

Investigation of Transmission Coefficient and I-V Characteristics of OPE-PY-Based Structures Using GOLLUM Program

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Abstract

Present study deals with the electronic properties of donor-bridge-acceptor(D-B-A) molecular systems. By employing the density functional theory, the calculations were carried out to analyze the applications of oligophenylene-pyridene OPE-PY-based structures. All calculations have been carried out using the Gollum program together with SIESTA code at the high end computation unit-Lancaster University-UK.

The results showed that, the high occupied molecular orbitals HOMOs are strongly localized on the anchor groups for the structure with pyridyl anchor group. The distribution of the frontier molecular orbitals suggests that the conductance may be dominated by transport through the low unoccupied molecular orbitals LUMOs for the configurations with pyridyl anchor group. The curve of the ionization potential of PY-based configurations structures goes toward low IP ($\text{OPE-PY-3} < \text{OPE-PY-2} < \text{OPE-PY-1}$), that means OPE-PY-3 structure needs a small energy to donating electrons in comparison with the others. Also, all the studied molecular systems have semiconductor properties with energy band gap in the order of $\text{OPE-PY-2} < \text{OPE-PY-3} < \text{OPE-PY-1}$. In addition, the lowest molecular length is for the structures with carbon triple bonds in the middle. The calculations of the transmission coefficient showed that, the value of the structures without side group is higher than that of the structure with side group. The electrical transport of these molecules could be control by switching from one type of anchor group to another one and that means these molecules could useful for sensing device-applications.

Keywords: Density functional theory, High occupied molecular orbital, Low unoccupied molecular orbital, Transmission coefficient and I-V characterization

تخمين معامل الانتقال ومميزات تيار- فولتية لتراكيب OPE-PY باستعمال برنامج GOLLUM

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الخلاصة

يتضمن البحث الحالي دراسة الخواص الالكترونية لأنظمة جزيئية واهب- جسر- قابل. بتطبيق نظرية دالة الكثافة، أجريت الحسابات لغرض تحليل تطبيقات التراكيب من نوع OPE-PY باستعمال برنامج Gollum وبرنامج SIESTA في وحدة الحسابات النهائية العليا في جامعة لنكستر- بريطانيا. تبين النتائج ان المستويات الجزيئية العليا المشغولة متمركزة بقوة على مجاميع البايرديل المثبتة للتركيب. ان توزيع المدارات الجزيئية يؤدي الى اقتراح ان التوصيلية يمكن تطبيقها بواسطة الانتقال خلال المستويات الجزيئية السفلى الفارغة للتركيب. ان منحني جهد التأين للتركيب يكون باتجاه انخفاض الجهد ($\text{OPE-PY-1} < \text{OPE-PY-2} < \text{OPE-PY-3}$) وأن تركيب OPE-PY-3 يحتاج الى طاقة صغيرة ليفقد الكتروناته بالمقارنة مع التراكيب الاخرى. كما أن جميع التراكيب تمتلك خواص شبه موصل مع فجوة طاقة بالترتيب $\text{OPE-PY-2} < \text{OPE-PY-1} < \text{OPE-PY-3}$. بالإضافة الى ذلك فإن الطول الجزيئي الاقصر كان للتركيب ذات أصرة الكربون الثلاثية في وسط التركيب. أن حسابات معامل الانتقال تبين أن قيمة الانتقال للتركيب بعدم وجود مجموعة مضافة تكون أعلى منها للتركيب بوجود مجموعة مضافة. أن الانتقال الكهربائي لهذه المجموعة من الجزيئات يمكن السيطرة عليه من خلال التحويل من نوع من المجموعة المثبتة الى نوع آخر وذلك يعني أن هذه الجزيئات مهمة في تطبيقات أجهزة التحسس.

الكلمات المفتاحية: نظرية دالة الكثافة، المستوى الجزيئي العلوي المشغول، المستوى الجزيئي السفلي الفارغ، معامل الانتقال ومميزات تيار- فولتية.

