Tuning the Electrical and Thermoelectric Properties of Phthalocyanine and Metallo-Phthalocyanine Molecular Junction

Alaa Ayad K. Al-mebir*,a,b; Mohammed D. Noori c; and Bahjat B. Kadhim a

a Department of Physics, Collage of Sciences, Mustansiriyah University, Baghdad, Iraq
b Department of Physics, Collage of Education for Pure Sciences, University of Thi-Qar, Thi-Qar, Iraq
c Department of Physics, Collage of Sciences, University of Thi-Qar, Thi-Qar, Iraq

* Corresponding Author: alaaayad.eps@utq.edu.iq

Abstract: In this work, a comparative study is presented that analyses the electrical and thermoelectrical properties of free base-Phthalocyanine (Bare-Pc) and Metallo-Phthalocyanine (MPc) molecule sandwiched between gold electrodes. The study investigates the transmission and conductance characteristics of Bare-Pc without central metal ion and with different transition metal ions at the centre of (Pc) such as (Mn, Co, Ni, and Zn) in two different molecular configurations, cis and trans. The results reveal that the conductance changed by varying the transition metal-centre in the order of Co > Ni > Zn in trans, and closely similar pattern Co > Ni > Mn in cis with higher values in trans configuration. This reflects the correlation between the spin-dependent transport properties with the transition metal-centre type and the molecular structure. Further, thermoelectrical properties such as thermal conductance ($k$), Seebeck coefficient ($S$) and figure of merit ($ZT$) are investigated. It was found that ($k$), ($S$) and ($ZT$) have higher values in case of trans configuration for Co-Pc, Ni-Pc and Zn-Pc structures. Thus, by varying the transition metal-centre type and the molecular configuration of (Pc) molecule, transport properties can be tuned to produce a good value of the transmission and electrical conductance, thermal conductance, Seebeck coefficient, and figure of merit of the (Pc) molecular junction for potential high conductance and efficient thermoelectric applications.

1. Introduction:
Nowadays, more than 10% of the world’s electricity that is used by computers and the internet is converted to heat. This wasted heat could be used to generate electricity economically by identifying new materials with a high thermoelectric efficiency [1]. The possibility of generating a voltage difference from a heat gradient, Seebeck effect, has been already introduced since the early 19th century [2]. This effect is devoted to enhancing electric current generation by investing the wasted heat that exists in some physical structures like automobile exhausts or accompanies some mechanisms such as...
most industrial manufacturing processes. Recently, much attention has been given to enhance the efficiency of this effect by studying the parameters that control the thermoelectrical properties, especially of molecular materials and devices [3-7]. Thermoelectric figure of merit (ZT) is mainly used to determine the efficiency of thermoelectrical materials. It is given by (ZT=S²GT/κ), where S is the Seebeck coefficient, G is the electrical conductance, T is the temperate and κ is the electronic thermal conductivity.

Although the commonly used thermoelectric materials are inorganic, however, there is an increased interest in using organic thermoelectric materials to avoid many downsides of using inorganic materials such as toxicity, availability, and high cost. Besides, the thermoelectric properties of inorganic materials can be tuned by considering nano-structuring characteristics [8, 9], thus, there is particular interest in exploiting the room-temperature characteristics of single-molecules attached to nanogap electrodes, which represents a nano-device. Up to now, 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], wiring circuit [16], magnets [17], quantum dots [18, 19] switches [20, 21], and biology systems [22, 23].

Among several potential organic molecular candidates for nano scale application, phthalocyanine (Pc) has attracted huge attention for many years due to its distinguished high chemical and thermal stabilities and ideal symmetric geometrical structure [24-26]. Its electronic structure, magnetic, chemical, as well as transport characteristics can be tuned by inserting host central metallic ion. Such materials are known as metallo-phthalocyanines (MPc) that have been considered in many applications from organic thin film transistors [27], chemical sensors [28] to optoelectronic and photovoltaic devices [29-32], and have been investigated with techniques such as scanning tunneling spectroscopy (STS) [33] photoemission spectroscopy [34], gas phase electron diffraction [35], nuclear magnetic resonance [36], etc. However, much of these studies were based on experiments approach, and thus more deep theoretical analysis needed to be addressed in this field.

