

## DESIGN OF SINGLE MOLECULE AROMATIC MOLECULAR SWITCHES WITH METAL ELECTRODES-A COMPUTATIONAL APPROACH

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Designed 1,4-benzene dithiol, 1,4-benzene diamine, and 1,4-benzene dicarboxylic acid based molecular switches with gold, silver, platinum and palladium metal electrodes by the first-principles approach. The electronic properties of the designed metal-molecule-metal sandwich structure are investigated with density functional theory (DFT) method. A series of benzene derivatives to explore the physical behaviour of conductance interpret in terms of nature of molecular backbone, anchoring group, contact geometry, nature of electrode material, molecular length, connectivity site, density of states, HOMO-LUMO gap, ionization potential and potential energy were systematically studied and compared. The findings of the present work clearly reveal that for the design of an efficient molecular switch, palladium and thiol are the best among electrode and anchoring group respectively. Palladium electrode shows high switching band gap ratio for ON and OFF state compared to Au, Ag, and Pt. The first principles approach can be used to screen and minimize the need for experimental approach which could be expensive.

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### 1. Introduction

Molecular electronics is an indispensable technological concept of rapid-growing interest since molecules constitute promising building blocks for future generation of electronic devices. Make use of single molecules as active components in electronic devices is one of the major goals in nanotechnology [1]. The bottom-up approach, based on the self-assembly of functional molecular building blocks into more complex architectures, designates an attractive alternative to silicon based nanoelectronics. These molecular systems can perform as gates, switches, memories or transport elements, providing new molecular functions that need to be well distinguished and understood [2]. But this Molecular electronics term is also used to refer to the distantly associated field of organic electronics and conductive polymers [3]. Which uses the properties of molecules to influence the bulk properties of the material. The organic compounds made up of small molecules, oligomers, or polymers and have found application in devices such as liquid crystal display (LCD), Organic light emitting diodes (OLED), and Organic Field Effect Transistor (OFET) [4]. At the electrode interface, an enormous accumulation of molecules is connected by a conducting phase. In contrast, single molecule systems, have in view at individual contact to single molecules or small arrays of identical and perfectly ordered molecule. This approach differs extremely from the bulk molecular system approach as it aims to utilize the physical properties of single molecule for nanosized electronic devices.

The single-molecule junction, which is the basic unit of molecular device, has been extensively studied since the first discovery in 1974 [5]. Since then several numerous experiments and theoretical studies have been performed through molecules placed between two nano electrodes within a nano gap. Since the pioneering work of Reed et al. who first measured by mechanically controllable break junctions (MCBJ), the conductance of a single benzene-1,4-

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dithiol (BDT) molecule attached to a gold surfaces, BDT has been considered the benchmark molecule for both theoretical and experimental studies [6]. Performed a systematic investigation of the evolution of the conductance of a benzene molecule with different electrodes and different anchoring groups combination. When junctions are formed using gold metal electrodes, thiol links are frequently used. However, the conductance of the single-molecule junction varies significantly from junction to junction, making it difficult to map the relation between molecular structure and junction conductance [7]. Measurements of single molecule junctions in a molecular switch with different metal electrodes results in a broad distribution of conductance, attributed to different binding geometries for ON and OFF. In particular, the conductance of aromatic molecules is strongly influenced by the orientation of the  $\pi$  system relative to the electrode-anchoring bond.

Interpreting charge transport through metal-molecule junctions and factors affecting the conductivity at the single molecule level is the first step in designing functional electronic devices using individual molecules. Single molecule junctions are electrode-molecule electrode sandwich structures [8]. They usually are formed by wiring a molecule between two metal electrodes via anchoring groups that come up with efficient electronic coupling and bind the organic molecular backbone to the metal electrodes. While molecular-scale switching has been reported in atomic quantum point contacts, single-molecule junctions provide the additional flexibility of tuning the on/off conductance states through molecular design by changing the electrode and anchoring group. Thus far, switching in single-molecule junctions has been imputed to changes in the conformation or charge state of the molecule. The molecule-metal nano electrode interaction plays a significant role in determining the structural design of molecular scale switches that are formed [9]. The motivation behind the present work is to design and modelling of an efficient molecular switch with gold, silver, platinum and palladium electrode and to investigate its switching as well as conductance dependence theoretically. The geometrical optimization of benzene based molecular switch with metal electrodes and its switching properties are investigated via HOMOLUMO gap and the results are explored.