1. Introduction

Molecular electronics which involve the investigations related to the electronic structure, electron transport and device exploitation of matter and their molecular degree [1]. Molecular electronics is the technology emerging extremity of semiconductor electronics, where a discrete molecule (up to few nanometres range) rather than the continuous semiconductor materials, are the components for electronic circuits [1, 2]. In electronics all the electronic operations take-place through the transport of the electron in the circuit. The ultimate miniaturization will be molecular level [3, 4]. One of the earlier studies of charge transfer in donor-acceptor systems was well studied by Robert Mullikan and Albert Szent-Gyorgi in 1940 [5]. From the above, it can be suggested that in such donor-acceptor systems where the charge transfer can be achieved easily would be suitable for the molecular electronic devices.

2. Theory

One possible way of tackling the many-body problem in terms of one particle wave functions is offered by Density Functional Theory (DFT) [6]. The Hohenberg-Kohn theorem states that the ground-state energy E of an N -electron system is an unique functional of the charge density n :

$$E = E[n] = \hat{T}[n] + \hat{V}_{ext}[n] + \hat{V}_{Ne}[n] + \hat{V}_{ee}[n]$$

where

$$n^{\sigma_1}(\vec{r}_1) = N_e \int |\psi^e(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_{N_e})|^2 d\sigma_2 d\sigma_3 \dots d\sigma_{N_e} d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_{N_e}$$

$$n(\vec{r}) = \int n^{\sigma}(\vec{r}) d\sigma = n^{\uparrow}(\vec{r}) + n^{\downarrow}(\vec{r})$$

Provided

$$\langle \psi^e | \psi^e \rangle = 1 ; \int n^{\sigma}(\vec{r}) d\sigma d\vec{r} = N_e$$

Where $n^{\uparrow}(\vec{r})$ and $n^{\downarrow}(\vec{r})$ are the densities of electron up and down, respectively, and N_e is the total number of electrons. If the density functional is known we will be able to solve the variation equation[7]:

$$[-\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(\vec{x})] \psi_i(\vec{x}) = \varepsilon_i \psi_i(\vec{x})$$

The set of eigen-states $\{\psi_i\}$ which are solutions to the above eigen value problem are known as Kohn-Sham states[7]. The effective potential V_{eff} corresponds to the effective single particle potential seen by an electron due to its interaction with the other $N-1$ Kohn-Sham states. This potential is defined as:

$$V_{eff}(\vec{x}) = V(\vec{x}) + V_H(\vec{x}) + V_{XC}(\vec{x})$$

The first term is the external potential and includes the potential originating from the nuclei as well as an external applied electric field if present. The term V_H corresponds to the classical Coulomb potential (Hartree potential) for an electron density $n(\vec{r})$. This term is obtained by solving the Poisson equation for the scalar potential[7]:

$$-\nabla^2 V_H(\vec{r}) = n(\vec{r})$$

Finally

$$V_{XC}(\vec{x}) = \frac{\delta E_{XC}}{\delta n}$$

V_{XC} is the exchange-correlation potential defined as the functional derivative of the exchange correlation energy, E_{XC} with respect to the electron density n .

3. Siesta Code

The basis set in SIESTA is a numerical basis obtained by solving the Schrodinger equation of the isolated atom immersed in a hard-wall potential. It reads

$$\phi_{n,l,m}(r, \theta, \varphi) = R_{n,l}(r)Y_{l,m}(\theta, \varphi)$$

where $R_{n,l}(r)$ is the radial function for orbital n and $Y_{l,m}(\theta, \varphi)$ is the real spherical harmonic for the orbital angular momentum l and magnetic quantum number m [8]:

$$\int |R_{n,l}(r)|^2 r^2 dr = 1$$

the radial part of our second- ζ retains the tail of the first- ζ outside a split-radius r_s and has a polynomial form inside [8]:

$$R_{n,l}^{2\zeta} = \begin{cases} r^l (a_l - b_l r^2) & \text{if } r < r_l^s \\ R_{n,l}^{1\zeta}(r) & \text{if } r \geq r_l^s \end{cases}$$

