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Prospects of aromatic hydrocarbons for applications in molecular devices: a comparative study based on density functional theory

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Abstract

Prospects of molecular devices for better efficiency and performance are in the spotlight for some decades. Molecular electronic devices are good candidates to overcome the problems of leakage current, gate thickness and high-power consumption in conventional silicon-based transistors. Aromatic hydrocarbons are promising candidates for these devices because of their unique structural, physical and chemical properties. In this paper we report comparative simulations of transport properties of three aromatic hydrocarbons viz. benzene, naphthalene and anthracene from first-principles calculations based on density-functional-theory (DFT). The charge transport properties of the aromatic hydrocarbons with regard to their implications in molecular devices are investigated by sandwiching them between 3×3 gold (Au) nanoelectrodes. The molecules are sandwiched with 3 atoms of the Au nanoelectrodes on each side of the molecule. To form a firm contact with the Au atoms, Sulphur (S) is used as a linker group because it readily forms a strong bond with the Au and thiols molecules. The computed properties include transmission spectra, device density of states and I-V characteristic of all the molecules by using DFT and non-equilibrium green function (NEGF). We predict better transport properties for dithiol benzene (DTB) molecular device with greater conductivity and different response of current at increasing voltages. On the other hand, dithiol naphthalene (DTN) and dithiol anthracene (DTA) molecular devices show ohmic behavior at the increasing voltages. We observe that the conductivity of the devices is decreased by increasing the number of atoms of the hydrocarbons. We also compare transport properties of hydrocarbon devices with the saturated alkane thiols and unsaturated oligo phenylene and noticed that tunneling barriers of aromatics are low as compared to the alkanes and oligo phenylene molecules and can be applied in different molecular devices like transistors, diodes and resistors.

Key Words: Molecular devices; DFT; Dithiol Benzene; Dithiol Anthracene; Dithiol Naphthalene; Gold Electrodes; Charge properties;

I. INTRODUCTION

We have reached to a scenario where 100 million transistors of 180 nm size can be assembled onto a silicon chip of few cm^2 [1]. Owing to such low dimensional devises with assembly of large number of transistors, it is a formidable task to stop leakage current from one transistor to the other side of the circuit and junctions. Device size is limited by diffraction to about one half the wavelength of the light used in the lithographic process [1-5]. Nevertheless, at low dimension of 50 nm it is not possible to dope silicon uniformly into the circuits that poses main hurdle in the design of low dimensional efficient device [6]. On the other hand, the techniques involving the creation and synthesis of the semi-conductor devices are reaching to their potential limit which calls for the development of new methods to overcome some related issues. Innovative techniques are required to develop semi-conductor devices of smaller size with ease and good efficiency [7-9]. These devices have diverse molecular behavior under various conditions. For instance, some molecules offer negative differential resistance subjected to electric field by changing the geometry [10, 11]. Some molecules show ohmic behavior with a well-defined linear response of current with the increasing voltage. However, some molecules show hysteresis curve and have a tendency to align their magnetic moments in the presence of the magnetic field, this is useful in magnetic storage devices [12-17]. On the other hand, some molecules reveal high conductance through molecular wires and can be used for communication purpose [18, 19].

Manipulation of single molecules and geometries by various methods, especially by the electromagnetic field, can induce changes in the electrical properties of the molecules [20, 21]. Up to this point, the digitization and miniaturization of electronic devices has been realized through different approaches. However, most attempts in this regard were hampered by costly computational demands and time constraints. In order to overcome some of the issues, interest is on rise to simulate devices of greater efficiency and smaller size up to the level of atoms and molecules. In fact, molecular electronics has been in the spotlight in recent decades and considerable scientific efforts have been extended to explore the prospects of molecular devices in various fields of science and technology. Novel computational tools and methods have enabled the researchers to explore the applications of single molecule as compact molecular resistors, transistors, switches, rectifiers, non-linear components and magnetic storage memories [10, 22-24].