## 2. Model and computational details

For the first principles study of a molecular switch, firstly, one should optimize geometrically suited molecule and electrode separately. In this work, the geometrical optimization of molecular backbone and the electrode have done independently and later in a fused form as a molecular device. The geometrical optimization is done by Gaussian 09 software [10] with BPV86 type exchange-correlation functional and the popular SDD basis set [11]. The Metal-Molecule Metal sandwich geometry for ON (top-hollow) and OFF (top-top) state is explored separately. Our prime goal is to investigate the metal electrodes Gold (Au), Silver (Ag), Platinum (Pt) and Palladium (Pd) for the modelling of a molecular switch. Our design includes four components left electrode, anchoring groups, molecular backbone and the right electrode. Anchoring group attached to both left and right of the molecular backbone forms the heart of the molecular switch. The density of state spectra (DOS) were calculated using GaussSum software at the same level of theory [12].

## 2. Results and discussion

### 3.1. Conductance across the designed single molecular switches

Investigated eight objectives to design the molecular switch by exploring the conductance across a single molecule-metal junction. The main eight causes are formulated as: 1) Nature of molecular backbone 2) Anchoring group 3) Contact Geometry 4) Nature of electrode material 5) Molecular length 6) Connectivity site of anchoring group on molecule 7) DOS, HOMO, LUMO and HOMO-LUMO gap 8) Ionization potential and Potential energy. The systematic study of electrode-anchoring group-molecule fusion is supreme for the modelling and design of a molecular switch [13].

### 3.2. Selection of molecular backbone for the design of a molecular switch

It is the central molecular part between the two metal electrodes besides the alligator or anchoring group. This molecular backbone determines the functionality of a single molecular device as molecular switch [14]. In this paper, for the design of a molecular switch, the prime goal is to select a conjugated, aromatic,  $\pi$  bonded molecules as a backbone and that holds two chemical stable states or geometry which in turn is evaluated as ON/OFF state of the switch [15]. The previous experimental results shown that oligo phenylene ethynylenes (OPE) are the good candidates for the molecular backbone, since it demonstrates a huge electronic conjugation between phenyl rings and also when connect with gold electrode it has two stable geometries and both states allow different conduction. [6]. Here selected and simulated for geometrical optimization of benzene derivatives as molecular backbone.

### 3.3. Dependence of Anchoring group in junction conductance of molecular switch

An anchoring group is a group of atoms that forms the interface between the molecular backbone and nano electrode [16]. A strong single molecule -electrode coupling is the significant step for designing a molecular switch. Different anchoring group with same molecular backbone will affect the HOMO-LUMO gap of the molecular switch and there by conductance too. To explicate the contribution of anchoring group in a molecular switch design, systematic studies are needed where the molecule remains the same and only the anchoring group is substituted. Venkataraman et al. [17,18] who studied junctions formed by lone-pair interactions of amine anchor group with gold proposed the idea to test if the spread in conductance arises purely from the nature of the gold-sulphur (Au-S) bond is to substitute the thiol anchor for other groups, such as amines ( $-\text{NH}_2$ ) which may bind in a different manner. In this work, 3 anchoring groups namely thiol ( $-\text{SH}$ ), amine ( $-\text{NH}_2$ ), and carboxylic acid ( $-\text{COOH}$ ) with the same molecular backbone, aromatic benzene ring were investigated systematically for the design of an efficient molecular switch. In these three anchoring groups,  $-\text{SH}$  forms the bond with electrode via S atom, whereas  $\text{NH}_2$  forms the bond with electrode via lone pair of electron in the nitrogen atom. Thus, these two anchoring groups have come under monodentate family since it has only one atom to bind across the electrode to get a stable and optimized geometry [8]. But  $-\text{COOH}$  is coming under bidentate family and it forms the bond with electrode using any two-binding site as carbonyl ( $-\text{C}=\text{O}$ ) or carboxylate ( $-\text{COO}^-$ ) sites giving different contact conformation between anchoring group and electrode [19,20].

To model a molecular switch, one should primarily consider the bond between anchoring group and nano electrode and that eventually leads to strong coupling. Observed Au, Ag, Pt, and Pd electrode with Sulphur atom forms the strong and robust covalent bonding compared to Nitrogen and Oxygen. [21]. Previous experimental results have given the idea of binding strength, contact resistance, junction formation probability and stability of thiol, amine and carboxylic acid as follows  $\text{Au-S} > \text{Au-NH}_2 > \text{Au-COOH}$  [22,23,24]. The contact geometry between the anchoring group of a molecular backbone and the nano electrode atoms is expected to differ from one contact to another. The geometrical optimization of anchoring groups with benzene ring give critical role of Hydrogen atom in the interface of thiol and carboxy acid, and details of the interaction of the Nitrogen lone pair in the amine group with all metal electrodes. Comparing to other two anchoring groups, amine has taken more time to get geometrically optimized because of the lack of covalent bond. Therefore, an anchoring group should possess high coupling strength, low contact resistance, regular binding geometry, sufficiently strong anchoring with high junction formation probability and relatively high electronic nature with good conduction for the design of ON and OFF state of molecular switch [25].

