Comparative study of symmetrical and asymmetrical B$_{40}$ molecular junctions

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Received: 6 July 2021 / Accepted: 17 February 2022 / Published online: 24 March 2022 © The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2022

Abstract
This work investigates quantum transport in symmetrical and asymmetrical borospherene-based molecular junctions with adenine. Adenine is one of the four nucleobases of DNA and was selected because of its excellent transport properties. The density functional/non-equilibrium Green's function (DFT-NEGF) mathematical approach was utilized, which was further used to calculate quantum transport parameters including the I–V curve, transmission spectra, highest occupied molecular orbital (HOMO)–lowest occupied molecular orbital (LUMO) gap (HLG), differential conductance, and transmission pathways. We observed that both symmetrical and asymmetrical B$_{40}$ molecular devices exhibit nonlinear behavior, thus leading to non-differential resistance. Also, the symmetrical B$_{40}$ molecular device demonstrated reduced HLG relative to the asymmetrical B$_{40}$ molecular device. This drop in HLG was due to a reduction in electron density. A high rectification ratio for the devices was observed at 0.2 V. Hence, symmetrical and asymmetrical B$_{40}$ molecular junctions are potential candidates for use in future nanoscale devices.

Keywords  Borospherene (B$_{40}$) · DNA · Transmission pathways · HOMO–LUMO gap · Negative differential resistance · Nanoelectronics

1 Introduction
Over the past four decades, increasing developments in the field of science and technology have completely changed the industry. “There’s plenty of room at the bottom,” an acclaimed lecture by Feynman [1], paved the way for nanotechnology, and many researchers have shown their curiosity in this field. Thus, over the years in the field of electronics, researchers have investigated the use of single molecules in devices. There have been many kinds of studies related to single molecular devices, but utilization of B$_{40}$ with DNA is another promising candidate for molecular electronic applications.

Deoxyribonucleic acid (DNA) was first isolated by Friedrich Miescher in 1869, but its value for electronic applications was not anticipated for many years. Extensive research has shown that DNA exhibits good conductivity, and researchers have investigated how the charge is transferred [2]. DNA is composed of a long wire-like structure formed by four nucleobases, i.e. adenine (A), guanine (G), thymine (T), and cytosine (C). Furthermore, it has been proved that by changing the length of DNA, its conductance can be varied. In addition, when formulating devices using DNA, the electrode material, nucleotide content, and Miller indices orientation have strong effects on the properties of the device [3–5]. The DNA molecule has the unique ability to duplicate itself, and thus it can be applied to develop molecular electronic devices. Cytosine and guanine nucleobases of DNA have also been examined individually [6]. The comparative study of the two nucleobases reveals excellent conductive properties in the case of cytosine, whereas guanine exhibits exceptional non-differential resistance (NDR). Borospherene (B$_{40}$) is another emerging material in the field of molecular electronics. In 2014 Zahi et al. discovered a highly stable B$_{40}$ molecule [7]. A comparative study was conducted by He et al. between B$_{40}$ and other boron clusters, and it was
deduced that B₄₀ exhibits strong absorbing capability [8]. Further research revealed that the borosherene cage encompasses two hexagons, one at the top and the other at the bottom, alongside four heptagons positioned at the sides [9]. Wang et al. analyzed the properties of B₄₀ by positioning the transition metals inside the fullerene cage. Mn, Fe, Co, and Ni were encapsulated, and it was determined that M@B₄₀ (M = Fe and Mn) was spin-polarized, whereas Ni-encapsulated fullerene remained unpolarized [10]. Borospherene has shown its capability as a sensor for the detection of various toxic gases due to the presence of both acidic and basic sites [11]. Kaur et al. utilized the chalcogen family elements with B₄₀ to investigate its electronic transport properties [12]. Maniei et al. used a lithium-doped variant in B₄₀ fullerene in order to capture NO₂ [13]. Although much research has already been conducted in the field of molecular electronics based on borospherene (B₄₀) and DNA, the two materials have not been investigated together in a single molecular device as symmetrical and asymmetrical junctions.