The first-principles calculations show the variation in conductance of the benzene molecule under the influence of light which suggests that molecule can be served as the molecular switch [25].Using the DFT calculations in combination with non-equilibrium green function (NEGF) method in comparison with the conventional gold Au electrodes with three different anchoring groups, i.e. thiol for dithiol benzene (DTB), methylene for dimethyl-benzene (DMB), and direct bonding for benzene (Phenylene).The electronic properties of these molecules are investigated by calculating the transmission spectra and density of states. The usage of the thiol linker group may open up new horizons in the field of molecular electronics [26]. The DTB molecule is investigated with Au metal electrodes. The transmission spectra and density of states are obtained with potential implications in various logical operations via switches and transistors [43]. Benzene-1, 4-dithiol is often used in molecular electronics, however full understanding of the electronic properties of this molecule is yet to be understood. Usually the geometries, considered in transport calculations, assume the connection of BDT between two Au leads via the S atoms while considering molecule's orientation either perpendicular or close to a perpendicular configuration relative to the Au metal electrode surfaces. Results obtained from *ab initio* calculations for an isolated molecule showed that the configuration with the largest adsorption energy has the DTB very close to being parallel to the metal Au electrode surfaces. It is argued that the discrepancies in the molecular break junction (MBJ) experiments may be overcome following the conformation and geometry based on the DFT calculations in combination with the NEGF [27] approach.

Study of electron transport phenomenon is observed for the DTB, DTN and DTA. The molecules are sandwiched between two Au electrodes for the purpose of creating molecular junctions. Conductance of each molecule is calculated in the histogram. The calculated conductance peaks suggest that these molecules, upon applying gate potential, can act as transistors which have potential applications in molecular electronics [28]. The connection is made between the molecules and electrodes using the mentioned in computational technique part. Then different electronic properties are calculated. The I-V characteristic curve suggests that the molecules of interest can be affected by the geometry of the electrodes and its effect on the current voltage relationship. The calculated I-V curve is in good agreement with the experimental results [29]. Full scale molecular orbital theory is used to investigate the benzene molecule sandwiched between the metal electrodes. Accurate position, bond length, bond angles and all the parameters related to the molecule and electrodes are considered carefully in this study as they have impact on the electronic properties of the system under consideration. The obtained results motivate to discover more effective ways to connect the molecules with the metal electrodes to achieve the novel properties and applications. The approximation used in the DFT undermines the HOMO-LUMO gap in the molecular system in comparison to the experimental results. LUMO and LUMO +1 may be approachable but they do not have impact on the properties of the system neither they take part in the conduction phenomenon of the system[30]. Ab initio investigation of the switching behavior of the DTB nano-molecular wire is studied by conducting experiments on the MBJ by using scanning tunneling microscopy (STM). It is found that the switching mechanism completely relies on the coupling between the molecule and the electrodes. In this communication, first-principal calculations are used to predict a novel type of more stable system, obtained by controlling the stability and activation barrier between a chemically bound state (the 'ON' state) and a physically bound (precursor) state (the 'OFF' state) for benzene derivatives adsorbed on a metal surface. All of the calculations are done using DFT formalism within PBE exchange-correlation functional along with NEGF approach [31]. Using the previous techniques calculated the transmission modes/channels and conductance was calculated using DFT technique. The electron transport study is also done on the basis of NEGF and DFT approach. The switching behavior of the benzene ring is studied and its relation with the electric field is also observed which tells that the electric field influences the switching behavior of the benzene and hence its conductivity and conductance. These parameters are critical in fabrication of molecular devices which completely depend upon the order and magnitude of the electric field which influences the internal structure of the benzene molecule. The change in the electric field can increase or decrease the conductivity of the benzene molecules. This can be seen in the calculated conductance of the molecule with the alternating electric field [32]. It was also observed that molecular junctions can exist without using thiol linker group. Junction can exist using some other linker groups as well like amine group is bonding with nitrogen [33] etc. At the single molecular level this technique provides a new way for the design and geometry of the molecular devices which can be used for various applications [34].