Studied the dependence of anchoring group with respect to the empirical formula, molecular junction conductance,  $G = A_N \exp(-\beta_N d)$  [26].  $A_N$  is a constant decided by the molecule electrode coupling strength and reflects the contact resistance.  $A_N$  is highly responsive to the type of anchoring group.  $\beta_N$  is the tunneling decay constant, a significant parameter that determines the capacity of electron tunneling mechanism through junction. But relative to coupling strength and contact resistance, the tunneling decay constant has small differences in their values for three anchoring groups. Our theoretical study strictly gives the dependence of  $\beta_N$  on the molecular

energy alignment with the fermi energy level of electrode rather than anchoring group [27]. For the design of a molecular switch, the best anchoring group is thiol (-SH), even though it is not much better than amine (-NH<sub>2</sub>). The worst anchoring group is carboxylic acid (-COOH) in terms of junction conduction. Among all the combinations of BDT, BDA and BDC with Au, Ag, Pt and Pd, BDC -Pd combination gives high switching ratio and BDC-Pt gives low switching ratio. Pd-S, Pd-N and Pd-O show good bandgap difference between ON and OFF state of molecular geometry among all the nano electrode-molecular backbone combination. Other best options for the design of molecular switches are Au-O, Ag-O, Au-N, Ag-S, Pt-N, Pt-S, Ag-N, Au-S from out DFT method. Further, Venkataraman et al [28] found that among selected anchoring group, amine is the best for fabrication of a single molecular junction device, even though Au-NH<sub>2</sub> bond is weak compared to the Au-S bond.

### 3.4. Selection of different electrode materials for the design of molecular switch

Basic requirement for the design of any molecular switch. Electronic properties of the molecular device are purely depending on the electrode material. If the electrodes are made of noble transition metals like Au, Ag, Pt or Pd it forms a good ohmic contact and good coupling between the molecular backbone and both left and right metal electrodes. Thereby metal electrodes are the traditional choice for nano electrodes. Whereas graphene nano ribbons are revolutionary electrodes for the molecular electronics. For Au, Ag, Pt and Pd which have work functions of 5.10, 4.26, 5.65 and 5.12 eV respectively [7]. The highest work function is for Pt metal. From the simulation results it is found that the Fermi energy of the electrodes and the energy offset between the Fermi energy and the HOMO of the molecule decreases with increasing work function.

*Table 1. (a) Energy gap between HOMO and LUMO when the molecule is insulated and attached to two nano metal electrodes; (b) Bond length and bond angle of BDT, BDA, BDC with Au (111); (c) Length of molecular backbone Vs HOMO-LUMO gap values for insulated and attached with Au (111).*

Molecule	Eg (eV) insulated	Eg (eV) attached with Ag (111)
BDT	5.5576	0.0343
BDA	4.62	0.0653
BDC	2.57	0.1116

(a)

Molecule with Au (111)	Metal-Molecule Bond Length (Å <sup>o</sup> )	Bond Angle (Degree)
BDT	2.35	109.47
BDA	2	116.59
BDC	1.92	108.38

(b)

Molecule	HOMO-LUMO gap (eV) when connected to Au (111)	No: of phenyl	HOMO-LUMO gap (eV) when not connected to an electrode
Monophenyl	0.05	1	5.5576
Biphenyl	0.1023	2	2.5868
Tetraphenyl	0.1051	3	2.322
Quaterphenyl	0.1099	4	2.1533
Quinquephenyl	0.1121	5	1.9891

(c)

Au and Ag are from group 11 transition metals and Pt and Pd are from group 10 transition metals. Group 10 possess significant d-orbital characteristics, that leads to the  $\pi$  bonding at the electrode molecule contact. That will obviously make an additional channel for electron tunnelling. Because of these reasons Pt and Pd display more conductance than s-orbital

characteristics, sigma bonding group Au and Ag. [29,30]. From the simulation results it is observed that Pd is more conductive than Pt and Au is more conductive than Ag. While considering the group 11 metals, besides Au, Ag is also a good option to design a molecular switch due to its strong optical enhancement property [31]. and its high catalytic activity for specific chemical reactions [32]. Moreover, Ag is analogous to Au in terms of atomic and electronic structure, and hence measurements that are feasible with Au electrodes should be attainable with Ag electrodes also. [8]. Hence, here proposing the idea of using Ag instead of Au for the traditional design of molecular switch.