In what follows, the aim in this work is to explore the potential of the metallo-phthalocyanine (MPc) molecular junctions shown in Fig. 1 for high-efficiency thermoelectricity. We will demonstrate the use of density functional theory DFT to calculate the transmission coefficient T(E), which describes electrons of energy E and spin σ=[↑, ↓] passing from one electrode to the other through the metallo-phthalocyanine (MPc) single-molecule, and then discuss the electrical conductance G obtained using the Landauer formula (see method). Here, we will present a comparative theoretical study of the transmission and conductance characteristics as well as Seebeck coefficient and figure of merit behaviour of phthalocyanine (Pc) and metallo-phthalocyanine (MPc) single-molecule as a promising material for thermoelectrical applications. As shown in Fig. 1 the single (Pc) molecule is sandwiched between gold electrodes in two different configurations cis and trans, and it used first in the form of free base (Bare-Pc) and then variety of different metals such as (M= Mn, Co, Ni, and Zn) are embedded in the centre of (Pc) molecule to present the comparison.

2. Methods:
First, the cis and trans molecular geometry that shown in Fig. 1 was optimized before building the junction model. Then, the geometry of each structure that consist of two gold electrodes and a single Bare-phthalocyanine (Bare-Pc) and metallo-phthalocyanine (MPc) molecule were optimized using the SIESTA code [37] implementation of density functional theory (DFT), with a double-ζ polarized basis set (DZP) and generalized gradient functional approximation (GGA-PBE) for the exchange and correlation functionals. We then merge the DFT Hamiltonian with our quantum transport code, GOLLUM [38] to calculate the transmission coefficient T₀(E) that refers to the probability that electrons with energy E and spin σ=[↑, ↓] can pass from the left to the right gold electrode through the single molecule. After that, the conductance was calculated using the calculated transmission coefficient T₀(E), and the
Electrical conductance $G$ is given by the Landauer formula, which is given by:

$$G = G_{(up)} + G_{(down)} = G_0 \int_{-\infty}^{\infty} dE T(E) \left[- \frac{\partial f(E, T)}{\partial E}\right],$$

where $f(E, T)$ is the Fermi distribution function given by:

$$f(E, T) = \left(\frac{e^{(E-E_f)/K_BT} + 1}{e^{(E-E_f)/K_BT} + 1}\right)^{-1},$$

where $K_B$ is Boltzmann’s constant and $G_0 = \left(\frac{2e^2}{h}\right)$ is the quantum of conductance. Further, the Seebeck coefficient which characterizes the ability of a thermoelectric material to convert heat to electricity 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. This leads to finally evaluate the figure of merit values given by:

$$ZT = S^2 T \frac{G}{\kappa},$$

where $T$ is the temperature and $\kappa$ is the thermal conductivity in which only the electronic part is considered while the phonon contribution is neglected as considered by most studied because there are no direct measuring methods.

![Figure 1](image)

Figure 1: Free base-Phthalocyanine (Bare-Pc) and Metallo-Phthalocyanine (MPc) single-molecule structure sandwiched between two gold electrodes in two different configurations cis and trans.

### 3. Results and Discussion

After obtaining the relaxed geometry of each system, molecule sandwiched between two gold electrodes in two different configurations cis and trans as shown in Fig. 1. In order to investigate the electrical and thermoelectric properties of each MPc, and since the d-orbitals of metallic atoms in the centre of phthalocyanine could be partially filled, so for each molecular
juncture we used the spin density functional theory (DFT) code SIESTA, to obtain the electron and spin transport properties, using the Gollum code. Here, the transmission function has been calculated for a majority and minority spin denoted by spin up (↑) and down (↓). The total function of the transmission is defined as \( T(E) = (T↑ + T↓) \).

Figure 2 illustrates the spin-up (red line), the spin-down (yellow line), and the total transmission coefficient (blue line) for Bare-Pc and MPc, where M=Mn, Co, Ni, and Zn in two different configurations, cis and trans. From the transmission curves, we can carry out a spin state test. In Fig. 2, the transmission curves of Bare-Pc in both configurations cis (a) and trans (b) show non spintronic properties since the spin up and spin down curves are equal. While the transmission curves of Mn-Pc in both configurations cis (c) and trans (d) and Co-Pc in both configurations cis (e) and trans (f) show spintronic properties. 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 in which both (Mn and Co) metals have unpaired electrons in the last d orbital. However, Ni-Pc and Zn-Pc show non spintronic properties in both cases cis and trans as shown in Fig 2. (g, h) and (i, j), respectively, because both (Ni) and (Zn) metals have paired electrons in the last d orbital. Also, it is found that transmission curves of Bara-Pc are higher in the case of trans connection (b) than in cis connection (a), which represented by the extra resonances / fanoresonances in the vicinity of Fermi energy predicted by DFT. This is also true in almost all followed (MPC) cases except Mn-Pc.
Figure 2: Shows the transmission coefficient of Bare-Pc in (a) cis and (b) trans, (Mn-Pc) in (c) cis and (d) trans, (Co-Pc) in (e) cis and (f) trans, (Ni-Pc) in (g) cis and (h) trans, (Zn-Pc) in (i) cis and (j) trans configurations.

