



Enhancing Electrical Conductance in Acene-Based Molecular Junctions: A Hybrid Approach

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Abstract

In an attempt to enhance electrical conductance and improve the formation probability of a molecular junction, a hybrid method was established. Charge transport and conductance-length dependence (exponential decay) in hybrid acene-based molecular junctions was investigated using Density Functional Theorem (DFT) in combination with Non-equilibrium Green's Function (NEGF) formalism. To diversify the electrical characteristics and device architectures of molecular junctions using heterogeneous structures, to achieve desirable electronic functionalities the low level acene were used to investigate such functionalities. The transmission coefficients $T(E)$, the Frontier Molecular Orbitals (FMO) in consideration of their gap (HOMO-LUMO gap) and the electrical conductance-length dependency were investigated. The results show that hybrid molecular junctions enhanced electrical conductance and is recommended for anthracene and pentacene molecules. It also show that the anchoring materials have a significant effects on the HOMO-LUMO gap of the junction. It is also observed that the hybrid molecular junctions show a non-exponential conductance decay. Lastly, we recommend that the practical implementation of these hybrid molecular junction will bring about a lot discoveries of functionalities and applications in nano electrical circuits.



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Introduction

In recent years, there has been significant interest in the study of charge transport in molecular junctions (MJs). These systems consists of a molecule sandwiched between two metal electrodes. Understanding the nature of charge transport across

these interfaces is of crucial importance for the improvement in molecular electronics. One class of molecules that has been studied as potential candidates for MJs is the acene family,¹ which includes molecules such as anthracene, tetracene and pentacene. Acenes belong to the family of

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aromatic compounds that have received significant consideration for invention of electronic devices.^{2,3} These molecules have extended π -conjugation, which allows for efficient charge delocalization and transport. Acenes and polyacenes are capable for charge transport due to the strong conjugation between the benzene rings.⁴ Moreover, they represent good model structures for understanding the properties of more complex configurations.^{5,6}

Some studies have shown that transport properties like conductance (G) depend on the system length⁷. At long-range, the molecular conductance generally indicates a linear length dependence linked with thermal activation and described by an illogical mechanism.⁸ At short-range, the transport does not depend on the temperature.⁹ At this range, the conductance exhibits an exponential decay with length of molecule and it is represented by equation 1 below.⁴⁰

$$G(L)=A\exp(\beta L) \quad \dots(1)$$

where L is the molecular length, A is a prefactor that depends on the molecule-electrode contact, and β is the decay (attenuation) factor related to the tunneling barrier of the molecular region. The fast degeneration of the conductance with molecular length (Equation 1) restricts the formation of molecular-based electronic components. Some previous studies,^{9,11,12} show the conductance of a chains of carbon-based compounds without anchoring groups. In these studies the electrodes are joined directly to the π -orbital organic molecules and revealed a conductance to be high and independent of molecular length with a very low formation probability. Another study analyzed the conductance of a molecules connected to electrodes via anchoring groups predicted a near length-

independent conductance.¹³ Other studies have compared the conductance of MJs with anchoring groups showing that the anchoring design governs the electron transport path. These MJs has a high formation probability but low conductance value.^{14,15}

In an attempt to enhance electrical conductance of a MJs, and improve its formation probability at the same time, a hybrid method was established. Charge transport in hybrid molecular junctions has been a topic of recent research interest.^{16,17} Hybrid molecular inorganic junctions have been investigated, showing a transition in the charge transport mechanism associated with the spin state conversion of the embedded spin crossover complex.¹¹

In this study, a combination of density functional theory (DFT) calculations and the non-equilibrium Green's function (NEGF) formalism were employed to investigate the charge transport properties of a hybrid acene-based MJs. DFT calculations are used to determine the electronic structure of the molecules and its interaction with the electrodes. This involves solving the Kohn-Sham equations to obtain the energy levels and wavefunctions of the system. The HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) energy levels of the acene molecules are crucial in understanding the charge transport behavior. The energy alignment of these levels with respect to the Fermi levels of the electrodes determines the charge injection and extraction process at the electrode-molecule interfaces. NEGF calculations are then performed to obtain the transmission spectrum. These theoretical investigations compliment experimental efforts and facilitate the design and optimization of molecular devices for various electronic applications.