Through DFT based calculations in this paper it is shown that molecular switch with Ag electrode junctions conduct through the HOMO orbital. By first principle studies it is examined that Au (111) nano electrode molecular switch junctions have a higher conductance than those formed with Ag, consistent with the work function difference for these two metals. Kim et al found that junctions formed with Ag can be elongated by longer distances than those formed with Au [33] leads to the low junction conductance of Ag. Energy gap between HOMO and LUMO when molecule is insulated and attached to two nano electrodes are examined thoroughly for thiol (-SH), amine (-NH<sub>2</sub>), and carboxylic acid (-COOH) anchoring group. The HOMO-LUMO gap is decreased when the molecular backbone is attached to left and right electrodes as an open system. Noticed the interesting fact that the molecule without electrode has the bandgap energy in the order of straight opposite to that of molecule attached to two nano electrodes. Calculated the values as BDT (5.56eV) > BDA (4.62eV) > BDC (2.57eV). But in literature review, experimental investigations show molecule with electrode has the Bandgap energy in the order BDT < BDA < BDC [34,35].

### 3.5. Contact Geometry

Investigated the key role of contact geometry in determining the “ON” and “OFF” state of a benzene ring based aromatic molecular switch. That means, the same molecular-metal junction can display different conductance values due to the different molecule-metal contact geometry, which generally play an important role in switching characteristics of a molecular switch. This is due to the different coupling strengths with different contact geometry [36]. Different headgroup substrate binding geometry forms different conductance state for a molecular switch. Typically, there are four binding site-substrate geometries have mentioned in the previous research papers both in theoretically and experimentally [37,38]. In this work, when simulated the all four contact geometries, it is noticed that, the top-hollow/hollow-top has medium HOMO-LUMO gap, top-top has high HOMO-LUMO gap, and hollow-hollow has low HOMO-LUMO gap. This result is consistent with previous experimental results [14]. Out of this top-top geometry shows low conductance and it corresponds to the “OFF” state of a molecular switch. It is a molecular junction where both ends sit on top sites of both electrodes. Whereas one headgroup is sitting on the 3-fold hollow site of the electrode and the other end is connected to the top sites is denoted as top-hollow, and it shows high conductance and it corresponds to the “ON” state of a molecular switch. The hollow-hollow geometrical configuration existence is relatively infrequent. The changes in the contact geometry may results in unstable molecule-electrode sandwich structure and that leads to the design of faulty molecular switch. In contact geometry, bond length, bond angle, rotation of angle and axis of molecule are the essential factors while simulation. Interestingly from the DFT studies it is observed that conductance of single molecular switch is directly proportional to the metal molecule interface bond length at contact geometry for all the metal nano electrodes in this work.

#### 3.5.1. Design of BDT, BDA, BDC based Molecular switch with Au, Ag, Pt and Pd

Designed different combinations of molecular switches with BDT, BDA, and BDC using the four metal electrodes Au, Ag, Pt and Pd. All combinations of this molecule with metal nano electrode exhibit two stable geometrical states corresponding to two different conductivity states ON and OFF. Out of these combinations, BDT molecule with Pd shows the characteristics of molecular switch low and high conductance values in accordance with the band gap. When consider the Pd-S junction in a Pd (111)-BDT-Pd (111) molecular switch simulation, it is very much clear that Pd junction shows high switching ratio compared to other electrodes. Furthermore,

it is predicted that the best metal for the design of a benzene derivative molecular switch with thiol anchoring group is corresponds to Palladium followed by Platinum, Silver and Gold. Order is as follows: Pd > Pt > Ag > Au. This is consistent with previous experimental results that the highest junction conductance is obtained for the Pd-S combination than Pt-S, Ag-S, Au-S [39]. The conductance of Pt and Pd are more than  $1G_0$  due to the presence of more than one conductance channel with transmission coefficient smaller than one [40,41]. Interestingly, it is discerned that Palladium -BDT sandwich structure reveals the characteristics of semiconductor bandgap. The band gap for ON is 0.1135 eV and for OFF is 0.1854 eV .The band gap energy has come close to InSb (Indium antimonide).It is a well-known narrow band gap semiconductor material from the group three and five and it is widely used in the infrared (IR) applications like IR detectors, thermal imaging cameras, forward-looking IR (FLIR) systems, IR homing missile guidance systems and IR astronomy.

Table 2. Band gap values for ON and OFF state of BDT, BDA and BDC switches with Au, Ag, Pt and Pd nano electrode.