The bridge sites on each molecule present the best adsorption with increased adsorption energies between the range (−0.90, −1.37, and −1.79 eV, fort benzene, naphthalene and anthracene respectively). Larger aromatic compound adsorption energies can also be computed using the proposed model and technique which is based upon the interaction energies and exchange-correlations among the molecule and electrodes under study[35]. Highly conductive single naphthalene and anthracene molecular junction with well-defined conductance are prepared. It demonstrate that π-binding method is the most promising approach to fabricate highly conductive and well-defined molecular structures which can be very beneficial in the making of more efficiency and high performance devices in the molecular electronics [36]. Ab initio analysis of conductance of naphthalene and anthracene are studied by connecting the molecules between the Au electrodes as for the benzene which is already discussed. It is found that in comparison to the alkanes, these aromatic hydrocarbons have lower tunneling barriers and hence their conductance is greater than the alkanes. It is also observed that the theoretical results obtained by DFT technique are 122 times greater than the experimental results. The discrepancy in the results is due to the defects in the molecule prepared for the experimental procedures. Transmission spectra's, density of states and HOMO LOMO calculations are performed for the study of these molecules [37]. We have calculated the current–voltage characteristics for positive and negative bias voltages using 3 x 3 leads of the Au electrodes. We observed that due to interaction with the applied electric field, the current–voltage curve of amino substituted benzene molecule exhibit-switching behavior as if it has two states i.e. OFF (0) and ON (1). Despite the asymmetric structure of benzene molecule substituted with hydroxyl group, there is no obvious rectification behavior in its current–voltage curve. Furthermore, we have calculated the current–voltage curve for benzenediselenol and it is found that the best anchoring atom depends on bias voltage which will decide the rectification or switching behavior of the molecule understudy [38].

II.COMPUATION DETAIL AND METHODOLOGY

In this section, first-principles DFT calculations combined with NEGF on the electronic and transport properties of benzene-based hetero-structure molecular devices have been investigated. Main focus is on the contact geometry between molecules and electrodes, and several anchoring groups have been considered for the investigation of the molecule. The current–voltage characteristics are calculated for positive and negative bias voltages. Transmission spectra, DOS. Results shows that the anchoring groups play a crucial role in determining the overall conductivity of the molecular devices. Negative differential resistance (NDR) and rectifying effect can be observed. Calculations are based on the first-principle DFT formalism along with NEGF method as implemented in atomistic toolkit (ATK) package[39]. In all the calculations, the single-ζ polarized basis set is adopted for elements of systems. The exchange correlation function is described by LDA-PBE. The mesh cutoff energy is set to be 150 Ry. The Brillion zone integration of $1\times1\times100$ k-points is chosen. The NEGF-DFT self-consistency is controlled by a numerical tolerance of

10^{-5} eV. The results show that the molecule is greatly influenced by the atoms in contact with the electrode leads [40].

III. RESULTS AND DISCUSSIONS

Au-DTB-Au transport properties

The geometries are optimized so that the device is formed without any errors and faults in the bond lengths and angles. Figure 1 is obtained after optimization of the Au-DTB-Au molecular device. Before optimization, the bond lengths of C-S,C-C, C-H, S-Au are taken 1.75 A^0 , 1.39 A^0, 1.10 A^0 , and2 A^0 for the DTB molecule respectively. After optimization their bond lengths are changed to 1.69 A^0, 1.40 A^0, 1.09A^0 and 2.42-2.45 A^0 respectively for three atoms of Gold which are in direct contact with the Sulphur (thiolate) atom as shown in Figure 1.

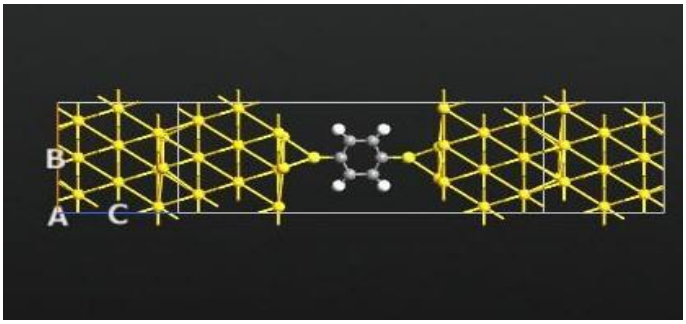

Figure 1: Au-DTB-Au device with Optimized Geometry

Figure 2 shows the projected density of states of Au-DTB-Au molecular device with the Au metal electrodes in the energy range of -5 to +5 eV. The fermi level is set at 0 eV by default the calculation.