In the present study, the transport properties of symmetrical and asymmetrical B₄₀ molecular junctions are investigated. Adenine (A) (C₅H₅N₅) is used due to its excellent properties in comparison to other nucleobases of DNA [14]. Adenine with B₄₀ is used in the molecular junction. We aimed to study various properties of B₄₀ fullerene with adenine. The transmission spectra, electron density, highest occupied molecular orbital (HOMO)–lowest occupied molecular orbital (LUMO) gap (HLG), and transmission pathways were examined. Figure 1 depicts both the asymmetrical and symmetrical devices, where blue atoms are nitrogen atoms, gray atoms are carbon atoms, white atoms are hydrogen atoms, and yellow atoms are sulfur atoms that act as linkers.

2 Methodology

DNA is a nano-molecule recognized as a material for use as molecular wire. It is an organic molecule that has the characteristics of self-replication. Thus, it becomes necessary to individually study the bases of DNA, and in this paper, we focus on adenine. The investigation was done by forming asymmetrical and symmetrical devices. For the first case, an asymmetrical device was formed with adenine and B₄₀, whereas a symmetrical device was formed by placing adenine on both sides of B₄₀ fullerene. For the formation of the device, the adenine and B₄₀ were sandwiched between two gold (Au) electrodes with sulfur as linker atoms [15].

All of the modeling and simulations were implemented using the Atomistix ToolKit interfaced with VNL software (ATK-VNL) [16]. Density functional theory (DFT) in association with non-equilibrium Green’s function (NEGF) was employed [17–20]. Gold is the most favorable material for electrodes because of its high stability at room temperature. The assembled device comprises three regions: the left electrode, right electrode, and scattering region. A double-zeta polarized basis set (DZPS) was employed for both devices, and the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA) was selected as a correlational function [21]. The orientation of the electrode was chosen to be <1, 1, 1>, and the length of the electrode was taken as 7 Å [22, 23].
The I–V (current–voltage) curve can be determined by imposing the Landauer–Büttiker formalism [24]. The formalism anticipates the relation between applied voltage and current, with the help of transmission probability \(T(E, V)\):

\[
I(V) = \frac{2e}{h} \int_{\mu_L}^{\mu_R} T(E, V) \left[ f\left(E - \mu_L\right) - f\left(E - \mu_R\right) \right] dE
\]  

(1)

In Eq. (1), \(T(E, V)\) represents the transmission function, and \(\mu_L, \mu_R\) represent the electrochemical potential of the left and right electrodes. The transmission function can be determined from the information about the portion of coupling between the electrodes and the molecule and the molecular energy level. The transmission was envisaged similarly [25]:

\[
T^k(E, V) = \Gamma_r \left[ \Gamma^k_1(E, V) G^k_M(E, V) \Gamma^k_{1L}(E, V) G^k_M(E, V) \right] \Gamma_L
\]  

(2)

In the above Eq. (2), \(\Gamma(E)\) demonstrates the coupling function which provides adequate information about the type of contact between the molecule and electrodes, and \(G_M(E, V)\) represents Green’s function. Suppose that the energy levels of the molecule are assumed to float towards a higher level with a value \(eV_{\text{mol}}\) which is proportional to the molecule’s electrostatic potential. In addition, it can be supposed that the energy levels of the molecules are fixed, while the substrate is assumed to float towards a lower level by an amount \(eV_{\text{mol}}\). Hence, for the two metallic electrodes, the electrostatic potentials can be represented as [26]:

\[
\mu_L = E_F - eV_{\text{mol}} = E_F - \eta eV
\]  

(3)

\[
\mu_R = E_F + eV_{\text{mol}} = E_F + (1 - \eta)eV
\]  

(4)

In Eqs. (3) and (4), \(E_F\) represents the equilibrium Fermi energy, \(e\) denotes the electron charge, and \(\eta\) denotes the distribution of the potential difference between the electrodes. It can be defined as \(\eta = V_{\text{mol}}/V\) [24, 25].