Molecule	State	Au (111)	Ag (111)	Pt (111)	Pd (111)
BDT	ON	Eg = 0.0557 eV	Eg=0.0343eV	Eg=0.077 eV	Eg=0.1135 eV
	OFF	Eg = 0.063 eV	Eg=0.0675eV \	Eg=0.1399eV	Eg=0.1854 eV
BDA	ON	Eg = 0.0245 eV	Eg=0.0365eV	Eg=0.0942eV	Eg= 0.0079eV
	OFF	Eg = 0.0654 eV	Eg=0.0653eV	Eg=0.0504eV	Eg=0.0457 eV
BDC	ON	Eg = 0.0079 eV	Eg=0.0326eV	Eg=0.0895eV	Eg=0.0010 eV
	OFF	Eg = 0.0266 eV	Eg=0.1116eV	Eg=0.3823eV	Eg=0.0242 eV

Moreover, it is predicted that the best metal for the design of a benzene derivative molecular switch with amine anchoring group is corresponds to Palladium followed by Platinum, Silver and Gold. Order is as follows: Pd > Au > Pt > Ag. This is strictly due do the different lone pair electron interaction of Nitrogen in the amine with different metal electrodes. Hence, it is concluded that for the BDA the electrode selection is purely depends upon the bond strength and stability between lone pair and electrode bond.

Table 3. HOMO, LUMO and band gap energies for ortho, para and meta BDT molecule with Gold, Silver Platinum and Palladium electrode.

Molecular backbone	Au (111)	Ag (111)	Pt (111)	Pd (111)
Ortho BDT	0.003 eV	0.0321 eV	0.1399 eV	0.0297 eV
Para BDT	0.063 eV	0.0675 eV	0.1578 eV	0.0327 eV
Meta BDT	0.099 eV	0.079 eV	0.3061 eV	0.1854 eV

Furthermore, it is predicted, the best metal for the design of a benzene derivative molecular switch with carboxylic acid follows: Pd > Ag > Au > Pt. This is may be due do the bidentate characteristics of carboxylic acid anchor group. It has different affinity with different metal electrodes via two bonding sites.

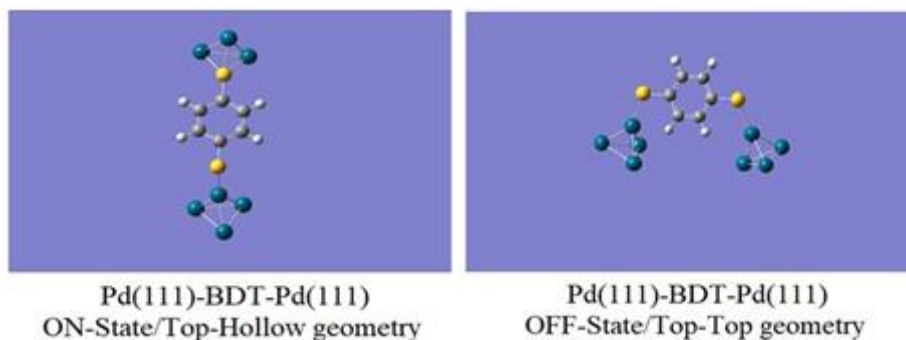


Fig. 1. Model of BDT with Palladium electrode used in the design of BDT based molecular switch.

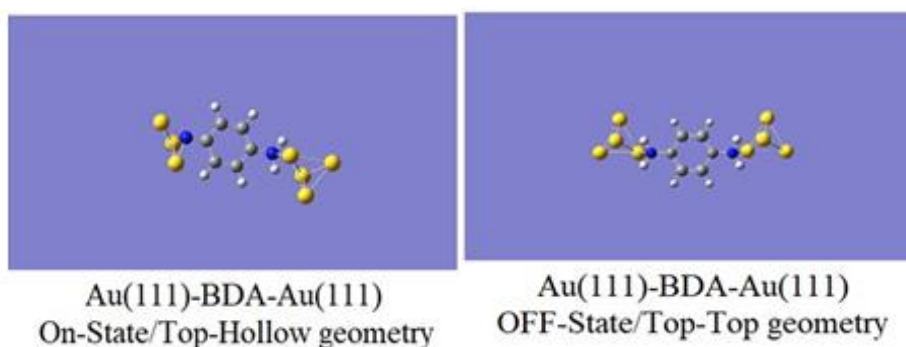


Fig. 2. Model of BDA with Gold electrode used in the design of BDA based molecular switch.