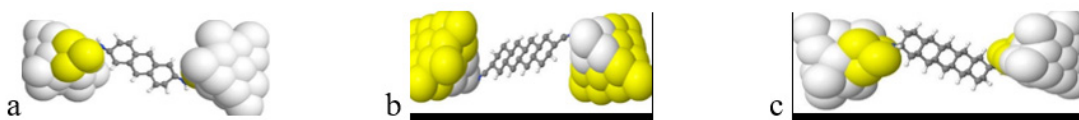


Fig. 1: Acene-based MJs with single contact to electrodes via amines anchor group

Method

This work involves a modelling of the extended structure, energy band calculations as well as charge transport simulations. Modellings of the structures

was done using modelling and visualization software called Jmol. Figure 1, illustrates some of the MJs formed using some members of an acene group. Throughout this work, gold (Au) was maintained

as an electrodes (leads/reservoirs) and they are connected in *para*-positions.¹⁸ The structure optimization and energy band calculations were performed using DFT technique as implemented in FHI-aims computer code,¹⁹ with the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional. Transport properties of the system were investigated using Non-equilibrium Green's Function (NEGF) formalism approach as implemented in the Aitrans computer code.^{20, 21, 22}

In the first phase, Hybrid MJs was investigated by comparing its properties to those that are made up using direct π -electrode contacts and π -anchor-electrode bindings. The first three acene member (i.e., anthracene, tetracene and pentacene) molecules connected to Au electrode via different anchoring groups²³ were considered. The anchoring materials used are amine (-NH₂), cyanide (-CN), sulphur (-S) and thiol (-SH). Figure 1 and 2 illustrate how an anchoring groups are connected to a) anthracene b) tetracene and c) pentacene molecules in a single and hybrid modes respectively. In the second phase, exponential decay and length dependence of the electrical conductance of the hybrid MJs was investigated.^{16, 24}

DFT is based on quite a rigid conceptual framework. For many-body problem, the Schrodinger equation becomes

$$\left[\sum_i^N \left(\frac{-\hbar^2 \nabla_i^2}{2m} + V(r_i) \right) + \sum_{i < j} U(r_i, r_j) \right] \Psi(r_1, r_2, \dots, r_N) = E \Psi(r_1, r_2, \dots, r_N)$$

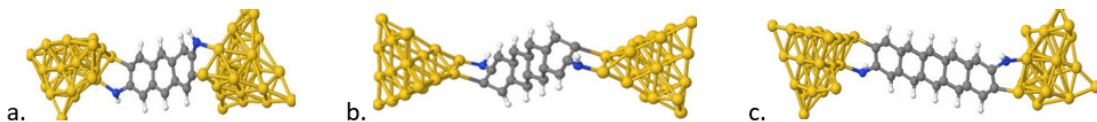


Fig. 2: Double contact (Hybrid) acene-based MJs with amines as anchor groups (a. anthracene MJ, b. tetracene MJ and c. Pentacene MJ)

Results

The results are presented in two different segments. In the first segment, a comparative study between MJs formed without anchoring materials, the others that the anchoring materials were used as well as the double-contact version (hybrid). In the second segment, conductance-length dependence as stated by equation 1 above was scrutinized.

It is assumed that the full Hamiltonian of the extended molecule (Figure 2) has been subject to partitioning into a sub-system M (molecule), a reservoir, M, and a mutual coupling.

$$H = H_M + H_R + V \quad \dots(3)$$

The coupling V is of the form

$$V = \sum_{m,k} v_{mk} d_m^\dagger c_k + H.c. \text{ while } d_m^\dagger, \text{ and } d_m$$

while d_m^\dagger , and d_m denote the creation/annihilation operators in M Hilbert space and c_k^\dagger, c_k the counterparts in R space.

