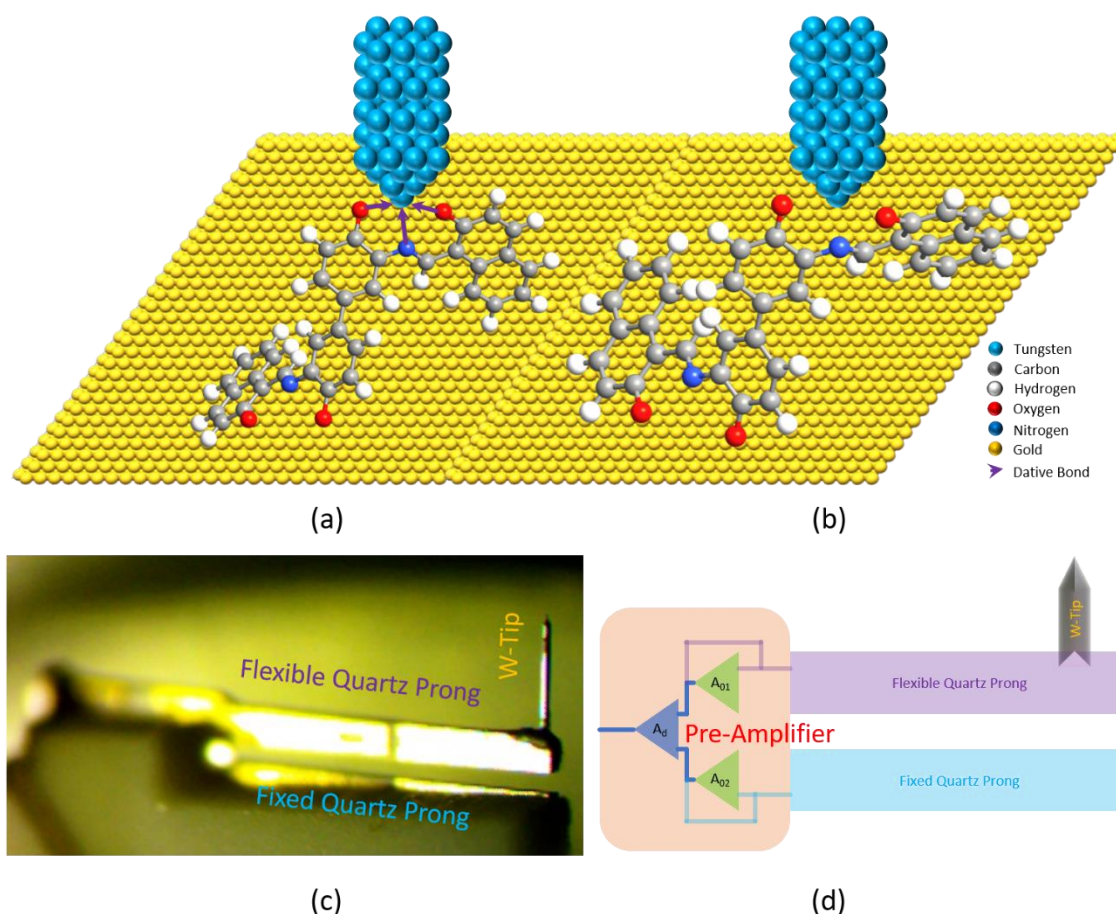


Fig.6.6 (a) Schematic representation of formation of dative bonds between tungsten atom at the tip with ligand molecule during positive biasing at the tip. (b) Breaking of coordination bonds between metal-ligand complex in the presence of negative biasing at W-tip. (c) Microscopic image of Q-plus sensor with mounted W-Tip. (d) Schematic representation of Q-plus sensor.

## 6.4 Conclusion

The Schiff's based ligand has been synthesized and characterized at molecular level with the help of STM. The ligand is proposed to form dative bonding with W-tip of Q+ Sensor while

performing IV characteristics with a few nanometers spacing between tip and substrate. The ligand in conjunction with transit metal element forms p-n junction at a bias voltage to make a conductive path for charge transfer in positive biasing. While in negative bias condition nitrogen and oxygen atoms forbid to share their lone pair of electrons with Tungsten atoms which results in both memory switching as well as rectification behavior of ligand-metal complex.