The constants a_l and b_l are determined by matching the wavefunction and its first derivative. The overlap matrix is defined as:

$$S_{ij} = \int d\vec{r} \phi_i(\vec{r} - \vec{R}_i) \phi_j(\vec{r} - \vec{R}_j)$$

with $i = \{i', I\}$, $j = \{j', J\}$ and R_I is the position of the I^{th} atom.

the Kohn-Sham Hamiltonian matrix is computed by evaluating integrals of the form:

$$H_{ij} = -\frac{\hbar^2}{2m} \int d\vec{r} \phi_i(\vec{r} - \vec{R}_i) \nabla^2 \phi_j(\vec{r} - \vec{R}_j) + \int d\vec{r} \phi_i(\vec{r} - \vec{R}_i) V_{eff}(\vec{r}) \phi_j(\vec{r} - \vec{R}_j)$$

Where $\hbar$ is Planck's constant, r and R are the coordinates for electrons and nuclei, respectively. For periodic systems, one must also include the coupling to the periodic mirrors of the unit cell with the Hamiltonian [8]:

$$H_{ij}(\vec{k}) = \sum_I H_{ij}^I e^{i\vec{k} \cdot \vec{r}_I}$$

4. Gollum Program

The simplest mean-field approach to describing quantum transport through nanostructures is to build a tight-binding Hamiltonian, which reproduces key electronic properties near the Fermi energy. This approach has been available for more than half a century and is still popular today when describing generic properties of materials such as graphene [9]. Tight binding parameters can be obtained by fitting to known band structures and then by varying spatially to describe external fields and other perturbations. However, such an approach does not easily capture the effects of interfaces between different materials or edge terminations of finite-size systems, whose properties are distinct from those of bulk materials. This problem was solved in part by the non-equilibrium Green's function technique [1–17], which combines with density functional theory (DFT) [18, 19] to obtain the self-consistent mean-field Hamiltonian of the system. It is subject to a finite bias voltage and, from it, the lesser Green's functions provide the non-equilibrium electronic density and current. This approach is utilized within the SMEAGOL code [1, 2], which was the first to describe spin-dependent and finite-

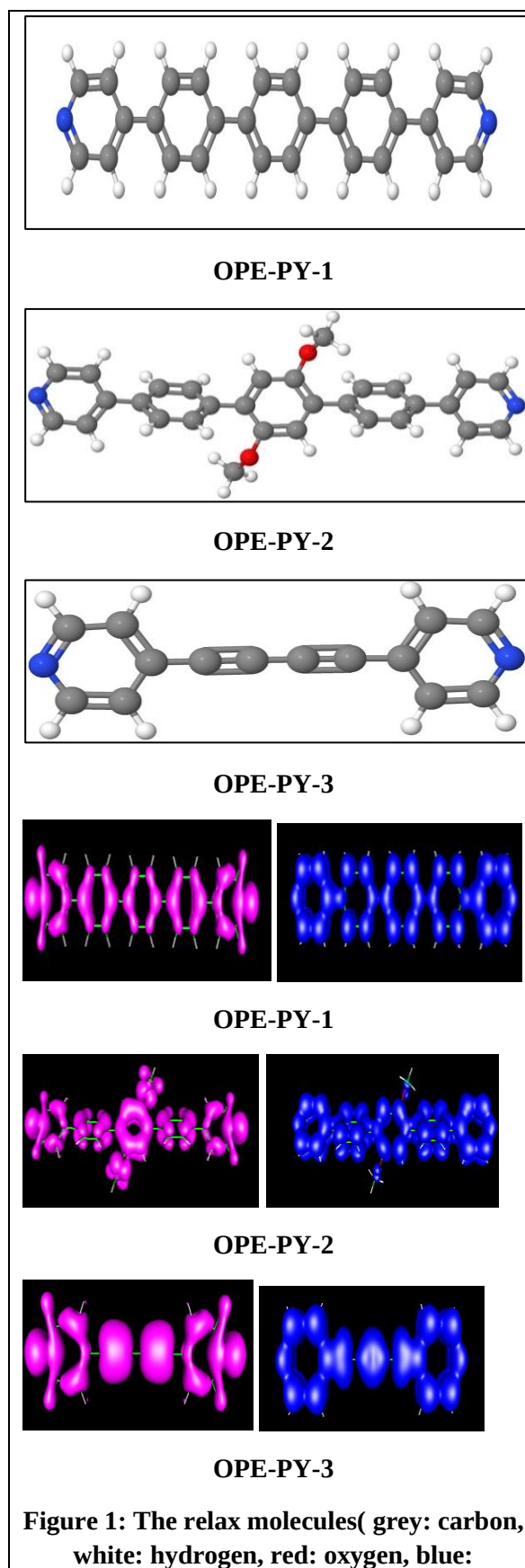
voltage transport properties of systems with inhomogeneous magnetic moments in the presence of spin–orbit scattering. The new code is called GOLLUM. The development of SMEAGOL [9, 10] allowed to understand that non-equilibrium transport codes are quite difficult to handle, in part because of their complex input data structures, which can create a steep learning curve, and also because they carry very heavy computational demands. As a consequence. The development of the new code GOLLUM to be more user friendly, with simple and easy to understand input and output structures, and with no accuracy parameters to tune.

