Coulomb Blockade and Single Electron Charging in DNA Bases

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ABSTRACT
To achieve the Coulomb blockade, three criteria have to be met: Bias voltage shouldn't exceed the charging energy; Thermal energy k_BT (≈0.026eV) must be below the charging energy and the tunneling resistance should be higher than the resistance quantum (h/e^2). The DNA base molecules Adenine (A), Cytosine(C), Thymine (T) and Guanine (G) were studied for the above conditions to verify their suitability to use in room temperature single electron devices. Charging energies or junction barriers as {LUMO- μ} and {μ - HOMO} for electron and hole transfer respectively are calculated using HF/STO-3G. The order for charging the bases for electron transport is A (0.65eV) < C (0.87eV) < G (0.95eV) < T (1.11eV) and for hole transport G (11.67eV) < C (11.92eV) <A (12.11eV) < T(12.57eV). Choosing bias voltages less than the charging energies, V-I characteristics are obtained using Virtual Nanolab showed that G and A displayed linear curves with resistance of $1.04x10^6$ kΩ and $4.3x10^6$ kΩ while T had resistance of $3.1x10^2$ kΩ when a voltage sweep of 0 - 0.5 V is applied. Cytosine exhibited the large resistance ($6.2x10^6$ kΩ) for the potential 0-0.4V which suddenly reduces to 17.8kΩ representing single electron transfer at 0.4V.

Keywords
Coulomb blockade; tunneling resistance; energy level diagram; molecular electronics; DNA bases; V-I characteristics.

1. INTRODUCTION
Molecular electronics using bio-molecules is one widely studied area in the pursuit of high speed, high density, low power consuming and low cost molecular devices. The main advantage of molecular devices over the semiconductor devices is that heat dissipation is negligible. This is due to the fact that the scattering process in such devices is elastic that gives rise to loss of momentum but no loss of phase. The idea of using organic molecules as electronic circuit component has been proposed back in 1974 where they theoretically proposed rectification in Donor-Acceptor system separated by saturated organic bridge [1]. Organic molecules, which can mimic the wire function, are the π-type systems, where electron transfer takes place through the backbone of fully delocalized π-bridges, and consequently energetically closely spaced frontier molecular orbitals (reduced HOMO-LUMO gap or in short, HLG) are the conduction channels. Due to very small HLG, the process is thermodynamically favorable and ultimately gives rise to efficient wire function [2-4]. Similarly, the molecules having the presence of the saturated –CH2- units can create nodes in their electron densities above the atomic nuclei. For this reason and also due to large HLG, they cannot transport electrical current. This enables aliphatic molecules or groups to act like resistors [5-6]. Starting from the Aviram-Ratner rectifier [1] to today's most widely studied rectifiers [5,7] the common construction principle of organic molecular rectifier adopted is still the same i.e. donor –bridge-acceptor system.

Coulomb blockade and high bias staircases play a crucial role in transport through single small molecules. Ben Jacob et. al. in 1998 proposed a single electron transistor from DNA strand with the understanding that chemical bonds can act as tunnel junctions in coulomb blockade regime [8]. Single electron tunneling transistor and a quantum bit elements have been explored with an assembly of two DNA grains (Sugar + base) connected through a phosphate bridge.

In this paper we are proposing an entirely different approach to use DNA bases Adenine(A), Guanine(G), Cytosine(C) and Thymine(T)) as molecular devices, where we placed DNA bases individually between the electrodes and characterize them for charge conduction. The characterization of these bases would in addition help in locating the appropriate operating point which can help in precise identification of DNA sequence by analyzing the flow of tunneling current through the bases. Recently, DNA sequencing technique has been demonstrated which is based on measurement of electron transfer through DNA nucleotides [9]. DNA bases by virtue of their unique property of self assembly, self replication [10] and their stability at high temperature and humidity can make them the master components for the molecular devices. With the interest the energy level diagrams and Current voltage characteristics are constructed for all the bases. The substantial HLG of the DNA bases accounts for the barrier to the charge transport. This barrier can be approximated as {μ - HOMO} or {LUMO- μ}, where μ is the work function of the metallic contact. The barrier values thus calculated revealed that we can find coulomb blockade in above DNA bases. The typical pattern of energy level shifting, quenching of HOMO-LUMO gaps on single electron charging corresponded to anionic and cationic states of the bases suggested coulomb oscillations in the device[11]. The V-I plots are generated with two probe setup of Virtual Nanolab to characterize the DNA bases for device application.