The transmission pathways can be utilized to investigate the flow of electrons in molecular junctions. They divide the transmission coefficient into local bond contribution, \(T_{ij}\). The pathways have the ability to split the system into two parts \((A, B)\), and then the pathways are all over the boundary between \(A\) and \(B\), summing up to the total transmission coefficient [27]:

\[
T(E) = \sum_{iA,jB} T_{ij}(E)
\]  

(5)

Table 1: HOMO, LUMO, and HLG

| Device    | HOMO   | LUMO   | HLG    |
|-----------|--------|--------|--------|
| A-B\(_{40}\) | -0.6881377 | 0.1159547 | 0.8040924 |
| A-B\(_{40}\)-A | -0.2107773 | 0.2594467 | 0.470224  |

3 Results and discussion

3.1 Quantum transport under equilibrium

The transmission spectra at 0 V are analyzed for both adenine-based molecular junctions. The arrangement of molecular orbitals along with the extent of coupling between the metallic leads is examined by exploring the transmission spectra at equilibrium. The transmission spectra explain which molecular orbitals are responsible for transmission along with the HOMO–LUMO gap. From Fig. 2 it can be seen that for adenine-B\(_{40}\)-adenine, the peak is closer to the Fermi level for negative bias voltage, signifying the dominance of LUMO orbitals in transmission. In the case of adenine-B\(_{40}\)-adenine, the peaks are closer to \(E_F\) for positive bias, signifying the dominance of LUMO orbitals in transmission.

The molecular energy spectrum of both devices at 0 V is also considered. The HOMO, LUMO, and HOMO–LUMO gap (HLG) of the devices are as tabulated in Table 1. From the table, it can be deduced that for the device in which adenine is placed on both sides of the borospherene, the HLG decreases in comparison to the device in which adenine is placed only on one side of the borospherene. The HLG for adenine-B\(_{40}\) is 0.804 eV, whereas for adenine-B\(_{40}\)-adenine it is 0.470 eV.
3.2 Quantum transport under non-equilibrium transport

To further investigate the quantum transport for the adenine-based molecular junction, the transport properties under non-equilibrium conditions were determined. In this context, transmission spectra were analyzed at various biases ranging from −1 to +1 V with a step size of 0.2 V. Figure 3 depicts comparative graphs for the two devices. In the case of adenine-B₄₀, the intensity of the peaks is higher and very close to the Fermi level, indicating the effortless flow of electrons from the left to the right electrode. For adenine-B₄₀⁻adenine, Figure 3 Transmission spectra at various voltages
a large number of peaks can also be seen, but with lower intensity and having sharpness in the peaks, which reveals that there is lower transmission between electrodes. Also, with the variation in applied bias, there is shifting of peaks, thus implying that with change in bias, the states engaging in conduction also change.

Also, from Fig. 3, a comparison was done between transmission at all the negative and positive biases. For the transmission spectra at −1 V, the adenine-B_{40} device has more peaks, which indicates higher transmission, and the adenine-B_{40}−adenine has fewer peaks, and sharp peaks can be seen, which indicates lower transmission. In contrast, for the positive bias at +1 V, the intensity of transmission further decreases for both devices. When the rest of the biases are compared for the negative bias, transmission is greater than the transmission at positive bias, which corresponds to the results of transmission spectra at −1 V and +1 V.

Along with other parameters, the current–voltage (I–V) curve was investigated. From Fig. 4, it can be seen that for adenine-B_{40}−adenine, the current is lower relative to the adenine-B_{40} device. Adenine-B_{40} shows symmetrical behavior for both positive and negative bias. Also, the current indicates the nonlinear behavior for both devices. The negative differential resistance (NDR) is distinguishable in the case of adenine-B_{40}−adenine in the positive bias range. This signifies that there will be a decrease in current with an increase in bias voltage.

Now the question arises as to why the current is lower in the adenine-B_{40}−adenine-based molecular junction even though the HLG is smaller. This is due to the weak bonding

Fig. 3 (continued)
of electrodes to the molecule, which corresponds to the lower value of the current. To probe this further, we assimilated the electron density for both devices. From Fig. 5 it can be seen that for the adenine-B$_{40}$ device, the electron cloud is more oriented around all the nitrogen atoms in adenine, as compared to adenine-B$_{40}$-adenine. This is why, even though the HLG is smaller for adenine-B$_{40}$-adenine, the current is still lower because of the lower electron density and larger work function value. Also, adenine has nitrogen atoms which possess high electronegativity and thus hold more free electrons. As a result, a reduction in the flow of current can be seen.