GOLLUM is a program that computes the charge, spin and electronic contribution to the thermal transport properties of multi-terminal junctions. The program has been designed for user-friendliness and takes a considerable leap towards the realization of ab-initio multi-scale simulations of conventional and more sophisticated transport functionalities. The simpler interface of GOLLUM allows it to read model tight-binding Hamiltonians. Furthermore, GOLLUM reads information from all the latest public flavors of the code SIESTA [20]. GOLLUM also incorporates an interface with some classical molecular dynamics programs, which enables it to handle interactions with the environment. In contrast with SMEAGOL, which only computes the magnitudes of the transmission coefficients of two-terminal junctions, GOLLUM has therefore the ability to compute non-equilibrium current–voltage curves.

5. Results and Discussion

Before computing transport properties, all molecules in this work were initially geometrically relaxed in isolation

to yield the geometries shown in Figure 1. The molecules under study have significant applications in molecular electronics.



nitrogen), and iso-surfaces of the HOMO (pink) and LUMO (blue) for each molecule

Figure 1 shows that the LUMOs are extended across the backbone for each molecule, and noticeable contributions from the phenylene rings and the pyridyl (PY) anchor groups [21]. In contrast, HOMOs are strongly localized on the anchor groups for the structure with pyridyl anchor group, while the HOMOs are strongly positioned on both phenylene rings and anchor groups. In addition, it is clear that there is a weight of the side groups on HOMOs, while the weight of these side groups is less on the LUMOs. Furthermore, the composition and distribution of these frontier orbitals suggest that the conductance may be dominated by transport through the LUMO for the configurations with pyridyl anchor group. Figure 1 illustrates that the middle phenylene rings in the molecules with side group have rotated after relaxation process. In contrast, there is no rotation of these rings in the molecules without side groups [21]. This result point out the first effect of the side groups on the structural properties of these molecules, which could affect the electronic properties of these structures. Table 1 illustrates the distances associated with these conformations after relaxation process.

Table 1: The distances from the relaxation of OPE-PY based structures

Molecule	OPE-PY-1	OPE-PY-2	OPE-PY-3
L (nm)	2.452	2.435	1.651
d_{N-N}(nm)	2.032	2.015	1.233
C=C(nm)	0.141	0.141	0.141
C-C(nm)	0.148	0.148	0.142

C–N(nm)	0.134	0.134	0.134
C–O(nm)	-	0.137	-
C–H(nm)	0.11	0.11	0.11
X(nm)	0.21	0.21	0.21

The molecular length L of the OPE-PY-3 based structure is smaller than that of OPE-PY-2 and OPE-PY-1 based structures. This result is ascribed to the nature of anchor groups and their interaction with gold atoms of the electrodes through the distance X. In addition, the lowest molecular length is for the structure with carbon triple bonds in the middle. Furthermore, the present of side groups (Methoxy) also result in rotation in the phenyl ring and thus affected the structural properties of these molecules, which may be influenced the electronic properties.