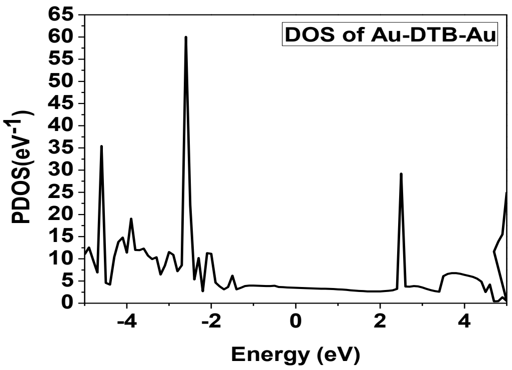

Figure 2: Projected Density of states for Au-DTB-Au

The charge transport properties in a molecular device, a molecule in a molecular junction through the molecular orbitals particularly through the frontier orbitals which are primarily positioned near the fermi energy level (E_f) set as zero here. These molecular orbitals undergo change and modifications when the device is connected to metal Au electrodes because of the electronic interactions. The highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) which take part in the electron transport are situated close to the fermi energy level (E_f). The fermi energy level is always calculated to be placed between the HOMO and LOMO states and HOMO is much close to the E_f than LUMO, which may imply hole-transport in the molecules related to the HOMO state. By calculating MPSH values, it is found out that 14 state is HOMO and LUMO states. 14 is the HOMO and 15 state is LUMO of Au-DTB-Au molecular device with the help ATK software packages. Au-DTB-Au shows broad transmission peaks near the fermi level which is consistent with the previous studies in this regard[41]. Intense and sharp peaks mainly arise from the molecular orbitals. There are no peaks in the graph from the energy range -2 to +2 eV which tells us that this is the gap between the HOMO and LUMO of the molecular device. By calculating molecular energy spectrum of the device it is found out that the gap between the two orbitals is 4.73 eV. The plateau created in this range means that there are no available states for the electron to occupy. The electron cannot be accommodated in the above mentioned energy range just like a forbidden energy gap in metals and semi-conductors. The projected density of states tells us the origin of the peaks arising in the graph. It is found out that the larger peaks closer to the fermi level are due to the overlapping of the s and p orbitals of the molecule and the Au metal electrodes. There are larger peaks in the energy range of 2.5 eV and -2.6 eV. The rest of the negative peak is not important because this is very far away from the fermi energy level.

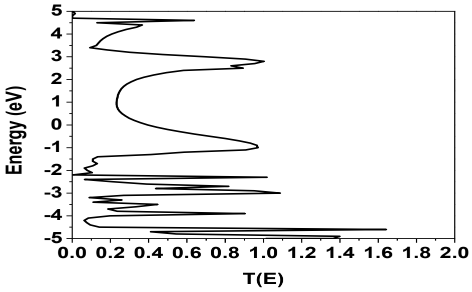

Figure 3: Transmission spectrum of Au-DTB-Au

Figure 3 demonstrates the transmission spectrum of the Au-DTB-Au molecular device in the -5 to +5 eV range. This shows the probability of the electrons in view of available density of states. The electrons can travel or has the maximum probability to be transmitted through these energy states. Since energy levels near the fermi level contribute more to the conductance, so it is reasonable to consider only these energy levels. Note that the peaks shown in the transmission spectra in the range of 2.82 eV and -1 eV are closest to the fermi level. Both peaks are showing transmission of 1 which is the maximum value meaning that the electron can surely pass through this mode/channel. The peaks at -2.32, -2.92 and 4.53 eV are showing transmission of even more than, i.e. 1.007, 1.009 and 1.63 respectively, which means that it has more than one transmission channels/ modes to be transmitted through this available density of state. The projected density of states and transmission spectra are consistent with each other confirming that the above-mentioned orbitals are responsible for the conductance and transmission of the electrons through the molecular device.