The total room temperature electrical conductance for Bare-Pc and MPc in both cis and trans configurations are shown in Fig.3a and Fig.3b, respectively. In both cis and trans configurations, the electrical conductance of Co-Pc, and Ni-Pc show higher values than of other cases. Fig.3c shows the total conductance at the DFT Fermi energy (EF=0 eV) and shows that the pattern of increasing conductance in trans is Co > Ni > Zn, and closely similar pattern in cis Co > Ni > Mn. Fig.3c also shows that the conductance of Bare-Pc and Mn-Pc has close values in both cis and trans cases.
Figure 3: Shows the electrical conductance \( G \) comparison between Bare-Pc, Mn-Pc, Co-Pc, Ni-Pc, and Zn-Pc in \textit{cis} (a) and \textit{trans} (b) configurations. (c) shows comparison of \( G \) values for all studied structures.

Thermal conductance \( k \) as a function of energy is found to be higher in \textit{trans} than \textit{cis} configuration in the vicinity of DFT predicted Fermi energy for Bare-Pc, Co-Pc, Ni-Pc, and Zn-Pc as shown in Fig. 4. While \( k \) is equal in \textit{cis} and \textit{trans} in the case of Mn-Pc.

Figure (4): Shows thermal conductance \( k \) as a function of energy of Bare-Pc, Mn-Pc, Co-Pc, Ni-Pc, and Zn-Pc in \textit{cis} (a) and \textit{trans} (b) configurations.
To test the thermoelectric properties of all structures in both configurations, we have obtained the Seebeck coefficient ($S$) as described in the Method section and shown in Fig. 5 (a and b) as a function of Fermi energy $E_F$. It should be mentioned that it is well-known that the Fermi energy $E_F$ predicted by DFT could be inaccurate. Thus, Fermi energy $E_F$ treat here as a single free parameter. The results demonstrate that both the magnitude and sign of thermopower ($S$) are sensitive to the metal atoms at the centre of the phthalocyanines, which determine the location of transport resonances relative to the Fermi energy. Fig. 5c shows the comparison between the room-temperature values of ($S$) for Bare-Pc and MPc evaluated at the DFT Fermi energy (EF=0 eV). It shows that the highest values of the thermopower occurs at the DFT-predicted Fermi energy are obtained in the presence of Ni, Co, and Zn in both cis and trans configurations. The lowest values of the thermopower of all are obtained for Mn, closely followed by Bare-Pc.

Figure (5): Shows Seebeck coefficient ($S$) curves of Bare-(Pc), Mn-Pc, Co-Pc, Ni-Pc, and Zn-Pc in cis (a) and trans (b) configurations. (c) shows the comparison of ($S$) values for all studied structures.

As a result, the figure of merit ($ZT$) can be obtained next as explained in the method and as shown in Fig. (6), which shows that ($ZT$) in trans connection is higher than cis connection in case of Co-Pc, Ni-Pc and Zn-Pc. This is due to the better transmission $T(E)$, electrical conductance ($G$), thermal conductance ($k$) and Seebeck coefficient ($S$) values in trans connection than cis connection in these structures. However, ($ZT$) values in cis connection are
higher in case of Bare-Pc and Mn-Pc due to their slightly higher \((S)\) values in \(cis\) connection. This can clearly interduce that \((ZT)\) values are very sensitive to the change of \((S)\) values as well as type of used configuration. High values of \((ZT)\), (greater than 1 as shown in Fig. 6c), are obtained for Co-Pc, Ni-Pc in \(trans\) configuration when \(E_F\) lies in an energy window in the vicinity of the DFT-predicted Fermi energy. Therefore, this suggests that these structures if used in \(trans\) configuration are promising candidates for thermoelectrical application.

![Graph showing ZT values](image)

**Figure (6):** Shows the figure of merit \((ZT)\) values of Bare-Pc, Mn-Pc, Co-Pc, Ni-Pc, and Zn-Pc in \(cis\) (a) and \(trans\) (b) configurations. (c) shows comparison of \((ZT)\) values for all studied structures.

