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# A Comparison Study On The Conductance Behaviour Of Self-Assembled Monolayers Of Various Aromatic Thiol Molecules Having Bio-Sensor Applications.

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**Abstract:**

A series self-assembled monolayers(SAMs) formed by various aromatic heterocyclic bisensor molecules have been studied to compare their conductance behaviour. Current-voltage (I-V) spectroscopic measurement of these SAMs were done using scanning tunneling microscope in the bias range of 1100mV to -1100mV. From the experimentally obtained I-V data, dI/dV curves were generated to compare the zero bias conductance of these biosenseor-molecular SAMs. It was found that Triazole molecule has the highest zero bias conductance.

## Introduction:

Interpretation of the charge transport behaviour through organic molecules has been achieved by different experimental methods such as scanning probe methods [1-6], cross oriented junctions of molecular wires [7-8] etc. Conductance determination by tunnel current-voltage measurement or commonly known as I-V spectroscopy using scanning tunneling microscope (STM) is a favored technique [9]. Non-metallic substrates such as graphene has also been used for such molecular conductance measurements using STM [10].

Specifically designed organic molecules are pivotal for various biosensor applications. One of such biosensing application is reading out DNA monophosphates or other biomolecular building blocks (e.g. RNA monophosphates, amino acids etc.) for the method development of nanopore DNA(or RNA or peptide) sequencing using electronic signal generation by STM. Hence, understanding the conductance property of these molecules and a

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comparison study on this front would be helpful in understanding their behaviour as biosensors for electrical signal measurements. In addition, this study would be beneficial for designing any new biosensor molecule for similar purpose. Four aromatic thiol molecules, namely Benzimidazole sensor (BnImR), Imidazole sensor (ImR), Pyrrole sensor (PR) and Triazole sensor (TR) were originally designed and synthesized for the mentioned purpose[11]. In this study, we have prepared self-assembled monolayers of these aromatic thiol biosensor molecules on metal electrodes and performed tunneling current-voltage spectroscopy measurements using metal probe of a scanning tunneling microscope(STM) as shown in figure1.

To understand the conductance behavior of these biosensor molecules, we prepared self-assembled monolayers (SAMs) and measured their tunneling current-voltage curve in the moderate bias range of +1100mV to -1100mV.

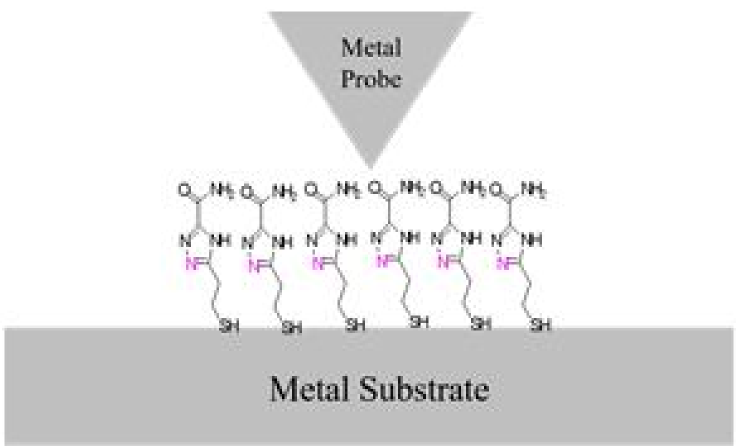


Figure1. Experimental orientation during the tunnel current-voltage spectroscopic measurements of SAM modified metal substrates using metal probe of an STM. The metal substrate and the metal probe are in the tunneling regime, while the molecular SAM(ImR SAM is shown here) is sandwiched between the two metal tunnel electrodes.

**Methods:**

SAM preparation: Synthesis of the aromatic thiol molecules and preparation of the SAMs on Palladium metal substrates has been done and characterized previously [11].

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Current-voltage measurements: Current-voltage measurements were done using home made Palladium STM probes installed in Pico-SPM STM instrument. For every measurement the current set-point was fixed at 200pA to maintain a similar probe-SAM surface distance for all the measurements. The voltage sweep was started from 0mV and gradually increased to +1100mV. Then it was gradually decreased to -1100mV and increased back to the starting point of 0mV to complete the sweep cycle. Change in the observed tunneling current was recorded simultaneously along with the voltage sweep.