For a small voltage and low temperature limit, the electrical conductance G_e of the molecular junction can be express as

$$G_e = \frac{I}{V} = G_o \tau_e(E_F)$$

Where G_o is the quantum of electrical conductance and has a value of $(2e^2)/h \approx 77.48 \mu S$, E is energy $\tau_e(E)$ is the transmission function for electrons passing from one electrode to the other electrode via the molecule (which can also be written as T) and E_F is the Fermi energy (chemical potential) of the electrode material. Therefore, from equation (4) above, we have¹⁰;

$$G/G_o = T(E_F) \quad \dots(5)$$

Double Contact (Hybrid MJs)

To improve the conductance as well as the formation probability of MJs, the hybrid (double-contact) MJs are formed. This is designed as a combination of direct-contact model and that of using anchor group simultaneously. In this mode, the charge transport path is assign via direct π -electrode binding, whereas, the anchoring of the molecule with the

metal electrode is assign via molecule-anchor-electrode path. Design, synthesis and structural characterization were performed. These MJs are anchored via four different anchoring groups.

Anthracene

At Fermi (E_F) level, the transmission coefficient $T(E_F)$ stands for the conductance of MJs as stated in

equation 5. Figure 3, below represents transmission coefficients for the MJs formed by three different techniques, which are the direct π -electrode binding, the direct π -anchor-electrode binding and the hybrid technique. Figure 5 a-d, are the $T(E)$ s of MJs made up using amines, cyanides, sulphides and thiols anchoring materials respectively.

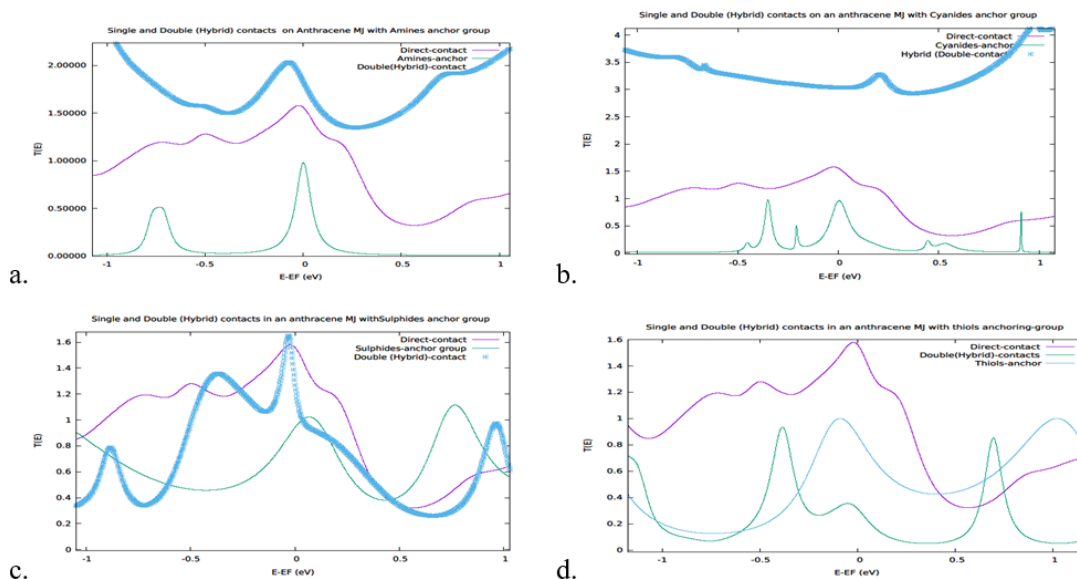


Fig. 3: Variation of a transmission of an anthracene MJs with direct, anchor and double-contact (hybrid) molecule-electrodes intercept

As it can be noticed in Figure 5a, the hybrid MJ has the highest value of $T(E_F)$ which is around 1.83, thus it has a higher conductance. The direct contact had $T(E_F)$ value of 1.56, and then that with anchor material with $T(E_F)$ value of 0.98. When a cyanides anchor is used (b), the similar results was obtained. The hybrid MJ has $T(E_F)$ value of 3.04 followed by the direct contact and then with anchor material whose $T(E_F)$ value is 0.95. For sulphides anchor material (c), the $T(E_F)$ value of hybrid MJ is 1.61 and that of the anchor binding is 0.94. Lastly, for the thiol anchoring, hybrid MJ has $T(E_F)$ value of 0.31 while the anchoring binding has 0.88.