2. METHODOLOGY
The molecular structures of the four DNA bases were created using HYPERCHEM 7. The backbone of the bases was removed from the molecule and the bond was terminated with a hydrogen atom. The molecular structures thus obtained were optimized using HF/STO-3G in Gaussian 03 program. The energy levels of the occupied and unoccupied molecular orbitals were obtained for the optimized structures to calculate the HOMO-LUMO gaps for each of the four molecules.

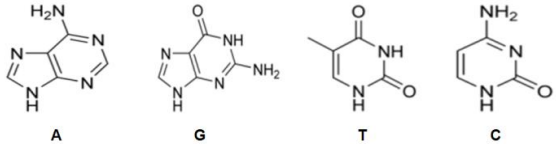

Fig 1: Structure of DNA bases Adenine (A), Guanine (G), Thymine (T) and Cytosine(C)

The current-voltage characteristics are calculated by inserting the DNA bases between two gold terminals in the two-probe setup of Virtual Nanolab software using double zeta polarized basis set.

Table 1. HUMO-LUMO Gaps for DNA bases Guanine (G), Adenine (A), Cytosine (C), Thymine (T)

Bases	HOMO	LUMO	HLG(eV)
Guanine	-6.17	6.44	12.62
Adenine	-6.61	6.15	12.76
Cytosine	-6.42	6.36	12.78
Thymine	-7.07	6.61	13.68

3. RESULTS AND DISCUSSIONS

3.1 Energy Level Diagram

To formulate the molecular devices the foremost task is to draw the energy level diagram. Energy level diagrams were obtained for neutral, anionic and cationic states of each base to understand the participation of energy levels for the charge conduction at room temperature. Energy levels as sketched below in Fig. 2 were obtained with Gaussian 03W program. Filled orbitals are represented by dark bold lines and empty orbitals by grey.

HOMO-LUMO Gaps (HLG) of four DNA bases Adenine, Thiamine, Guanine and Cytosine were obtained as summarized in Table.1. Since, the HLGs for all the bases is quite large as compared to the thermal energy (~K_BT =0.026eV) at room temperature (300K), all the bases are suitable for their use in room temperature electronics. Further analysis was carried out on ionic states of DNA bases by adding and removing an electron on the molecule. If we assume that Electron conduction is through LUMO and hole conduction is through HOMO. Hence when an electron is added to the molecules the energy levels of the MOs are elevated (Fig..2.) and thus LUMO are raised to quite high energy(>>k_BT) that results in formation of a larger barrier height as LUMO moved farther from the electrochemical potential level of the metallic contact μ. The process is well depicted in the Fig.2. for all the four bases , where addition of electron is represented by -1 state to the left of neutral (0) state and similarly addition of another electron (-2 state) further enhances the barrier height. Along with the increase in barrier height for LUMO the HLG gap shifts from N to (N+1)th state with reduced gap which aligns the occupied MOs with the Fermi level of the contact. Hence the coulomb blockade is washed out as the lower states come in resonance with the electrochemical potential of the electrode. Alternatively considering the cationic states, it is observed that energy level spectrum is shifted downward leading to the formation of coulomb well, as some of the unoccupied MOs are lying below the electrochemical potential. Therefore electron can very easily fall into the energy levels of the molecules on making contact with electrode. If these anionic and cationic states are related to single electron charging through gate bias then this phenomena can be compared to coulomb oscillations.