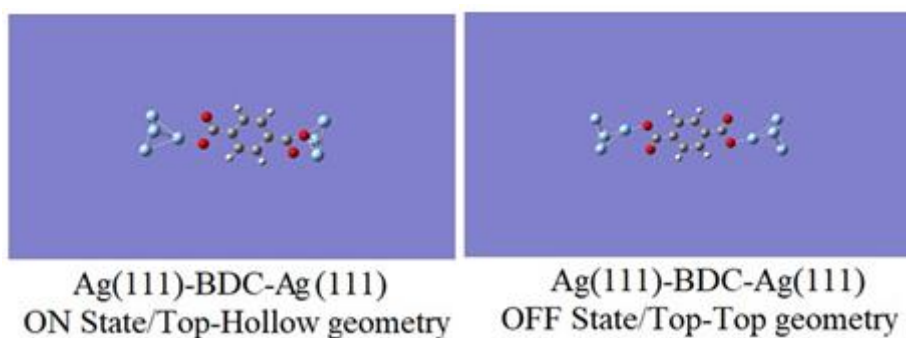


Fig. 3. Model of BDC with Silver electrode used in the design of BDC based molecular switch.

### 3.6. Molecular length dependence in junction conductance of molecular switch

From above mentioned empirical equation, Quantum conductance can be described as  $G = A_N \exp(-\beta_N d)$ . Where  $d$  is the length of molecular backbone. In the tunnelling transport mechanism, an exponential decay of the molecular junction conductance is noticed for molecular length raise. So, in fact for the design of specific molecular device, a shared effect of molecular length, conjugation and a selected anchoring groups are relevant.

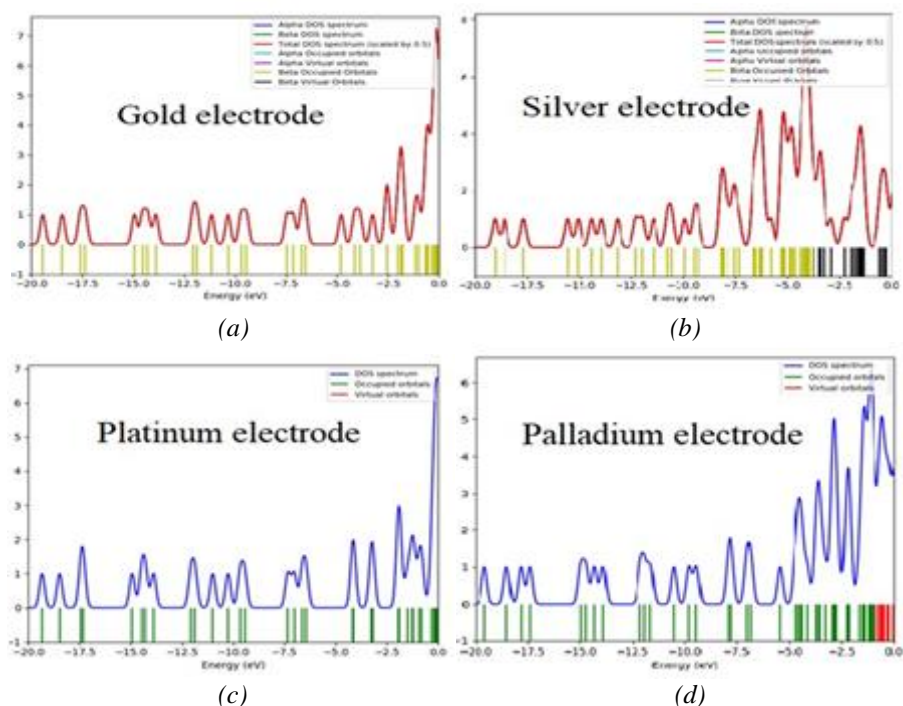


Fig. 4. (a) DOS of BDT based switch with Au (111) for ON State; (b) DOS of BDT based switch with Ag (111) for ON State; (c) DOS of BDT based switch with Pt (111) for ON State; (d) DOS of BDT based switch with Pd (111) for ON State.

The first principles calculation of monophenyl, biphenyl, tetraphenyl, quaterphenyl and quinquephenylene top-top geometry with different metal electrodes Au, Ag, Pt and Pd have done. By varying the number of phenyl rings one can systematically study the molecular length dependence of junction conductance by exploring its HOMO-LUMO gap. The HOMO energy, LUMO Energy and HOMO-LUMO gap values obtained in this work fitted well with empirical equation. Noticed the interesting fact from the DFT study that the molecule without electrode shows the band gap energy inversely proportional to the molecular length, that is monophenyl (5.5576 eV) > biphenyl (2.5868 eV) > tetraphenyl (2.1533 eV) > quaterphenyl (2.1533 eV) > quinquephenylene (1.9891). Monophenyl with Au, Ag, Pt and Pd electrode shows very low band gap compare to another molecule with more than one benzene ring. Hence, the conclusion is when consider the number of phenyl rings for the design of a molecular switch the metal electrodes has no role. But it is observed that the length dependence of quantum conductance is strongly affected by anchoring group. The measured conductance decays exponentially with molecular backbone length with a decay constant that is essentially the same for Au, Ag, Pt and Pd electrodes.