### 4. Conclusion

We have investigated the electrical properties of free base-Phthalocyanine (Bare-Pc) and Metallo-Phthalocyanine (MPc) molecule sandwiched between gold electrodes in two different molecular configurations, \(cis\) and \(trans\). SIESTA implementation of density functional theory (DFT) has been used to carry out the analysis. Transmission calculations \(T(E)\) of Bare-Pc and MPc, where \(M=Mn, Co, Ni, and Zn\) were presented, and it shows that \(T(E)\) is higher in \(trans\) connection in all cases except for Mn-Pc. Also, the electrical conductance \((G)\) results show that the highest value recorded in \(trans\) configuration for Co, Ni, and Zn. It was found that the conductance varies through this family of molecules in the order \(Co > Ni > Zn\) in \(trans\), and closely similar pattern \(Co > Ni > Mn\) in \(cis\). Therefore, single molecule junctions in the order \(Co > Ni > Zn\) in \(trans\) configuration can be considered as a potential system for high-conductance (Pc) single-molecule applications. Further, thermoelectric properties were investigated by calculating the thermal conductance \((k)\), Seebeck coefficient \((S)\) and figure of merit \((ZT)\). It was found that \((k)\) is higher in \(trans\) than \(cis\) configuration.
in the vicinity of DFT predicted Fermi energy in all structures except Mn-Pc. Also, it was found that the energies of transport resonances can be tuned through the choice of central metal atom, leading to rather large positive and negative thermopowers ($S$) range from $\sim -60 \mu V/K$ for Mn-Pc in cis configuration to $\sim 205 \mu V/K$ for Ni in trans configuration. Consequently, enhanced ($ZT$) values (greater than 1) obtained in trans connection in case of Co-Pc and Ni-Pc which suggested them to be highly recommended and promising candidates for the application of thermoelectrical field.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
This work is supported by the Ministry of Higher Education and Scientific Research, Al-Mustansiryah University and University of Thi-Qar, Iraq.

References
[1] Noori, M.D., S. Sangtarash, and H. Sadeghi, The Effect of Anchor Group on the Phonon Thermal Conductance of Single Molecule Junctions. Applied Sciences, 2021. 11(3): p. 1066.
[2] Seebeck, T.J., Ueber die magnetische Polarisation der Metalle und Erze durch Temperaturdifferenz. Annalen der Physik, 1826. 82(3): p. 253-286.
[3] Al-Jobory, A.A. and M.D. Noori, Thermoelectric Properties of Metallocene Derivative Single-Molecule Junctions. Journal of Electronic Materials, 2020. 49(9): p. 5455-5459.
[4] Noori, M., H. Sadeghi, and C.J. Lambert, Stable-radicals increase the conductance and Seebeck coefficient of graphene nanoconstrictions. Nanoscale, 2018. 10(40): p. 19220-19223.
[5] Noori, M., et al., High cross-plane thermoelectric performance of metallo-porphyrin molecular junctions. Physical Chemistry Chemical Physics, 2017. 19(26): p. 17356-17359.
[6] Al-Jobory, A.A. and M.D. Noori, Electrical and thermal properties of GaAs 1− x P x 2D-nanostructures. The European Physical Journal D, 2019. 73(10): p. 223.
[7] Noori, M., H. Sadeghi, and C.J. Lambert, High-performance thermoelectricity in edge-over-edge zinc-porphyrin molecular wires. Nanoscale, 2017. 9(16): p. 5299-5304.
[8] Yanagi, K., et al., Tuning of the thermoelectric properties of one-dimensional material networks by electric double layer techniques using ionic liquids. Nano letters, 2014. 14(11): p. 6437-6442.
[9] Poudel, B., et al., High-thermoelectric performance of nanostructured bismuth antimony telluride bulk alloys. Science, 2008. 320(5876): p. 634-638.
[10] Leary, E., et al., Bias-driven conductance increase with length in porphyrin tapes. Journal of the American Chemical Society, 2018. 140(40): p. 12877-12883.
[11] Leary, E., et al., Detecting mechanochemical atropisomerization within an STM break junction. Journal of the American Chemical Society, 2018. 140(2): p. 710-718.
[12] Noori, M., Quantum Theory of Electron Transport Through Photo-Synthetic Porphyrins. 2017, Lancaster University.
[13] Low, P.J. and S. Marqués-González, Molecular wires: an overview of the building blocks of molecular electronics, in Single-Molecule Electronics. 2016, Springer. p. 87-116.
[14] Ke, S.-H., H.U. Baranger, and W. Yang, Models of electrodes and contacts in molecular electronics. The Journal of chemical physics, 2005. 123(11): p. 114701.
[15] Schull, G., et al., Atomic-scale engineering of electrodes for single-molecule contacts. Nature nanotechnology, 2011. 6(1): p. 23.
[16] Lörtscher, E., Wiring molecules into circuits. Nature nanotechnology, 2013. 8(6): p. 381.
[17] Bartolome, S.J., F. Luis, and J.F. Fernández, Molecular magnets. 2016: Springer.
[18] Al-mebir, A.A.K. and S.A. AL-Saidi, *Tuning Optoelectronic Properties of Double Quantum Dot Structure Using Tight-Binding Model for Photo-Electric Applications*. NeuroQuantology, 2021. 19(3): p. 1.