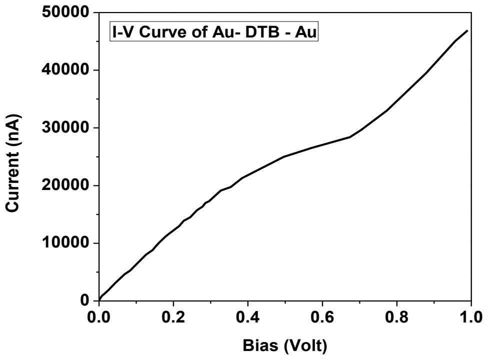

Figure 4: Linear response curve of the Au-DTB-Au

The linear current response curve of Au-DTB-Au molecular device is shown in Figure 4 for voltage up to 1V. In Figure 4, the current has a maximum value of 40000 nA at 1V. At lower voltages upto0.5 eV, the current shows a linear relationship with the voltage. Above 0.5 eV, a slight discrepancy in the linear behavior of the current with the voltage is observed. Shown conclude that at lower voltages the device is Ohmic whereas the device shows a non-Ohmic behavior with the increasing voltages.

Au-DTN-Au transport properties

The geometries are optimized so that the device is formed without any errors and faults in the bond lengths and angles. Figure 5 is obtained after optimization of the Au-DTN-Au molecular device. Before optimization, the bond lengths for the molecules of C-S, C-C, C-H, and S-Au are taken 1.75 A^{0} , 1.41 A^{0},1.09 A^{0}, and 2 A^{0} respectively. After optimization, their bond lengths are changed to 1.73 A^{0}, 1.42 A^{0}, 1.10A^{0} and 2.43-2.47 A^{0} respectively for three atoms of Gold which were in direct contact with the Sulphur (thiolate) atom as shown in Figure 5.

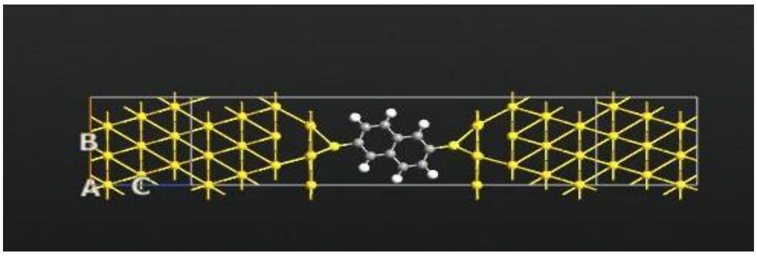

Figure 5: Au-DTN-Au with Optimized geometry

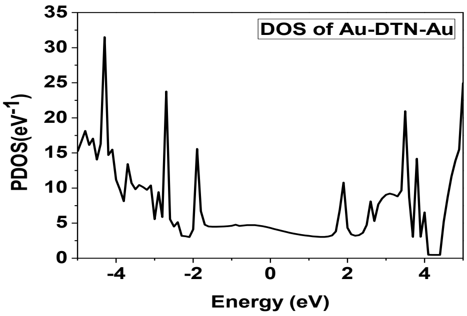

Figure 6: Projected Density of states of Au-DTN-Au

The Projected density of states of the Au-DNT-Au molecular device with the Au metal electrodes in the energy range of -5 to +5 eV is shown in Figure 6. We only consider the peaks near the Fermi level which is set to 0 by default. There are peaks at around 2 eV and -2 eV. There are no peaks between the range -1.86 to +1.93eV suggesting that this is the forbidden energy gap between HOMO and LUMO orbitals of the device. By calculating MPSH values, it is found out that the energy gap between HOMO and LUMO is 3.79 eV. We only consider the energy levels near the fermi level which contribute mostly in the conduction of the electrons. There are peaks at -2.7 eV and +2.5 eV as well, which indicate the available energy states for the electron to occupy. These peaks are due to the s and p orbitals of the molecule and Au metal electrodes.