Figure 4, is the frontier orbitals energies for the hybrid anthracene MJs formed using four different anchor materials. The HOMO-LUMO gap of these compounds decreases significantly from 0.049 to 0.008 eV. It can be seen that, the sulphides anchor MJ, the gap has wider gap followed by cyanides and

thiols with gap of 0.018 and 0.012 respectively. MJ made up with amines as anchor group has a least HOMO-LUMO gap of 0.008.

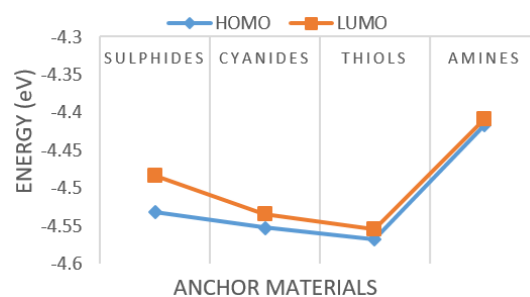


Fig. 4: Variation of the Frontier Molecular Orbitals (HOMO and LUMO) of anthracene hybrid MJs with anchoring materials

Tetracene

For the tetracene MJs, the transmission coefficients $T(E)$ for a MJs formed using direct-contact, π -anchor

and hybrid methods against energy (E) are displayed in Figure 5 (a-d). In these figures, the MJJs are

designed using amines, cyanides, sulphides and thiols as anchor groups respectively.

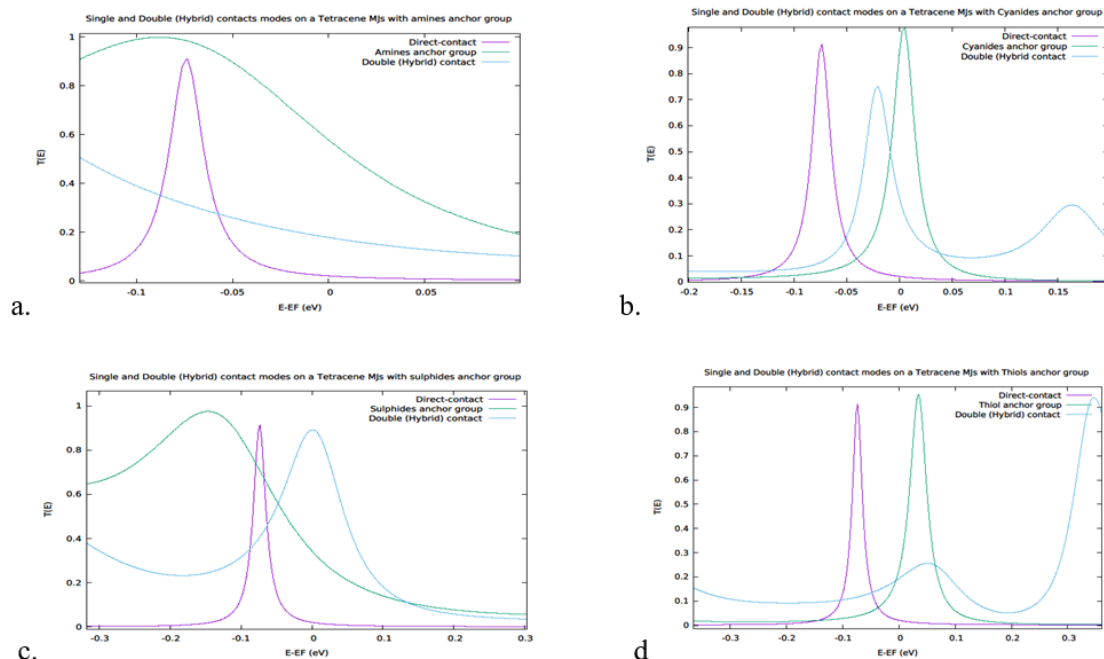


Fig 5: Variation of a transmission of tetracene MJJs with direct, anchor and double-contact (hybrid) molecule-electrodes intercept.