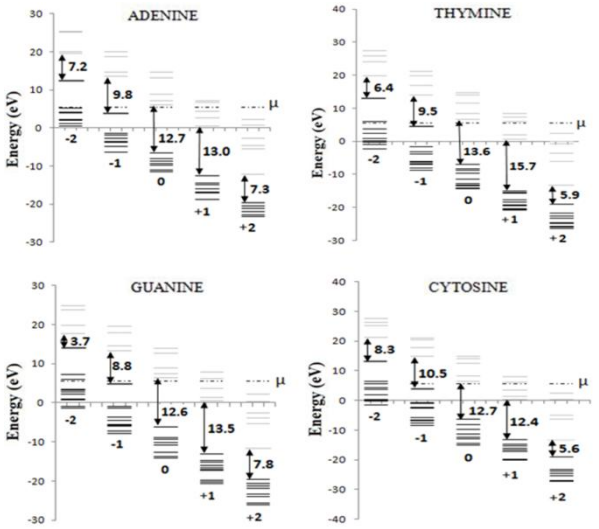

Fig 2: Energy level diagrams for the DNA molecules

Table 1. HUMO-LUMO Gaps for DNA bases Guanine (G), Adenine (A), Cytosine (C), Thymine (T)

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3.2 Electronic conduction through the molecule

When the molecule is placed between the metallic contacts e.g. gold, without applying the bias voltage and the contacts are coupled (Chemisorbed or adsorbed) to the base, the electrons flow in and out of the device bringing them all in equilibrium with a common electrochemical potential μ. In this equilibrium state the average number of electrons in any energy level is typically not an integer, but is given by the Fermi function:

$$f_0(E-\mu) = \{1+\exp[(E-\mu)/K_BT]\}^{-1} \quad (1)$$

The electrochemical potential for the Gold contact is 5.5eV. Energy levels far below the μ are always filled so that f_0 =1, while energy levels far above μ are always empty with f_0 =0. Energy levels within a few K_BT of μ are occasionally full and occasionally empty so that the average no. of electrons lies between 0 and 1: $0 \leq f_0 \leq 1$, and these are the levels which participate in conduction and current flows.

Now current flow under bias will depend on the number of energy levels available around E= μ. It does not matter whether the energy levels are occupied or empty [12]. And if the empty levels are available near E= μ it will make the molecular device n-type and if filled levels are in close proximity then it will act as p-type. From the Table.1. it is clear that in all the bases LUMO is located closer to the electro chemical potential (μ) of the contacts which is 5.5eV for gold and 5.36eV for platinum. Hence all can act as n-type devices.

The threshold voltage needed to turn the device ON is thus determined by the energy level difference between electrochemical potential μ and the lowest available empty state. These values can also be termed as junction barriers of the gold-base junction and can be taken as the energy level difference between electrochemical potential μ and the available state (unoccupied or occupied i.e. LUMO or HOMO for the molecules), Δ written as;

Δ_e = LUMO- μ for electron transport

Δ_h = μ- HOMO for Hole transport

The values of Δ_e and Δ_h are calculated for gold (μ = 5.5eV) and platinum (μ = 5.36eV) tabulated as below in Table 2.

Table 2. Barrier heights for electron and hole transport for DNA bases

Bases	Δ_e = LUMO- μ		Δ_h = μ- HOMO	
	Platinum	Gold	Platinum	Gold
G	1.08	0.95	11.53	11.67
A	0.79	0.65	11.97	12.11
C	1.00	0.87	11.78	11.92
T	1.25	1.11	12.43	12.57

From Table 2, it can be concluded that if a potential of -0.95V (which is a threshold for electron transport) is applied across Guanine with gold contact, charge will be able to overcome the junction barrier. Similarly, threshold of A, C and T are - 0.65V, -0.87V and -1.11V respectively. If we compare the values, order for charging or triggering the molecule for electron transport is A (0.65eV)< C (0.87eV)< G(0.95eV)< T (1.11eV). Further, for hole transport Threshold potential for G (11.67eV)< C (11.92eV), A(12.11eV)< T(12.57eV). This is in accordance with the fact Guanine also is the locus site for hole transport [13]. If the Gold electrodes are replaced by platinum electrodes then these junction barriers are shifted according to its chemical potential as obvious from the Table. 2. Δ_e is enhanced while Δ_h is reduced when compared with gold for all the Bases.