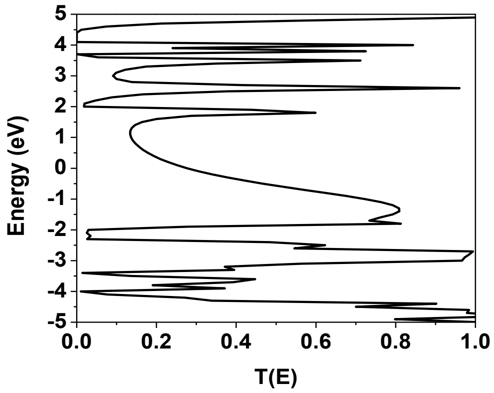

Figure 7: Zero biased Transmission spectra (T) of Au-DTN-Au

The transmission spectra of the Au-DTN-Au molecular deviceis shown in Figure 7. There are peaks in the -2.68 eV , -1.73 eV, +1.72 eV, and +2.62 eV. There is slight change in the spectra of the molecular device because we have connected it with the Au metal electrodes now. The peaks at energy -1.73 eV and +1.72 eV are not showing max transmission of 1 which is necessary for the electron to transmit through channel/mode. They have transmission probability of 0.6 and 0.8 respectively meaning the probability for electron to pass through these channels are low and electron may or may not transmit through it. The peaks at -2.68 eV and +2.62 eV have the maximum transmission of 1 meaning that the orbitals corresponding to these energy ranges have the highest probability for the electrons to be transmitted through them.

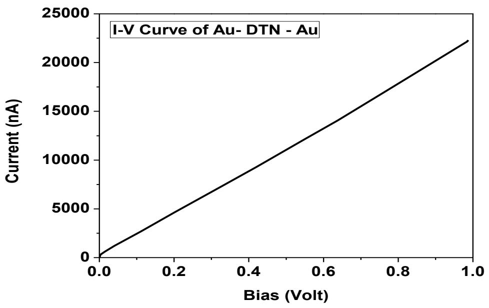

Figure 8:Linear response curve of the Au-DTN-Au

The linear response behavior of Au-DTN-Au molecular device can be seen in Figure 8. The linear response is measured for the voltages in the range from 0-1 V in the step size of 0.2

voltages. It can be seen that the maximum current for the device is 24000 nA at voltage 1V. Unlike Au-DTB-Au, this molecular device is showing a linear response to the increasing voltage suggesting that this device is Ohmic in nature.

Au-DTA-Au transport properties

The geometries are optimized so that the device is formed without any errors and faults in the bond lengths and angles. Figure 9 is obtained after optimization of the Au-DTA-Au molecular device. Before optimization, the bond lengths for the molecules of C-S, C-C, C-H, and S-Au are taken 1.75 A^0C, 1.42 A^0, 1.09 A^0, and 2 A^0. After optimization their bond lengths changed to 1.73 A^0, 1.43 A^0, 1.10A^0 and 2.43-2.52 A^0 respectively for three atoms of Gold which were in direct contact with the Sulphur (thiolate) atom as shown in Figure 9.

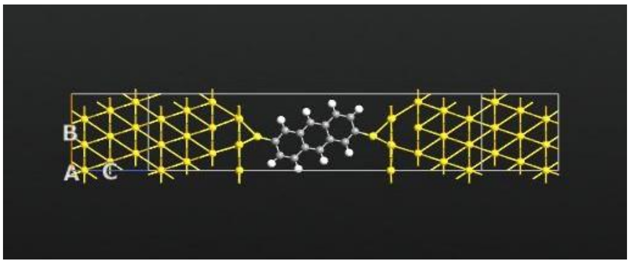

Figure 9: Au-DTA-Au with Optimized geometry

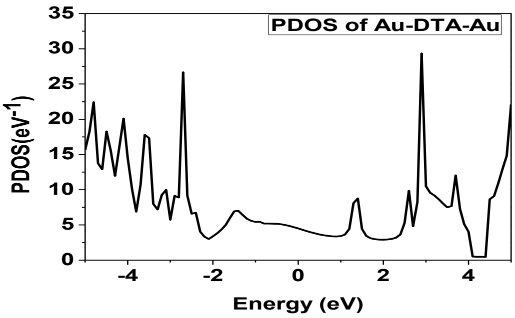

Figure 10: Projected density of states for Au-DTA-Au

The projected density of states of the Au-DTA-Au molecular device with the Au metal electrodes in the energy range of -5 to +5 eV is shown in Figure 10. The Fermi energy level of the device (E_f) is set as zero. There are peaks at around -1.46 eV and +1.35 eV. The forbidden energy gap between HOMO and LUMO orbitals of the device. By calculating MPSH values, it is found out that the energy gap between HOMO and LUMO is 2.81 eV. It means that these orbitals have the tendency to occupy electrons.