Table 4. Absolute value of ionization energies (I) and Potential energies for designed molecular switches calculated from the simulation.

Molecule	State		Au (111)	Ag (111)	Pt (111)	Pd (111)
BDT I=6.375eV P. E= 0.196 x 10 <sup>-14</sup> Joules	ON	I	0.9883 eV	4.4823 eV	0.7834 eV	0.9709 eV
		P. E	0.996 x 10 <sup>-14</sup> Joules	0.996 x 10 <sup>-14</sup> Joules	0.943 x 10 <sup>-14</sup> Joules	0.975 x 10 <sup>-14</sup> Joules
	OFF	I	1.05 eV	4.5609 eV	1.0484 eV	0.9908 eV
		P.E	1.156 x 10 <sup>-14</sup> Joules	1.16 x 10 <sup>-14</sup> Joules	1.08 x 10 <sup>-14</sup> Joules	1.14 x 10 <sup>-14</sup> Joules
BDA I=5.01Ev P. E= 0.0849 x 10 <sup>-14</sup> Joules	ON	I	1.0936 eV	4.0134 eV	1.0313 eV	1.0528 eV
		P. E	0.945 x 10 <sup>-14</sup> Joules	0.945 x 10 <sup>-14</sup> Joules	0.885 x 10 <sup>-14</sup> Joules	0.885 x 10 <sup>-14</sup> Joules
	OFF	I	1.14 eV	4.040 eV	1.0528 eV	1.0988eV
		P. E	1.07 x 10 <sup>-14</sup> Joules	1.07 x 10 <sup>-14</sup> Joules	0.998 x 10 <sup>-14</sup> Joules	0.998 x 10 <sup>-14</sup> Joules
BDC I=2.57 eV P. E= 0.279 x 10 <sup>-14</sup> Joules	ON	I	1.0139 eV	4.0866 eV	0.6789 eV	0.9907 eV
		P. E	1.11 x 10 <sup>-14</sup> Joules	1.11 x 10 <sup>-14</sup> Joules	1.05 x 10 <sup>-14</sup> Joules	1.05 x 10 <sup>-14</sup> Joules
	OFF	I	I=1.0652eV	I=4.098 eV	I=0.6992 eV	I=1.0158 eV
		P. E	1.21 x 10 <sup>-14</sup> Joules	1.21 x 10 <sup>-14</sup> Joules	1.14 x 10 <sup>-14</sup> Joules	1.14 x 10 <sup>-14</sup> Joules

The bandgap for each series improves exponentially with molecular backbone length for all four metals, with tunnelling decay constants that are not too different on Ag, Pt and Pd compared with Au. This is consistent with previous results that find that, in this tunnelling transport regime with the electrode Fermi energy relatively far from the HOMO,  $\beta$  is generally independent of electrode work function. [7,21]

### 3.7. Role of connectivity site of anchoring group in junction conductance of molecular switch

It is the site on molecular backbone where the anchoring groups are attached to form a bond with electrode. Ortho-BDT (1,2 benzene dithiol), para-BDT (1,4 benzene dithiol), and meta BDT (1,3 benzene dithiol) with Au, Ag, Pt and Pd electrodes were simulated separately for the detailed understanding of conductance with electrode in terms of HOMO-LUMO gap. In this paper the quantum interference (QI) effect in the charge transport through single-molecule junctions has been theoretically investigated for the design of a molecular switch [42]. It is found that the constructive and destructive interference in the charge transport mechanism provides to the design and development of molecular switch with remarkable ON/OFF ratio, proposing a potential implementation of efficient single molecular switching devices. According to the simulated bandgap value, the conductance of BDTs is, Ortho BDT > para BDT > meta BDT. The result is highly consonant with recent experimental results by Yang et al. [43]. Obtained HOMO-LUMO gap in the order Ortho BDT < Para BDT < Meta BDT for Au, Ag, Pt, Pd. Calculated band gap of ortho BDT is 0.003eV, very less compared to all the combination of electrode and BDT given in table. Ortho-BDT with gold electrode only shows the high conductive nature, comparing to other electrodes. Experimental results [42,43] shows Ortho BDT with gold electrode displays high conductivity of  $10^{-1}G_0$ . Among ortho, para and meta BDT it is explored that the ortho BDT is the best suitable molecule and Au (111) is the corresponding electrode for the good junction conduction. Therefore, we are proposing a molecular switch design with ortho BDT and Au (111) for the better result. From Table 3 it is understood that for the design of a molecular switch, the meta BDT is the worst option for all the nano electrodes (Au, Ag, Pt, Pd) considered here. The best option is Ortho and then Para. Regarding best junction conductance of ortho BDT, the order for electrode selection is Au > Pd > Ag > Pt. Similarly, for para BDT the order is Au > Ag > Pt > Pd and for meta BDT order is Ag > Au > Pd > Pt for the high junction conductance of OFF state of molecular switch.