[19] AL-Saidi, S.A. and A.A.K. Al-mebir, *Asymmetric Double Quantum Dot Structure as Nanoscale Diode*. University of Thi-Qar Journal, 2018. 13(4): p. 1-17.

[20] Liu, Z., S. Ren, and X. Guo, *Switching effects in molecular electronic devices*, in Molecular-Scale Electronics. 2019, Springer. p. 173-205.

[21] AL-Saidi, S.A., A.A.K. Al-mebir, and M. Hallool, *Characteristics of Thymine Molecule System Behave as Molecular Electronic Device*. Misran Journal of Academic Studies, 2019. 18(35): p. 130-143.

[22] Al-mebir, A.A.K. and S.A. AL-Saidi. *Theoretical Investigation of Base Pairs-Dependent Electron Transport in DNA System*. in Journal of Physics: Conference Series. 2020. IOP Publishing.

[23] Al-Saidi, S.A. and A.A.K. Al-mebir. *Electronic Properties Simulation of Guanine Molecule*. in Journal of Physics: Conference Series. 2020. IOP Publishing.

[24] McKeown, N.B., *Phthalocyanine materials: synthesis, structure and function*. 1998: Cambridge University Press.

[25] de la Torre, G., G. Bottari, and T. Torres, *Phthalocyanines and subphthalocyanines: Perfect partners for fullerenes and carbon nanotubes in molecular photovoltaics*. Advanced Energy Materials, 2017. 7(10): p. 1601700.

[26] Denekamp, I.M., et al., *A simple synthesis of symmetric phthalocyanines and their respective perfluoro and transition- metal complexes*. Applied Organometallic Chemistry, 2019. 33(5): p. e4872.

[27] Boileau, N.T., et al., *Metal phthalocyanine organic thin-film transistors: Changes in electrical performance and stability in response to temperature and environment*. RSC advances, 2019. 9(37): p. 21478-21485.

[28] Chaabene, M., et al., *New zinc phthalocyanine derivatives for nitrogen dioxide sensors: A theoretical optoelectronic investigation*. Journal of Molecular Graphics and Modelling, 2019. 88: p. 174-182.

[29] Islam, Z.U., et al., *Fabrication and Photovoltaic Properties of Organic Solar Cell Based on Zinc Phthalocyanine*. Energies, 2020. 13(4): p. 962.

[30] Feng, S., et al., *Phthalocyanine and Metal Phthalocyanines Adsorbed on Graphene: A Density Functional Study*. The Journal of Physical Chemistry C, 2019. 123(27): p. 16614-16620.

[31] Walter, M.G., A.B. Rudine, and C.C. Wamser, *Porphyrins and phthalocyanines in solar photovoltaic cells*. Journal of Porphyrins and Phthalocyanines, 2010. 14(09): p. 759-792.

[32] Urbani, M., et al., *Phthalocyanines for dye-sensitized solar cells*. Coordination Chemistry Reviews, 2019. 381: p. 1-64.

[33] Sedghi, G., et al., *Single molecule conductance of porphyrin wires with ultralow attenuation*. Journal of the American Chemical Society, 2008. 130(27): p. 8582-8583.

[34] Lozzi, L., et al., *Cu Pc: C 60 blend film: A photoemission investigation*. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 2006. 24(4): p. 1668-1675.

[35] Mastryukov, V., et al., *The molecular structure of copper-and nickel-phthalocyanine as determined by gas-phase electron diffraction and ab initio/DFT computations*. Journal of Molecular Structure, 2000. 556(1-3): p. 225-237.

[36] Filibian, M., et al., *Low-energy excitations in the electron-doped metal phthalocyanine Li 0.5 MnPc from Li 7 and H 1 NMR*. Physical Review B, 2007. 75(8): p. 085107.

[37] Soler, J.M., et al., *The SIESTA method for ab initio order-N materials simulation*. Journal of Physics: Condensed Matter, 2002. 14(11): p. 2745.

[38] Ferrer, J., et al., *GOLLUM: a next-generation simulation tool for electron, thermal and spin transport*. New Journal of Physics, 2014. 16(9): p. 093029.