Investigation of Electric and Thermoelectric Properties of Phthalocyanine monomer/dimer Molecular Junctions

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Abstract: In this work, we carried out a theoretical calculation to present the electrical and thermoelectrical properties of five monomers/dimers structures based on Phthalocyanine molecule sandwiched between gold electrodes. The calculation was preformed based on density functional theory (DFT) implemented by SIESTA. The results reveal that the transmission calculations T(E) of all five monomers/dimers show no spin dependent with highest value for monomer structure around Fermi energy. The phthalocyanine monomer structures show higher conductivity calculation around the Fermi energy in comparison to conductivity values of phthalocyanine dimer structures. Further, thermoelectric properties such as Seebeck coefficient (S), thermal conductance (k) and figure of merit (ZT) are also presented. It is found that the highest positive Seebeck coefficient (S) value belongs to zinc phthalocyanine monomer, while the highest negative (S) value belongs to free base phthalocyanine dimer structure over a wide range of Fermi energies. Moreover, zinc phthalocyanine monomer structure shows highest thermal conductance (k), while phthalocyanine dimer structures exhibit lowest thermal conductance (k) in the vicinity of DFT predicted Fermi energy. As a result, high room-temperature figure of merit (ZT ≈1.7) is reported for free base phthalocyanine dimer, which might be due to the low thermal conductivity and high Seebeck coefficient and electrical conductance values, which makes it a preferred candidate for potential thermoelectric applications.

1. Introduction:
Electricity generation from the wasted heat has taken much attention by focusing on studying the thermoelectric properties and identifying new materials with a high thermoelectric efficiency [1]. The main concept of thermoelectric comes from the Seebeck effect which has been already introduced since the early 19th century [2]. This effect refers to the process of generating a voltage difference from a heat gradient. It focuses on enhancing electric current generation by investing the wasted heat that exists in some physical structures like automobile exhausts or using the wasted heat accompanies
some mechanisms such as most industrial manufacturing processes. Recently, much attention has been given to tune the parameters that control the thermoelectrical properties, especially of molecular materials and device structures [3-7]. The efficiency of thermoelectrical materials is mainly determined by thermoelectric figure of merit (ZT), which is given by \( ZT\propto S^2GT/k \), where \( S \) is the Seebeck coefficient, \( G \) is the electrical conductance, \( T \) is the temperate and \( k \) is the electronic thermal conductivity.

Regarding the material used as thermoelastic, there is an increased interest in using organic thermoelectric materials to avoid many downsides of using inorganic ones including toxicity, less availability, and high cost. Besides, inorganic materials thermoelectric properties can be tuned by considering nano-structuring characteristics [8, 9]. Therefore, there is particular interest in exploiting the room-temperature characteristics of molecules attached to nanogap electrodes, which represents a nano-device. So far, different experimental and theoretical studies have been carried out to develop and control electronic molecules [4, 10-12]. They have been tuned for future nano electronics circuits applications such as molecular wires [13], electrodes [14, 15], quantum dots [16, 17] switches [18, 19], and biology systems [20, 21].

Phthalocyanine (Pc) has attracted huge attention for many years due to its distinguished high chemical and thermal stabilities as well as ideal symmetric geometrical structure [22-24]. Phthalocyanine characteristics such as electronic, structure, magnetic, chemical, as well as transport can be tuned by inserting host central metallic ion in the centre. Such materials are known as metallo-phthalocyanines (MPC) that have been considered in many applications from organic thin film transistors [25], chemical sensors [26] to optoelectronic and photovoltaic devices [27-30]. They have been investigated with techniques such as scanning tunneling spectroscopy (STS) [31] photoemission spectroscopy [32], gas phase electron diffraction [33], nuclear magnetic resonance [34], etc. However, much of these studies were based on experiments approach, and thus more deep theoretical analysis needed to be addressed in this field.