As it can be observed, the transmission of a tetracene MJ using direct method is 0.021. When amines was used as molecule-electrode anchor (a), the $T(E_F)$ value rises to 0.59 and for a hybrid MJ, the $T(E_F)$ falls to 0.18. For the cyanides anchor tetracene MJJs (b), the $T(E_F)$ value is 0.91, while it

is 0.32 for its hybrid. When the sulphides anchor groups are applied, the $T(E_F)$ value is 0.35, while it is 0.89 for its hybrid form. Lastly, the $T(E_F)$ value for tetracene MJ with thiols anchor group is 0.23 and it is 0.19 for the hybrid.

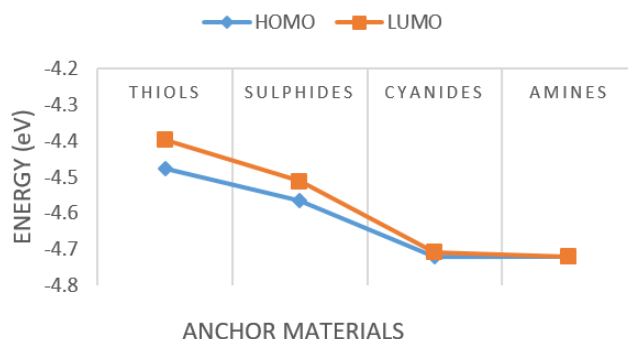


Fig 6: Variation of the Frontier Molecular Orbitals (HOMO and LUMO) of tetracene hybrid MJJs with anchoring materials

The figure above (Figure 6), shows the variation of HOMO and LUMO and their relative gap (HOMO-

LUMO gap) with respect to the type of an anchoring material used. The maximum gap here is 0.078 eV

for the thiols anchor group. Here also, the amines anchor hybrid MJ had the minimum HOMO-LUMO

gap of 0.002 eV. Sulphides and cyanides anchored hybrid MJs has 0.053 and 0.013 eV respectively.