The rectification ratio (RR) can be calculated as $R = \frac{|I(V)|}{|I(-V)|}$. The graph given in Fig. 6 shows the RR for both devices. The calculated RR values shown in Table 2 illustrate a clear picture of minor variations in RR values with an increase in bias. The adenine-B$_{40}$ device shows a maximum RR of 2.11 at 0.2 V, whereas adenine-B$_{40}$-adenine shows a maximum RR of 1.25 at 0.2 V. The RR for both devices decreases with an increase in bias voltage. Devices that depict prominent NDR and good RR are good candidates for tunnel diodes, with vital relevance in high-speed logic circuits.

To further understand how the current flows in the central scattering region of the molecular junction, we analyzed the transmission pathways. The transmission pathways are also known as local currents, which are represented by arrows superimposed on the molecular geometry. The red arrow indicates the transmission in the direction of the net current, whereas the blue arrow shows components in the opposite direction, thereby reducing the net current. Figure 7 shows the local current of adenine-B$_{40}$ and adenine-B$_{40}$-adenine. It can be seen that for adenine-B$_{40}$, the current flows along the spherical surface, not directly through the cage, and has

Fig. 4 I–V curve for a adenine-B$_{40}$ and b adenine-B$_{40}$-adenine
a greater number of channels, thus increasing the conductance. On the other hand, for adenine-B\(_{40}\)-adenine, the flow of current is also along the spherical surface of the cage but it has fewer channels than the first device.

### 4 Conclusion

The electron transport properties of borospherene in symmetrical and asymmetrical molecular junctions with adenine were elucidated. The density functional theory and non-equilibrium Green’s function (DFT-NEGF) duo was used in ATK-VNL software. Transport parameters including transmission spectra, HLG, electron density, conductance, I–V curve, and transmission pathways were investigated.

By analyzing the transmission spectra at equilibrium, it was inferred that the LUMO orbitals play the dominant role in transmission for asymmetrical devices, whereas for symmetrical devices HOMO is dominant. Symmetrical junctions had reduced HLG due to lower electron density, as nitrogen has high electronegativity which holds a greater number of free electrons. The highest current was observed for asymmetrical junctions relative to symmetrical junctions. Nonlinear behavior was observed for both devices, due to which the NDR comes into the picture. The highest rectification ratio for both devices was observed at 0.2 V, and was 2.11 for the asymmetrical device and 1.25 for the symmetrical device.

| Voltage | A-B\(_{40}\) | A-B\(_{40}\)-A |
|---------|--------------|----------------|
| 0       | 0            | 0              |
| 0.2     | 2.11         | 1.25           |
| 0.4     | 1.645        | 0.3            |
| 0.6     | 0.97         | 0.35           |
| 0.8     | 0.713        | 0              |
| 1       | 0.588        | 0.28           |

![Fig. 5](image1.png) Electron density of a adenine-B\(_{40}\) and b adenine-B\(_{40}\)-adenine

![Fig. 6](image2.png) Rectification ratio

![Table 2](image3.png) Rectification ratio
Thus, borospherene-based symmetrical and asymmetrical molecular junctions are potential candidates for use in future nanoscale devices.

Acknowledgements The authors acknowledge the University with the Potential for Excellence (UPE) scheme of UGC for providing us the computational facility of the Virtual Nano Lab in Guru Nanak Dev University, Amritsar, for carrying out this research work.

Authors' contributions HK came up with the idea, wrote the introduction section. She performed the necessary modeling and simulations and analyzed the results. JK interpreted the results and proofread the manuscript. RK interpreted the results and edited the manuscript.

Funding This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Data availability Not applicable.

Declarations

Competing interests On behalf of all the authors, the corresponding author states that there is no conflict of interest.

Consent for publication All authors give their consent.

Consent to participate All authors give their consent.

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