While it is important to mention here that if the sum of thermal energy K_BT and the energy from voltage supplied is not enough to overcome the barrier the current will be blocked representing the coulomb blockade. Hence, at zero bias the charging energies for all the bases are much larger than the thermal energies at room temperature satisfying the second condition for coulomb blockade.

3.3 V-I Plots

To study the current voltage characteristics the DNA bases are placed between two gold electrodes one as source and other as drain. The positive voltage V_S is applied at source fixing the drain potential V_D at 0V. This potential difference will maintain them at distinct potentials i.e.

$$\mu_2 - \mu_1 = qV_S, \quad (2)$$

giving rise to two different Fermi functions :

$$f_1(E) = f_0(E-\mu_1)=\{1+\exp[(E-\mu_1)/K_BT]\}^{-1}, \quad (3)$$

$$f_2(E) = f_0(E-\mu_2)=\{1+\exp[(E-\mu_2)/K_BT]\}^{-1}, \quad (4)$$

Each contact seeks to bring the channel into equilibrium with itself. The quest to achieve equilibrium causes the current to flow from source to drain.

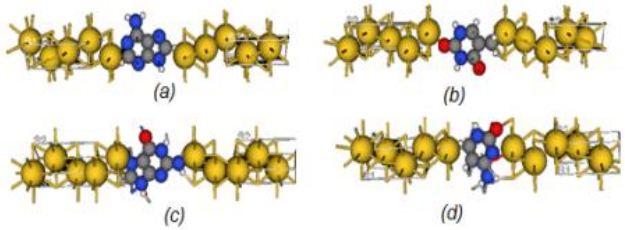

Fig 3: DNA Bases inserted between gold terminals (a) Adenine (b) Thymine (c) Guanine (d) Cytosine.

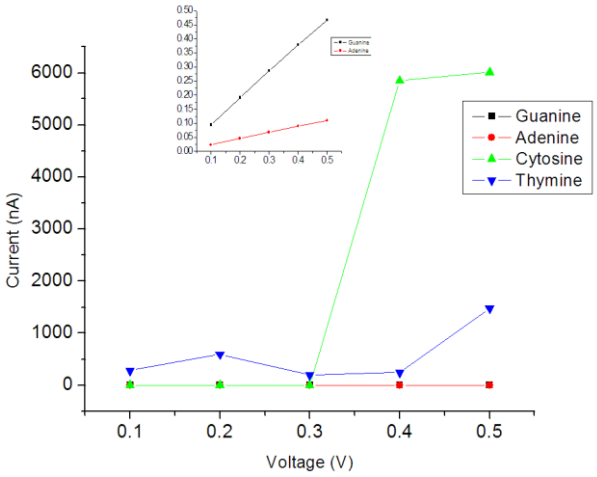

Fig 4: V-I plot for all bases (V= 0-0.5V). Cytosine shows sudden electron conduction at 0.4V displaying ON –OFF switching characteristics. Nanaoscale variation for Adenine and Guanine from 0-0.3 V is shown in Inset which is Ohmic

These DNA bases were inserted between two gold terminals in the two probe setup of virtual nanolab software with the contact arrangement shown in Fig. 4. The molecules are chemisorbed onto the electrodes, and the above orientation is fixed, although these molecules being asymmetric, the Current voltage characteristics will be varying greatly with orientation. A voltage bias V_S varying from 0-0.5V was applied to the four respective bases and the corresponding current values are plotted as in Fig. 5.