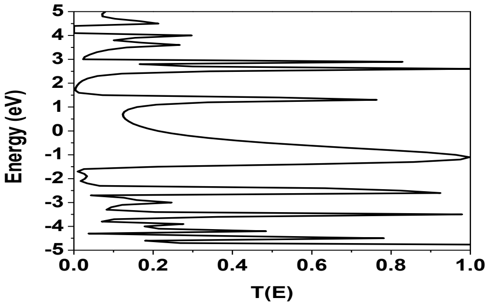

Figure 11: Zero biased tranmissioon spectra of Au-DTA-Audevice

We calculated the transmission spectra of this molecular device confirming the transmission of the electrons through these orbitals. Figure 11 shows the transmission spectra of the Au-DTA-Au molecular device. In this figure peaks can be seen at around -1.17 eV, -2.61,+1.30 eV,+2.60 eV energies which arise mainly due to the s and p orbitals of the molecules and electrodes. The transmission spectra tell us that the peaks at -1.17 eV and +2.61 eV have the highest probability of the electron to be transmitted through their corresponding orbitals mentioned in the PDOS of this molecular device. The peaks at -1.17 eV and +2.61 eV shows the transmission of maximum value of 1 meaning that these electrons have only one channel/mode to travel through and they have the highest probability to pass through these transmission channels. The rest of the peaks far away from the fermi level and are in significant because they do not contribute much to the conduction in molecular device.

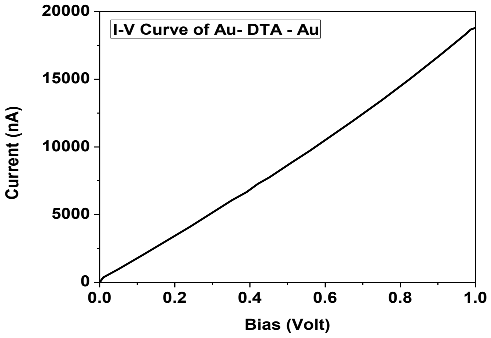

Figure 12: Linear response curve of the Au-DTA-Au

The I-V characteristics of the Au-DTA-Au devices shown in Figure 12. It shows the relationship of the current to the increasing voltages from 0-1 voltage range. It is seen from the Figure 10 that maximum current through the device is around 19000 nA at 1 volt. The I-V curve suggests that the current increases linearly with the increasing voltage. The device shows an Ohmic behavior with the increasing voltage. Unlike benzene and Naphthalene molecular device, Anthracene molecular device showed much lower conductivity and current with the increasing voltage in the 0-1 volt range. This can be understood on the basis of the energy gaps between HOMO and LUMO orbitals of the molecular device. Benzene molecular device despite having more energy gap between the molecular orbitals shows ~~ed~~ more conductivity as compared to Naphthalene and Anthracene molecular device.

IV. CONCLUSION

Aromatic hydrocarbons Benzene, naphthalene and Anthracene molecular devices are prepared using 3x3 Au metal electrodes by combining them with 3 gold atoms directly with the molecule. Their transmission spectra, device density of states and I-V characteristics are studied and compared with each other. It isfound out that molecular orbitals contribute towards the transmission spectra. The PDS corresponded towards the transmission spectra giving almost same peaks at almost same positions. We come to know about the orbitals which contributed in the transmission of the electrons. The I-V characteristic curves suggest that Benzene molecular device shows Ohmic behavior on lower voltages and non Ohmic behavior on higher voltages. Naphthalene and Anthracene molecular devices show almost a straight response to the applied voltages. They show Ohmic behavior at almost all the voltages. Due to these results it is concluded that benzene, naphthalene and anthracene behave differently under applied voltages and can be used in various applications of molecular electronics such as resistors, transistors, diodes and negative differential resistors.

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