Figure 2 shows the relation between the ionization potential IP and the length of the studied molecular systems, IP was calculated according to Koopman^s theorem($IP = -E_{HOMO}$). It is clear from figure 2 that the curve of the ionization potential of PY-based configurations structures goes toward low IP ($OPE-PY-3 < OPE-PY-2 < OPE-PY-1$). The ionization potential of OPE-PY-3 based configuration is less than the others, that means this molecule needs a small energy to donating electrons in comparison with the others.

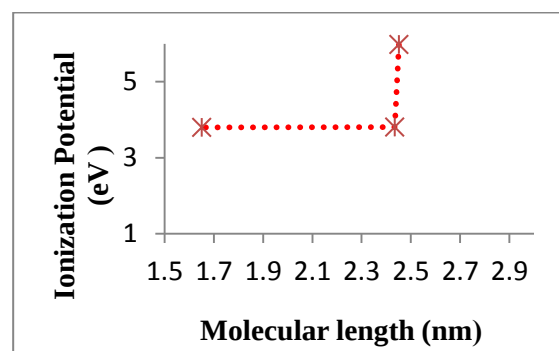


Figure 2: The ionization potential of the studied molecules.

Figure 3 shows the influence of the type of configuration on the electron affinity EA of the studied molecular systems, EA was calculated according to Koopmans theorem ($EA = -ELUMO$). It is clear from this figure that the EA of the PY-based configurations was increased with increasing the length of the molecular system due to the linear combination atomic orbitals, OPE-PY-1 molecule has the largest value of electron affinity, and this is not a reflection of the electronic structure of HOMO and LUMO, but it is a different global electronic property.

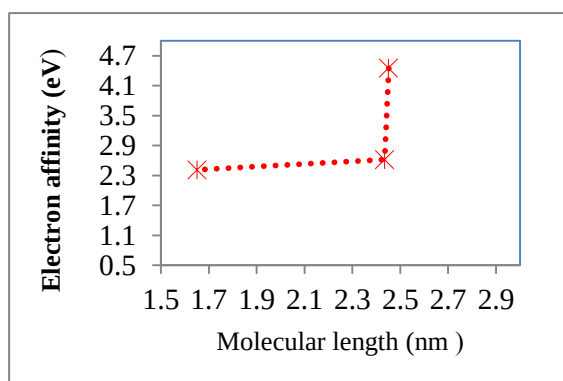


Figure 3: The electron affinity of the studied molecules.

Figure 4 shows the relation between the energy band gap and the length of each molecule of the configuration PY-based structures. As seen in this figure, the E_g depends on the construction of the nanobridge between the donor and the acceptor. Generally, all the studied molecular systems have semiconductor properties with energy band gap in the order of $OPE-PY-2 < OPE-PY-3 < OPE-PY-1$.