Herein, the aim of this work is to explore the properties of different monomers/dimers structures based on phthalocyanine (Pc) molecular junctions shown in Fig. 1 for high efficiency thermoelectricity. Density functional theory (DFT) is considered to calculate the transmission coefficient \( T(E) \), that describes electrons of energy \( E \) and spin \( \sigma=\{\uparrow, \downarrow\} \) passing from one electrode to the other through the phthalocyanine (Pc) molecule. The electrical conductance \( G \) is then obtained using the Landauer formula (see method). Thus, a comparative theoretical study is presented to show the transmission and conductance characteristics as well as Seebeck coefficient and figure of merit behavior of the five proposed monomers/dimers systems based on phthalocyanine (Pc) as a promising material for thermoelectrical applications. As shown in Fig. 1, the (Pc) molecule is sandwiched between gold electrodes in five monomer and dimer different structures to present the comparison.

2. Methods:
Firstly, geometrical optimization of each phthalocyanine molecule sandwiched between two gold electrodes shown in Fig. 1 carried out using the SIESTA code [35] implementation of density functional theory (DFT), with a double-\( \zeta \) polarized basis set (DZP) and generalized gradient functional approximation (GGA-PBE) for the exchange and correlation functionals. We then merge the DFT mean-field Hamiltonian of each ground state structure with our quantum transport code, GOLLUM [36] to calculate the transmission coefficient \( T_{\sigma}(E) \) that refers to the probability that electrons with energy \( E \) and spin \( \sigma=\{\uparrow, \downarrow\} \) can pass from the left to the right gold electrode through the molecule. After that, the conductance calculation was carried out using the calculated transmission coefficient \( T_{\sigma}(E) \), and Landauer formula, which given by: \( G = G_{\uparrow} + G_{\downarrow} \), and \( \int_{-\infty}^{\infty} dE \mathbf{T}(E)\mathbf{[-}\mathbf{f}(E,T)$/\partial E]. \), where, \( f(E, T) \) is fermi distribution function which given by: \( f(E, T) = [e^{(E-E_f)/K_BT} + 1]^{-1} \), where \( K_BT \) is Boltzmann’s constant and \( G_0 = (2e^2/h) \) is the quantum of conductance. Then, we obtained the Seebeck coefficient which refers to the ability of a thermoelectric material to convert heat to electricity,
which is defined as \( S = -\frac{\Delta V}{\Delta T} \), where \( \Delta V \) is the voltage difference generated between the two ends of the junction when temperature difference \( \Delta T \) is established between them. Finally, we evaluated the figure of merit values by using \( ZT = \frac{S^2 GT}{\kappa} \), where \( T \) is the temperature and \( \kappa \) is the thermal conductivity in which only the electronic contribution is considered while the phonon contribution is neglected as there are no direct measuring methods.

![Figure 1: Illustrates the investigated molecular structures that consist of five different possible structures as: phthalocyanine monomer free-base structure (1), monomer zinc structure (2), dimer free-base structure (3), dimer zinc-free-base structure (4), and dimer zinc structure (5).](image)

3. Results and Discussion

Since phthalocyanine sometimes shows spintronic properties [37-41], with this notation, all calculation in our work will be spin dependent. Therefore, we calculate the transmission function \( T^{\uparrow} \) for majority and \( T^{\downarrow} \) for minority spins. The total transmission function is defined to be \( T(E) = (T^{\uparrow} + T^{\downarrow}) \).

Fig. 1 shows five different investigated phthalocyanine structures, two monomers (a), and three dimers (b). Those studied structures can be described as follows; structure 1 refers to a free base phthalocyanine monomer \( (M=2H) \), structure 2 represents a zinc phthalocyanine monomer \( (M=Zn) \), structure 3 refers to a phthalocyanine dimer with two free base phthalocyanine \( (M_1=2H, M_2=2H) \), while structure 4 comprises two phthalocyanine one with zinc and the second free base \( (M_1=Zn, M_2=2H) \). Finally, structure 5 refers to a zinc phthalocyanine dimer \( (M_1=Zn, M_2=Zn) \) [42, 43].

Fig. 2a and b show the spin up (red line), the spin down (green dashed line), and total transmission coefficient (blue line) for the phthalocyanine monomer for \( M=2H \) (a), and for
M=Zn (b). Fig. 2c-e show the spin dependent and total transmission functions for the phthalocyanine dimers for M$_1$=M$_2$=2H (c), for M$_1$=Zn, M$_2$=2H (d), and for M$_1$=M$_2$=Zn (e). It can be demonstrated that the transmission functions are independent of spin, which confirms that all structures 1 to 5 are not spin polarized. This can be explained by referring to the square planar molecular geometry used in this work, and orbital diagram of transition metal according to crystal field theory.