### 3.8. Density of states (DOS) spectrum

DOS delivers the interpretation about the density of charge for various energy intervals along a molecular switch device [44]. Density of states of a molecular switch gets modified with respect to the number and types of benzene rings present in the molecular backbone. However, the density of charge varies in molecular switch between ON and OFF states. When the coupling strength with the electrode is good enough, then DOS of that particular molecule-electrode combination gets modified by the broadening and shifting of the discrete energy levels of a molecule. That will obviously lead to the increment in junction conductance. Hence broadening can be determined by the coupling interaction between the molecular backbone with its two metal nanoelectrodes. Whenever electron orbitals are converging, the DOS becomes wider and higher and that directs to more conduction the density of energy is observed to be more along the gold electrode regions due to its metallic nature (the swirls in the DOS spectrum shows higher electron density). [45] But, in the molecular backbone the density of electrons is found to be low. Since the molecule-anchoring group combination is bonded with Au, Ag, Pt, Pd electrodes through different atoms, the density of charge varies in different region. Moreover, metal electrodes have high atomic number the density of states is found to be more rather than the molecular backbone, which comprises of hydrocarbons in the middle portion of molecular switch.

### 3.9. Ionization potential and Potential energy

Theoretically, whenever the ionization potential of a molecule decreases the conductivity of that molecule increases, and whenever the potential energy of a molecule increases, stability of that molecule decreases [46]. By applying the Koopmans' Theorem, the ionization potential is seen to be the negative value of HOMO energy of that particular molecular device. [11] From the Table 4 it is understood that top-hollow (ON) geometry shows high conductance compare to top top geometry and ON State geometry (or Top-Hollow) is more stable than the OFF-State geometry (or Top-Top) for every combinations of metal electrodes selected in our work. BDT molecule in ON state with Pt electrode shows top stability compare to other electrodes. For BDA and BDC Pt and Pd sandwich structures have high stability whereas Au and Ag electrode have less stability. As

a conclusion from our DFT method study it is examined that BDC is not a good option for designing the molecular switch because of its stability less nature to exist. Good options are BDT and BDA. Also, Simulation results indicate, slightly higher conductivity and better stability for ON state of molecular switch than OFF state.

#### 4. Conclusion

Molecular switches with 1,4-benzene dithiol (BDT), 1,4-benzene diamine (BDA), and 1,4benzene dicarboxylic acid (BDC) with gold, silver, platinum and palladium electrodes have been designed for both top-hollow (ON) and top-top (OFF) state separately. The electronic properties of the designed molecular switch, electrode-anchoring group-molecular backbone combinations are investigated using density functional theory (DFT) method. It is noticed that the selection of base functions, bond lengths and angles is critical to get a geometrically optimized molecular switch. A series of benzene derivatives to explore the physical behaviour of conductance interpret in terms of nature of molecular backbone, anchoring group, contact geometry, nature of electrode material, molecular length, connectivity site, DOS, HOMO-LUMO gap, ionization potential and potential energy were systematically studied and compared.

According to our results for the design of a benzene derivative molecular switch, the best anchoring group is thiol (-SH), even though it is not much better than amine (-NH<sub>2</sub>) and the worst anchoring group is carboxylic acid (-COOH) in terms of junction conduction, stability, and coupling strength. It is explored that to design a molecular switch with high switching ratio, Pd is the best electrode comparing to Au, Ag, Pt and the length of the molecular backbone should be minimum for the design of high junction conductance molecular switch. But Gold is the most extensively used nano electrode material owing to its intense mobility, high conductivity, and excellent fabricability, chemically inertness and so easy to work with under ambient conditions. Among ortho, para and meta BDT, ortho BDT is the best suitable molecule and Au (111) is the corresponding electrode for the design of an efficient molecular switch in terms of junction conductance. Observed slightly higher conductivity and better stability for ON State of molecular switch than OFF state.

The results in this paper are broadly consistent with the previous experimental results. Zero bias conduction can be predicted by first principle study, but the precision of prediction hangs on the adsorption structure, nature electrode material, anchoring group, and the correctness of electronic structures estimated by density functional theory method.

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