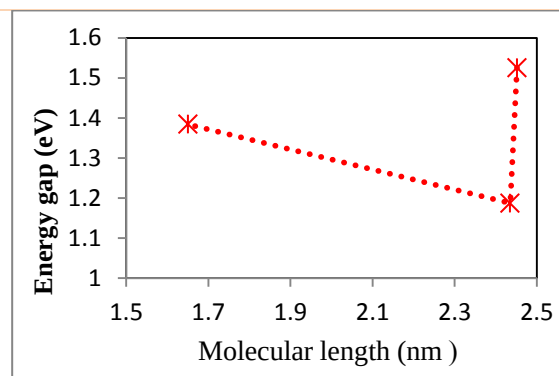
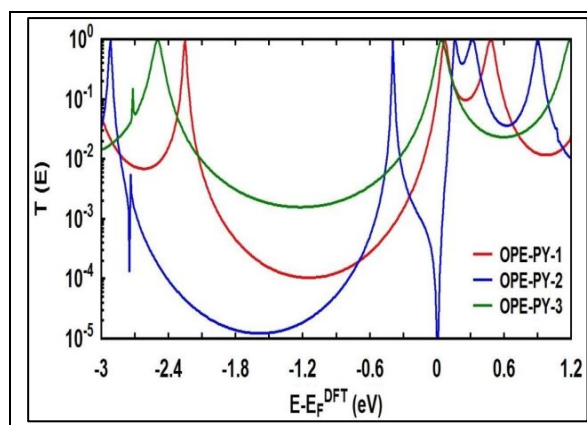
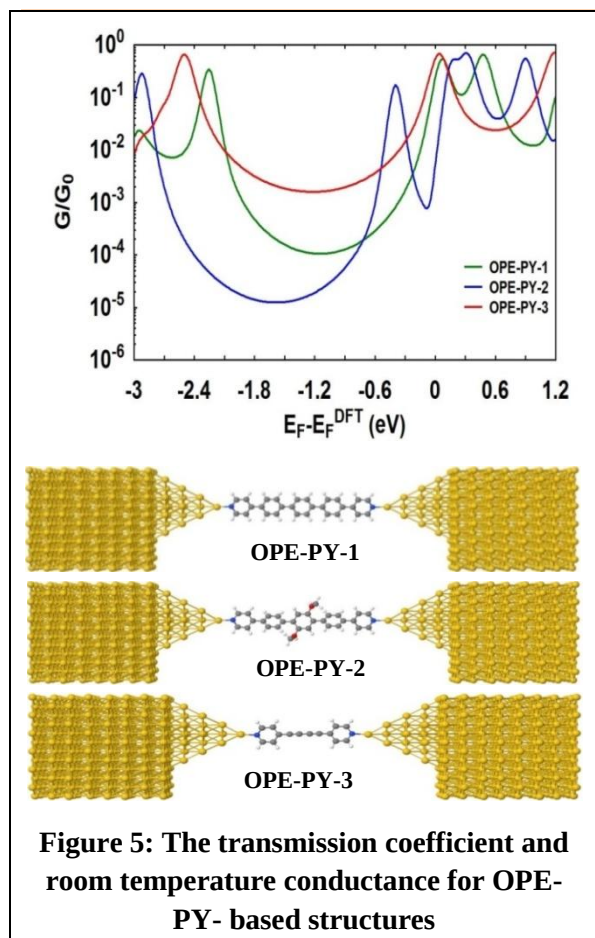


Figure 4: The energy band gap of the studied molecules.

Transmission and Conductance

The transmission coefficient is calculated by using GOLLUM program. The room temperature conductance is obtained by averaging $T(E)$ over an energy range of order $k_B T$ in the vicinity of $E = E_F$. Figure 5 shows the transmission coefficient as a function of the electrons energy and the room temperature conductance as a function of the Fermi energy for OPE-PY-based structures.





There are several points are apparent promptly. First, The transmission value of the structures without side group is higher than that of the structure with side group, and this could be ascribed to the effect of the Methoxy group (O-NH_3), since this kind of side group causes rotation of the middle phenylene rings, and that could affected the tuning between the energy channels or levels of the molecule and the gold electrodes result in a quantum destructive interference between the waves that propagate from the left gold lead to the right gold lead, which reduce the transmission. This explanation has been supported via the apparent of the LUMO anti-resonance peak at theoretical Fermi energy ($E_F = 0.0 \text{ eV}$) as shown in the transmission curve and conductance curves of OPE-PY-2. On the other hand, it could be observed that the transmission of the molecule with two carbon triple bonds in

the middle is the highest. This could be understood in term of the impact of the molecular length, since the molecular length of this structure (OPE-PY-3) is the lowest one, and that means the tunnelling distance decreases, which increases the value of transmission. This result has been supported by room temperature conductance curves. Finally, all molecules have shown LUMO dominated transport, and this confirmed via HOMO-LUMO results.

Current-Voltage Characteristics

To determine and understand the electrical behavior of these structures we did current-voltage calculations for all structures by using GOLLUM. Figures 6 and 7 show the forward current and the revers current as a function of the applied voltage, respectively, at theoretical Fermi energy ($E_F=0.0 \text{ eV}$) and ($T=300 \text{ K}$) for PY-based structures.