Close scrutiny of the graph reveals that the magnitude of current flow through Adenine and Guanine is in the nA range as shown in inset of Fig.5. While Cytosine also follows the trend of nA current till current suddenly rises to μA for an applied voltage of 0.4V and maintains the large value of current at 0.5V also. In comparison Thymine maintains its characteristics at 0.1 μA through out the voltage range till 0.4V where a sudden increase of 10fold is observed. From the V-I plots we can broadly classify the DNA bases to be used in two domains: nA Range and μA range, DNA bases G and A (double ring structures; purines) are covered under nA range and C & T (single ring structures; pyrimidines) are covered under μA range. Further, it is interesting to mention that small currents through smaller cross section give very large current density whenever charge is transferred through it and in case of molecule it does not matter how small the currents are, current densities are going to be large as the size of the molecular device is very small. Recent study by Tsutsui et. al.

[9] has experimentally demonstrated flow of current in pico ampere range where the applied bias is varied from 0.25-0.75V when DNA bases are passed through a nanoprobe, the difference may be understood in terms of backbone effects. Adhering to the current based classification, V-I characteristics are interpreted separately in each domain for the respective bases.

3.3.1 Nano-scale current domain; double ring structures

Fig.5. revealed that the two double ringed DNA bases Adenine and Guanine display current conduction in the range of nA on applying voltage varying from 0-0.5 V which was further extended to 1.5V to identify any significant changes in the pattern of the characteristics (Fig.6.). The linear characteristics upto 1.2V of both the molecules Adenine and Guanine suggest electron tunneling offering a consistent resistance of 4.3 $x10^9$ and 1.04 $x10^9$ ohm respectively. This also means that Guanine has comparatively larger conductivity. This difference in the resistance can be accounted due to the presence of doubly bonded oxygen on Guanine enriching the π-electron cloud. Further, increase in voltage (upto 1.5V) leads to the saturation of current. The characteristics of these molecules predict them to be used as high resistance linear devices.

3.3.2 Micro-scale current domain; single ring structures

The magnitude of current flowing through single ring DNA bases Cytosine and Thymine is much larger than that in the A and G bases. For small values of voltage Cytosine offers a large resistance which results in a nanoampere current (as shown Inset of Fig. 7). When the voltage is increased the resistance suddenly vanishes at 0.4V. This leads to a flow of a very large current in microampere range. The behavior of the cytosine molecule typically depicts ON/OFF type of switching. As the ratio of current change is of the order of 10^5, Cytosine offers excellent opportunities for its use in digital electronics as switches or memory devices. Moreover nanoscale variation is shown in inset of Fig. 7 is also ohmic for Cytosine. Thymine displays very less resistance as compared to other DNA bases. The current is in the order of microampere range for the various applied voltages. Further we calculated the resistances for all the four bases and these are listed in TABLE 3. It is seen that magnitude of resistance is much larger than Quantum resistance (h/e^2=26kΩ) which satisfy the criteria for single electron tunneling.

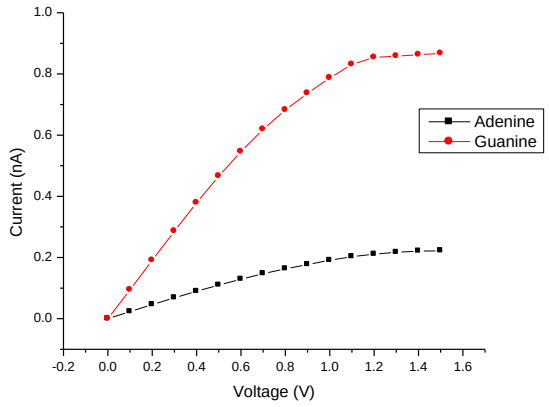

Fig.5. V-I Plots for Guanine and Adenine show constant resistance with saturation at 1.2 V