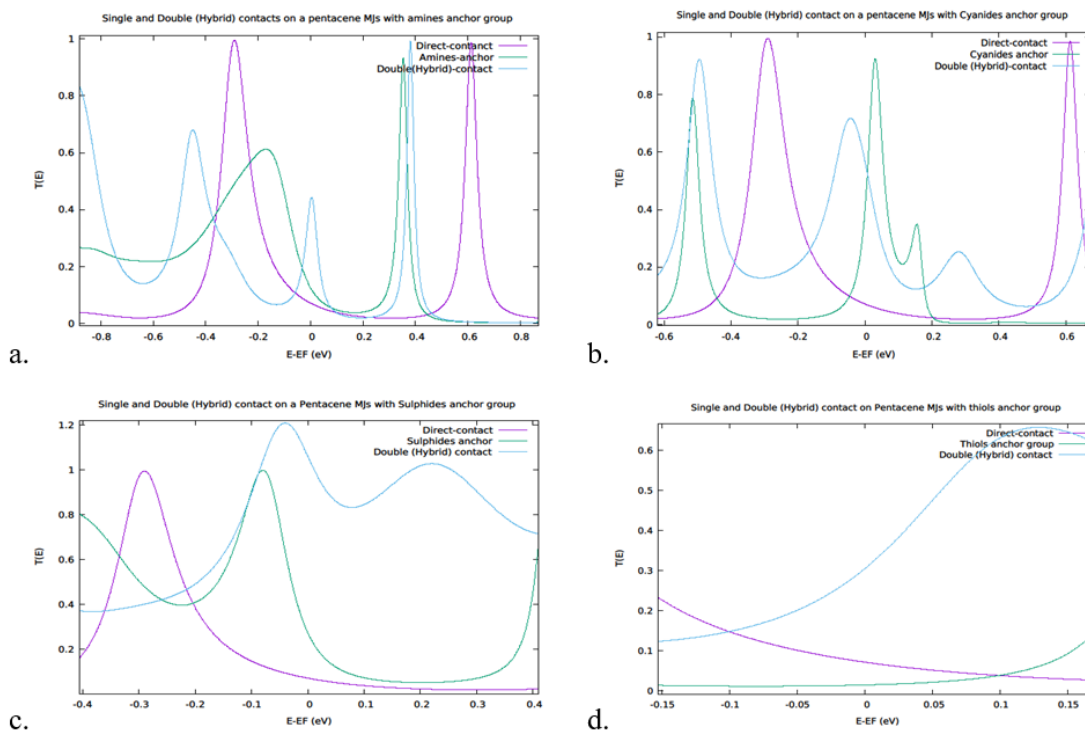


Fig 7: Transmission coefficient versus energy of pentacene MJs with direct, anchor and double-contact (hybrid) molecule-electrodes binding using a) amines anchor group b) cyanides anchor group c) sulphides anchor group d) thiols anchor group

Pentacene

Pentacene is the next member of acene after tetracene. Here also, the MJs are formed using a pentacene molecules the same way as the anthracene and tetracene. The transmission coefficients at Fermi energy level $T(E_F)$ are presented in figure 7 below. The direct π -electrode, π -anchor-electrode and the hybrid modes of MJs are investigated here.

For direct contact mode, the transmission coefficient at Fermi energy of an electrode $T(E_F)$ is 0.071. When amines anchor groups are used, the $T(E_F)$ is 0.12 and it is 0.42 for the hybrid MJ. The $T(E_F)$ of cyanides anchored MJ is 0.38, while it is 0.56 for the hybrid. For the sulphides and thiol anchored MJs, the $T(E_F)$ values are 0.27 and 0.015 while for their corresponding hybrid MJs, it is 1.07 and 0.30 respectively.

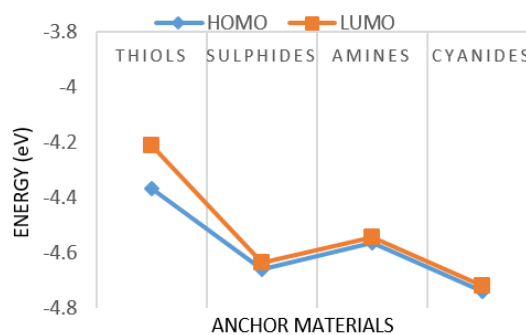


Fig. 8: Variation of the Frontier Molecular Orbitals (HOMO and LUMO) of pentacene hybrid MJs with anchoring materials

The frontier molecular orbitals of a hybrid pentacene MJs varies according to the anchor group used in forming it. Thiols anchor group has the widest HOMO-LUMO gap of 0.16 eV. Next to this amount is

sulphides anchor group with gap of 0.023 eV. Amines and cyanides anchor groups are having the least gap with 0.018 and 0.017 respectively.

Length Dependence in Acene-based MJs

Here, the length dependency and exponential decay (equation 1) was investigated. The conductance at

zero bias of the compounds anchored in different configurations (i.e., direct, anchor and hybrid) was presented. Figure 9 (a-d) shows the conductance of these MJs within the exponential decay region ($N \leq 5$) (Valdiviezo, 2021).