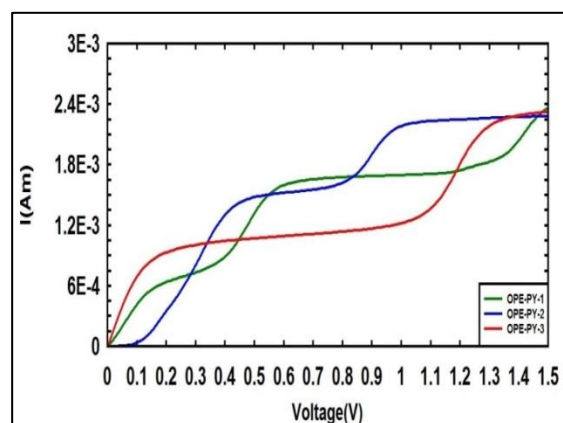


Figure 6: The forward current as a function of the applied voltage at theoretical Fermi energy ($E_F=0.0 \text{ eV}$) and ($T=300 \text{ K}$) for PY-based structures

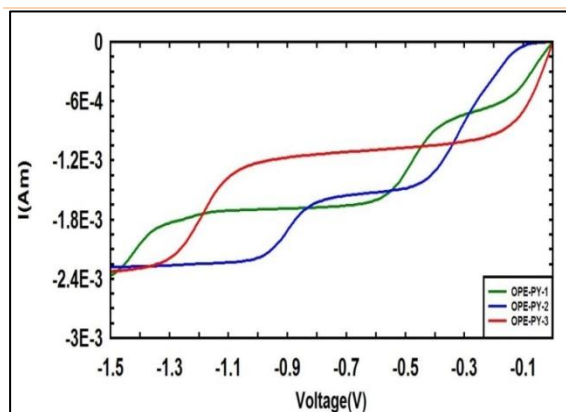


Figure 7: The revers current as a function of the applied voltage at theoretical Fermi energy ($E_F=0.0$ eV) and ($T=300$ K) for PY-based structures.

The above figures show clearly the molecular electronic for sensing device-applications, at bias voltage $\frac{eV}{2} = -1.5 \rightarrow 1.5$ eV applied on the donor part ($\varepsilon_D = \varepsilon_D^o + \frac{eV}{2}$) and decreasing the energy on the acceptor part ($\varepsilon_A = \varepsilon_A^o - \frac{eV}{2}$), we showed a perfect molecular electronic of forward bias of 1.5 eV and revers bias of -1.5 eV. The results show that the sensing in the revers bias behave as a very high resistance nearly of amount of $G\Omega$ and this is very important because the resistance in real dimensions nearly of amount of $M\Omega$. On the other hand, the sensing in the forward bias behaves as a very low resistance allowing a highly increasing current.

A very valuable result obtained from above behavior, since this behavior reduces completely the high temperature effects that appear in the old devices (macro devices). Furthermore, our calculations also suggest that the symmetric interaction with the electrodes have rather limited influence on the sensing behavior of a D-B-A system. The

sensing results from the lowering of the energy gap between the HOMO of the molecule and the Fermi level of the metal in the forward bias and in the reverse bias. The results of our theoretical calculations show a qualitative agreement with that of the real system which done by using DFT.

6. Conclusions

Theoretical calculations on OPE-PY-based structures as donor-bridge-acceptor molecular systems have been carried out in order to analyze the applications of these molecules. From the detailed structure-property analysis, a few important observations can be outlined as shown below:

1. HOMOs are strongly localized on the anchor groups for the structure with pyridyl anchor group, while the HOMOs are strongly positioned on both phenylene rings and anchor group. Furthermore, the composition and distribution of these frontier orbitals suggests that the conductance may be dominated by transport through the LUMO for the configurations with pyridyl anchor group.
2. The lowest molecular length is for the structure with carbon triple bonds in the middle. Furthermore, the present of side groups (Methoxy) also result in rotation in the phenyl ring and thus affected the structural properties of these molecules, which may be influenced the electronic properties.
3. The transmission value of the structures without side group is higher than that of the structures with side group. the transmission of

the molecule with two carbon triple bonds in the middle is the highest.

4. There is competition between the effect of the binding energy and the effect of the quantum interference.
5. The sensing in the forward bias behaves as a very low resistance allowing a highly increasing current.

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