**Results and discussions:**

The tunneling current-voltage spectroscopy data for BnImR, ImR, PR and TR is shown in figure2. The I-V curve for all the SAMs show linear ohomic behaviour in the close proximity of fermi level ($E_F$) i. e. 0mV bias, whereas non-linearity becomes prominent as the applied voltage increases. BnImR, ImR and PR show almost overlayed I-V spectroscopy curves and TR shows higher tunnel current value compared to the other three molecular SAMs for any voltage bias.

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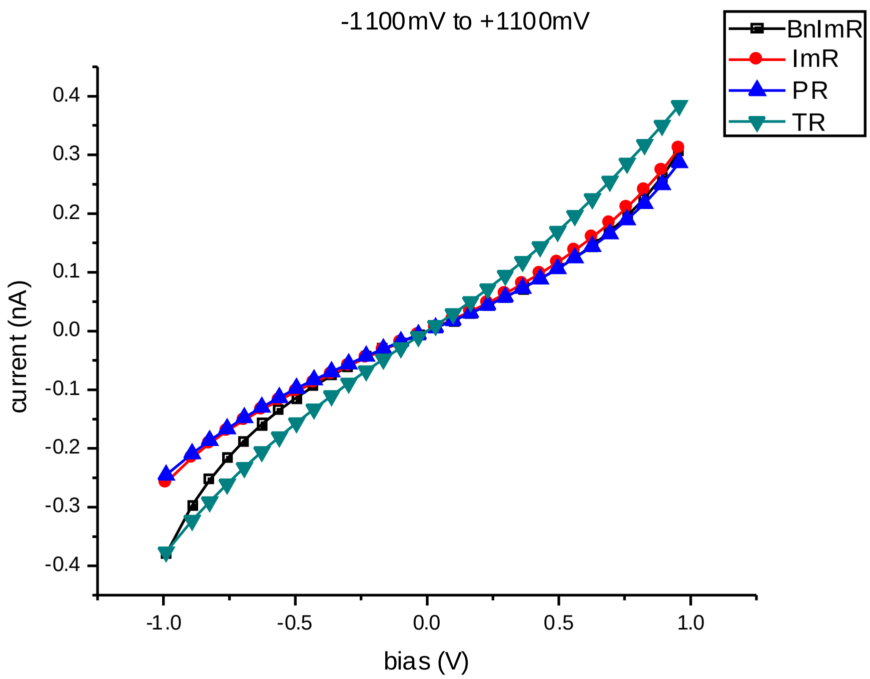


Figure2. Current-Voltage curves for BnImr, ImR, PR and TR SAMs in the voltage range of +1100mV to -1100mV. TR is clearly showing highest variation with change in bias, compared to the other three molecular SAMs. For this voltage range ohomic (linear) behaviour is not maintained through-out.

To verify the linear ohomic I-V behaviour of the SAMs, a small voltage range of +200mV to -200mV was considered (as shown in figure 3), which clearly indicates the linearity of the I-V curve in this narrow voltage range. A closer look at this data suggests that ImR allows higher tunnel current compared to BnImR and PR, after TR, at the voltage range close to the fermi level ($E_F$). However, the I-V curve (in figure 2) shows that with increasing bias range, there can be some extent of bias dependence as at the higher positive voltage range ImR SAM shows second highest tunnel current although at higher negative voltage range BnImR SAM shows superior tunnel current compared to ImR and PR.

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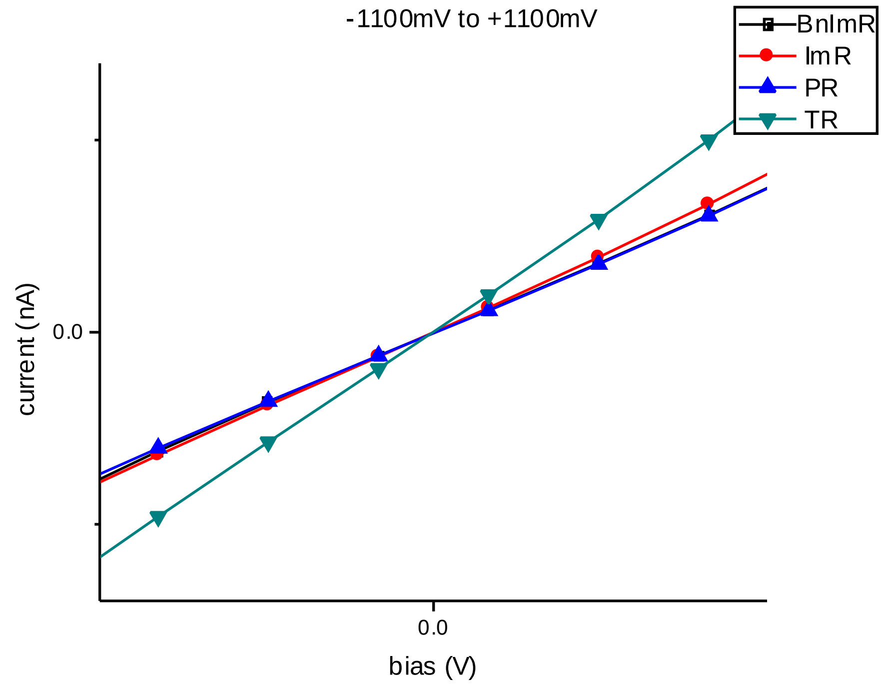