![Graphs showing transmission functions](image)

Figure 2: Shows the spin-dependent and total transmission coefficient as a function of energy for; (a) the phthalocyanine monomers for M=2H, (b) for M=Zn, (c) the phthalocyanine dimers for M$_1$=M$_2$=2H, (d) for M$_1$=Zn, M$_2$=2H, and (e) for M$_1$=M$_2$=Zn.

Fig.3a shows the total transmission coefficient as a function of energy for all structures 1 to 5. It can be seen clearly that only the phthalocyanine dimer structures show fano-resonances, which is close to the Fermi energy in the free base phthalocyanine dimer. However, when zinc atom presents in the phthalocyanine dimer, these fano-resonances start to shift apart from the Fermi level.

Fig.3b shows the corresponding electrical conductance versus Fermi energy. It reveals that the phthalocyanine monomer structures 1 and 2 have the highest conductivity value in the area around the Fermi energy in comparison to conductivity values of the phthalocyanine dimer structures 3, 4, and 5.
Figure 3: Shows the total transmission coefficient as a function of energy (a), and the room temperature electrical conductance for all structures (b).

Fig. 4a shows the Seebeck coefficients as a function of Fermi energy $E_F$. It reveals that the zinc phthalocyanine monomer 2 has the higher positive value of Seebeck coefficient while, the free base phthalocyanine dimer 3 has the higher negative value of Seebeck coefficient than other phthalocyanine structures over a wide range of Fermi energies. The electronic contribution to the thermal conductance has been shown in Fig.4b. It can be seen that the zinc phthalocyanine monomer 2 has the highest thermal conductance, while phthalocyanine dimer structures exhibit the lowest thermal conductance.

Figure 4: Shows the Seebeck coefficient $S$ (thermopower) (a), and electronic contribution of the thermal conductance for all five phthalocyanine structures (b).

Fig.5 shows the figure of merit ZT over a range of Fermi energies at room temperature. As it can be seen, the highest value of ZT belongs to the free base phthalocyanine dimer 3, whereas the phthalocyanine dimer 4 shows the lowest value. In spite of that the zinc phthalocyanine monomer 2 shows a high value in electrical conductance and thermopower but due to the highest value of thermal connectivity which appear in the denominator in the ZT equation (see method), this lead to reduce the ZT value of this structure.
Therefore, this suggests that the free base phthalocyanine dimer \(3\) structure if used in \textit{trans} configuration are promising candidates for thermoelectrical application.

![Figure 5: Shows figure of merit ZT over a range of Fermi energies at room temperature for all five phthalocyanine structures.](image)

### 4. Conclusion

In this work, we have compared the electric and thermoelectric properties of phthalocyanine (Pc) molecule sandwiched between gold electrodes in five monomers and dimers structures. The calculation was carried out based on density functional theory (DFT) implemented by SIESTA. Transmission calculations \(T(E)\) of all five monomers/dimers were presented and showed no spin dependent with higher values for monomer structures around Fermi energy. The highest conductivity value in the area around the Fermi energy was recorded for the phthalocyanine monomer structures compared to conductivity values of the phthalocyanine dimer structures. Further, the Seebeck coefficient \(\langle S\rangle\), thermal conductance \(\langle k\rangle\) and figure of merit \(\langle ZT\rangle\) were calculated to investigate the thermoelectric properties. It was found that Seebeck coefficient \(\langle S\rangle\) values varies from positive to negative values for zinc phthalocyanine monomer \(2\) and free base phthalocyanine dimer \(3\) structures over a wide range of Fermi energies. The zinc phthalocyanine monomer structure shows the highest thermal conductance \(\langle k\rangle\), while phthalocyanine dimer structures exhibit the lowest thermal conductance in the vicinity of DFT predicted Fermi energy. Consequently, our results show that the free base phthalocyanine dimer possesses a high room-temperature figure of merit. This high \(ZT\) value can be attributed to the low thermal conductivity, in addition to the high values of Seebeck coefficient and electrical conductance. By combining all these transport properties, a room-temperature figure of merit of \(ZT \approx 1.7\) can be obtained.

### Conflicts of interest

There are no conflicts to declare.

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