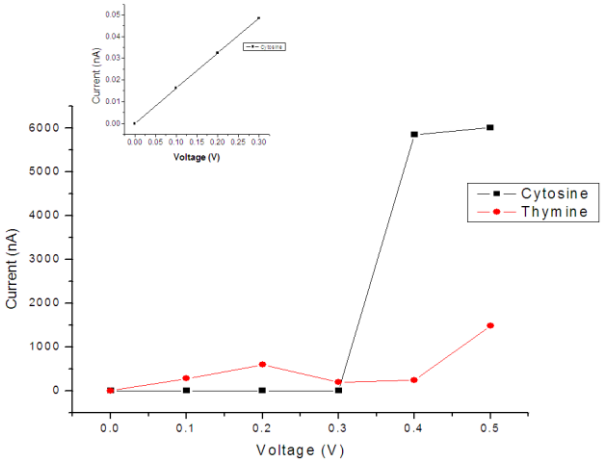

Fig 6: V-I Plot for Cytosine and Thymine. Thymine has very less resistance among all the bases and Cytosine has high bias staircase in micro ampere range. Nanoscale variation from 0-0.3 V for cytosine is shown in inset which is ohmic in nature.

Table 3. Resistance of Guanine (G),Adenine (A) Cytosine(C) &Thymine (T), calculated from the linear slopes of V-I characteristics

DNA Bases	Tunneling Resistance in KΩ
Guanine	$1.04x10^6$
Adenine	$4.3x10^6$
Cytosine	$6.2x10^6$ for OFF state 17.8 for ON state
Thymine	$3.1x10^2$

It is observed that DNA base Cytosine has the highest resistance among the four bases which suddenly falls to 17.8 kΩ at 0.4 V which further rises to high value of $6.25x10^2$kΩ forming a high bias staircase. The decrease can be attributed to single electron transfer in the conduction channel. Similarly Adenine and Guanine also exhibit large values of resistance satisfying the third condition for formation of coulomb blockade. DNA base Thymine offers a resistance of $3.1x10^2$kΩ resulting in flow of large tunneling currents.

4. CONCLUSION

Coulomb blockade is a unique phenomenon of molecular devices which appears when bias voltage and thermal energy are much below the charging energy, tunneling resistance is much higher than the resistance quantum. DNA bases are studied in terms of energy level diagrams for Junction barriers or charging energies. The order for charging or triggering the molecule for electron transport is A (0.65eV)< C (0.87eV)< G(0.95eV)< T (1.11eV) and for hole transport threshold potentials for G (11.67eV)< C (11.92eV), A(12.11eV)< T(12.57eV). These are much higher than the thermal energy (~K_BT =0.026eV) and suggests room temperature single electron effects. Choosing the bias voltage of 0-0.5V less that charging energies, all the bases have been characterized for the current flow through them. The molecule G and A displayed linear curves with resistance of $1.04x10^6$ kΩ and $4.3x10^6$ kΩ while T had comparatively very small resistance of $3.1x10^2$ kΩ when a voltage sweep of 0 - 0.5 V is applied.

The fourth DNA base C exhibited a typical characteristic in which the large resistance of the molecule ($6.2x10^6$ kΩ) for the potential 0-0.4V suddenly reduces to 17.8kΩ representing single electron transfer at 0.4V. Comparing the tunneling resistances with resistance quantum(~26KΩ), all the bases are satisfying the third condition for coulomb blockade except Cytosine for which resistance suddenly falls 17.8 kΩ (< 26 kΩ) showing single electron effects 0.4V. Resistance further rise to high value as the voltage is increased, so high bias staircase is expected. It has been concluded that all the bases showed tunneling and the amount of current varies from nA for purines (A & G) to μA for pyrimidines (C & T) depending on their double and single ring structures.

Further, characteristics can be taken for these bases by taking various orientations and directions to study the asymmetry in the characteristics but this is not covered in this paper. In addition, the performance can be altered by applying third terminal to the two probe setup acting as gate to verify single electron effects as suggested by energy level diagrams for anionic and cationic states.

Finally, it is inferred that four DNA bases G, A, C &T can be used in molecular electronics for various applications. G&A can be used as high resistance linear devices. T can be used in large current domain applications. Cytosine exhibits the typical graph which renders it for suitable for use in digital circuits.

The distinct electronic properties of four DNA bases combined with their self assembly and selectivity properties can be explored for next generation electronic devices and molecular sensors.

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