Figure3. Current-Voltage curves for BnImr, ImR, PR and TR SAMs in the voltage range of +200mV to -200mV. For this narrow voltage range, ohomic behaviour is maintained as the plots are fairly linear.

The dI/dV curves indicates the semi-metallic behaviour of the metal substrate-molecular SAM system and provide insights on the conductance behaviour of the different SAMs by comparing their “zero bias conductance”. TR clearly shows significantly higher dI/dV value at zero bias, whereas the other three molecular SAMs shows much similar levels of dI/dV values. This could be explained of the basis of more nitrogen atoms for triazole molecules, providing better metal-molecule contact and proving more transport channels.

 

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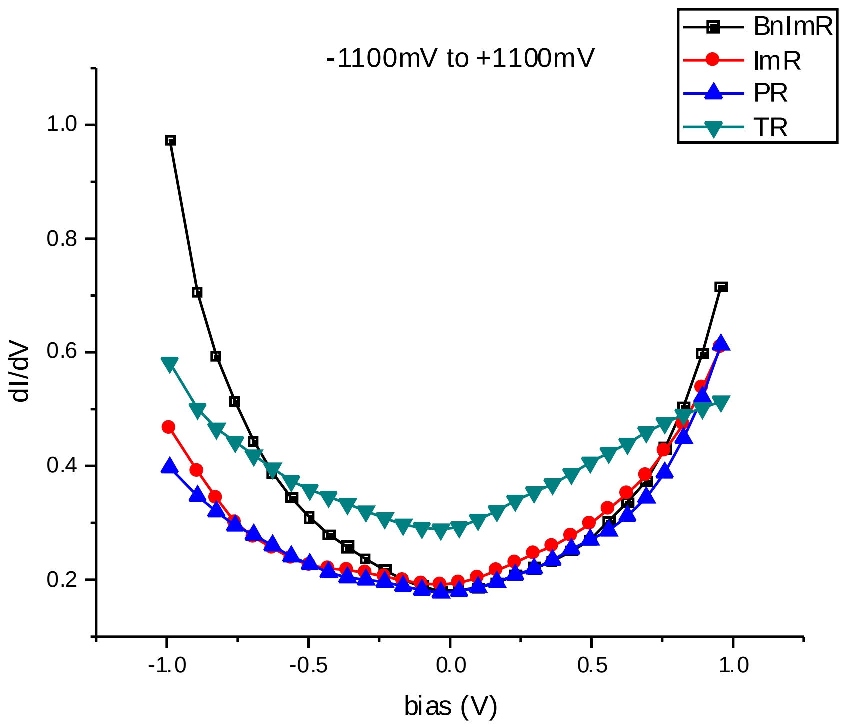


Figure4. dI/dV curves obtained from the I-V data for various molecular SAMs. TR shows highest zero bias conductance. Some bias dependence of the dI/dV values could be seen as we go towards higher bias values.

**Conclusion:**

The primary motive of this study is to understand the conductance properties of the four different aromatic thiol molecules that we use as biosensor in various metal-molecule-metal transport junctions experiments. Triazole has shown higher rate of change of the tunnel current in the STM metal-molecule-metal junction with changing sweeping voltages between the STM probe and the SAM modified metal substrate. The dI/dV curves showed that the zero bias conductance for Triazole is prominently higher that the other molecules. As mentioned before this could be attributed to the higher number of nitrogen atoms in the Triazole molecule creating better contact between the molecules of the SAM and the metal surface. This facilitates the transport for the Triazole SAM. Though, we understand that the actual orientation of the molecules on the metal surface affects the conductance of the overall SAM as well. Nevertheless, our learning interest predominantly lies towards finding out the

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molecular SAM having highest conductance value and Triazole came out as the standout candidate.

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