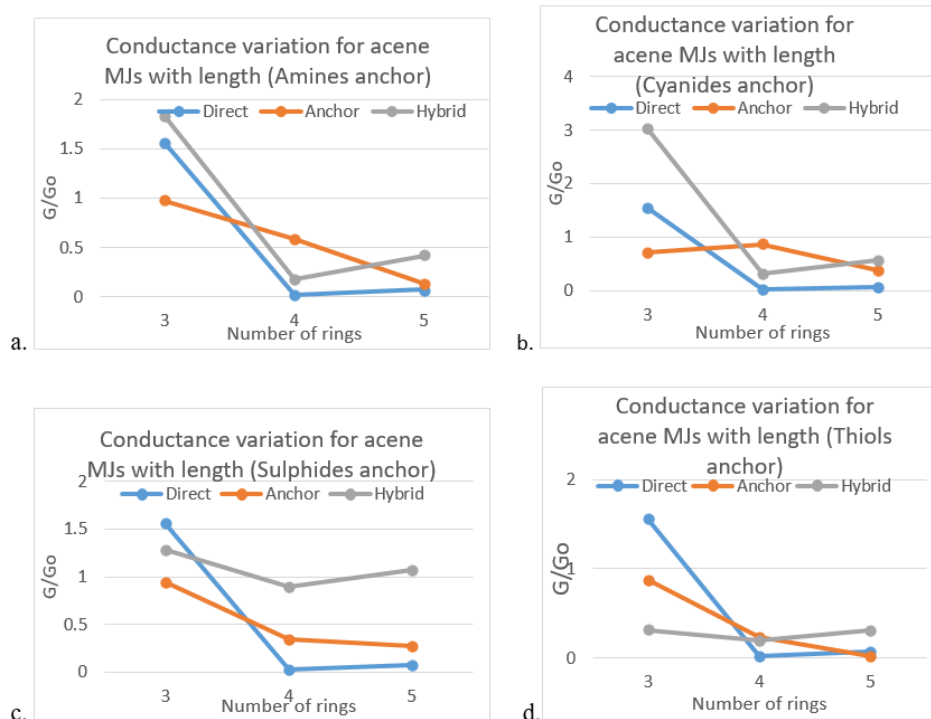


Fig 9: Zero bias conductance of acene-based MJs for different interfaces

For both anchoring groups (amines, cyanides, sulphides and thiols) in Figure 9 (a to d), the hybrid and direct π -electrode did not show any definite conductance decay. The results shows that the conductance does not depends on the molecular length. For the case of π -anchor-electrodes formation, the conductance decays with molecular length except for the case of cyanides anchoring group (Figure 9b). These results shows that, the anchoring materials plays a significant role in the nature of conductance behavior of MJ. It also show that the hybrid MJ does not obey the exponential decay rule in equation 1.

Discussion

The findings show that, apart from improving the formation probability, the hybrid method increases

the conductance of an anthracene MJ for all the anchor groups used. Also, the HOMO-LUMO gap varies with the type of anchoring material. It show that the amines anchor material increases the level of the FMOs and has a minimum HOMO-LUMO gap, thus it excites charges more than the other materials and it is recommended to be used in making such MJ.

For the tetracene molecule, the results show that the hybrid method does not improve the conductance of MJs, except for the sulphides anchor group. For the FMOs, the amines anchor group has the least HOMO-LUMO gap even though the energies dropped significantly. Hybrid method of MJ is not recommended with tetracene molecule, but if

necessary, the sulphides anchor group should be used even though it has wide HOMO-LUMO gap.

The results also show that, the hybrid method enhanced the conductance as well as the formation probability of pentacene MJ for all the anchor groups used. So also, the HOMO-LUMO gaps are minimum for the amines and cyanides anchoring groups. It is highly recommended to use a hybrid method to make a pentacene MJ with any of amines or cyanides as anchoring material.

Lastly, the results also demonstrate that, the lower acene derivatives have a non-exponential length dependence of the conductance. The connection to the electrodes (coupling) dictates the conductance behavior. This signifies that, the molecules anchored through anchoring materials demonstrated a traditional conductance decay with length, whereas molecules anchored via hybrid method and those with direct π -metal contact exhibit conductance fluctuations with molecular length. Thus, by improving the conductance and overcoming the exponential conductance decay, hybrid MJs will be a very good and cost effective organic molecular components of the next-generation nano electrical circuit.

Conclusion

In conclusion, by using the DFT in combination with NEGF calculations, we have demonstrated that the hybrid method can improve the conductance and formation probability of an anthracene and pentacene MJs. The conductance of tetracene MJ can only be improve when sulphides are used as an anchoring group. Energy band calculations suggested that the anchoring groups influenced the variation of HOMO, LUMO and the gap between them. It shows that for anthracene and pentacene MJs, the amines anchor materials produced a minimum HOMO-LUMO gap. Our results also shows that the hybrid MJs demonstrate a non-exponential conductance decay, but rather it shows a linear dependence in some cases.

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Conflict of Interest

The authors do not have any conflict of interest.

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