University of Thi-Qar Journal of Science (UTJsci)
E-ISSN: 2709-0256, P-ISSN: 1991-8690, Vol. 10, No. 2, Dec. 2023

The Effect of Linker Group on Thermoelectric Properties of Dimer Zinc Porphyrin-Based Molecular Junctions

1st Dhia S. Alkhafaji
Department of Physics/ Faculty of Science/ University of Mazandaran
Thi Qar / Iraq
dhiyaa1982@gmail.com

2nd Mohammed D. Noori
Department of Physics/ Faculty of Science/ University of Thi-Qar
Thi Qar / Iraq
mo845692@gmail.com

3rd Hossain M. Moghaddam
Department of Physics/ Faculty of Science/ University of Mazandaran
Mazandaran / Iran
milani@umz.ac.ir

Received: 2023-11-21, Revised: 2023-12-12, Accepted: 2023-12-17, Published: 2023-12-26

***Abstract*— The discovery of high-efficiency organic thermoelectric materials has the potential to pave the path for various energy-gathering innovations and the development of translucent, pliable thin-film materials for Peltier coolers. Our study involves a comparison of the electrical and thermoelectric characteristics of five zinc porphyrin configurations. The results show that changing the linker between zinc diner units has an essential effect on the electrical conductance and thermopower values of these structures. Consequently, the thermoelectric figure of merit ZT will change which means the thermoelectric efficiency change. We also observed a notable augmentation in the Seebeck coefficient when the linker connecting the Zinc porphyrin dimers is either (C - N) or (C - C). The augment in the Seebeck coefficient can be ascribed to a variety of factors. One plausible reason for this phenomenon is the dissimilarity in the electronic structure and energy levels between the zinc porphyrin molecule and the carbon-hydrogen linker. This dissimilarity has the potential to induce a modification in the density of states in the vicinity of the Fermi level, ultimately leading to an amplified thermopower.**

***Keywords*— Zinc porphyrin; electrical conductance; thermopower; molecular junctions**

I. INTRODUCTION

Waste heat electricity generation has garnered significant attention, with a particular focus on exploring the thermoelectric attributes and identifying novel materials with enhanced thermoelectric efficiency [1, 2]. The fundamental concept of thermoelectricity is rooted in the Seebeck effect, which was initially proposed in the early nineteenth century [3, 4]. This phenomenon involves the generation of an electrical voltage gradient from a thermal gradient and aims to harness the wasted heat in specific physical systems, such as automotive exhausts, or the excess heat produced by various industrial processes, to enhance electrical current production [5, 6]. The field of molecular electronics has experienced a surge of interest since the pioneering work of Aviram and Ratner, who introduced the concept of a molecular diode for downsizing electronic components [7-10]. Molecules, being the smallest building blocks capable of performing specific electrical functions, offer structural versatility that can be tailored and modified. Aromatic organic molecules, due to their high chemical stability and conjugation, hold significant promise in the realm of molecular electronics [11, 12] . Among various metal complexes, porphyrins and their derivatives exhibit a remarkable array of optical and electronic properties that render them indispensable in diverse fields, including biochemical processes, catalysis, electronics, photonics, nonlinear optics, and more. The porphyrin structure can be described as a planar aromatic system with a central cavity capable of hosting various metals like Co, Zn, Fe, and others, forming metalloporphyrins. In recent years, there has been extensive experimental and theoretical [13-17] research on porphyrins and metalloporphyrins, emphasizing the need to investigate the fundamental relationships between their structure and electrical properties at the single-molecule level to construct molecular devices. In order to discover more about the electrical transportation characteristics of individual molecules, a variety of techniques for forming molecular junctions and assessing their conductance have been designed [13, 18]. Various investigations have been carried out to date to design and control electronic molecules [13, 19]. These developments are geared toward future applications in nanoelectronic circuits, such as molecular wires [20] electrodes [21] wiring circuits [22] magnets [23] quantum dots [24] switches [25] and biological systems [26]. Recently, there has been a strong emphasis on fine-tuning the parameters that govern thermoelectric characteristics, especially concerning device architectures and molecular materials [6]. ZT, or the thermoelectric figure of merit, is a crucial measure of the efficiency of thermoelectric materials. It may be computed using the formula $ZT=S^2GT/\kappa$, in where S stands for the Seebeck coefficient, G for electrical conductance, T for temperature, and κ for electronic thermal conductivity. Low (κ), high (G), and high (S) materials are therefore in demand. Additionally, studying the thermoelectric characteristics of

https://doi.org/10.32792/utq/utjsci/v10i2.1133

metalloporphyrins attached to gold electrodes has shown that different types of linkers can adjust molecular energy levels in relation to the electrodes' Fermi energy (EF), which in turn can adjust the thermoelectric properties of metalloporphyrins [27, 28]. This discovery makes metalloporphyrins even more appealing for molecular-scale thermoelectric devices. Hence, an exploration of their transport properties is anticipated to shed light on how alterations in the horizontal bonding of porphyrin molecules affect charge transfer distributions and subsequently influence their thermoelectric properties. Consequently, our research aims to contribute to the theoretical advancement of studies focused on the thermoelectric properties of dimer zinc porphyrin junctions for potential high-efficiency thermoelectric devices, the results indicate that various linker types can indeed alter the electrical and thermoelectric properties, emphasizing the necessity of theoretical modelling in the study of electron transport in various molecules.

II. METHOD

In Figure 1, SIESTA was utilized to optimize the geometrical structure of each zinc porphyrin molecule wedged between two gold electrodes [29]. Density functional theory is implemented using a double-polarized basis set and a generalized gradient functional approximation for the correlation and exchange functionals. The quantum transport code Gollum combined with the underlying mean-field Hamiltonian (H) [30] by using each ground state structure's DFT mean-field Hamiltonian [19]. The transmission coefficient should be determined. The Landauer formula may be used to obtain the electrical conductance G formula, which is G= G0. $\int_{-\infty}^{\infty} dE$ (E-$E_f)^n \, T_{el}(E)[-\frac{\partial f(E,T)}{\partial E}]$, was then used to calculate the conductance using the estimated transmission coefficient, where f (E, T) is the fermi distribution function and G0 = $2e^2/h$ is the quantum of conductance. Moreover, the capacity of a thermoelectric material to transform heat into electricity is defined by the formula S = −ΔV/ΔT. Here, ΔV stands for the voltage that is produced when a temperature differential of ΔT is developed between the junction's two ends.

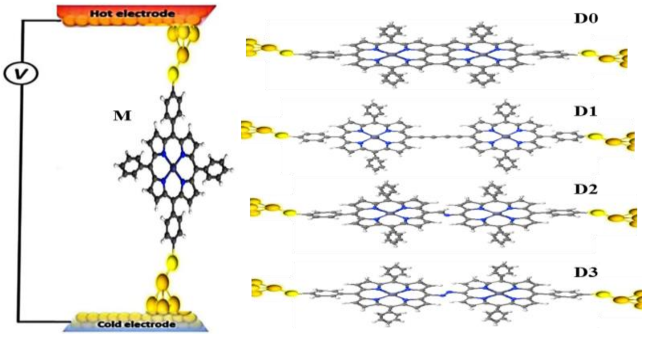

Fig: 1 depicts the molecular structures under investigation, encompassing the monomer zinc structure **M**, a dimer zinc structure with strong coupling labeled as **D0**, and a dimer with moderate inter-porphyrin coupling, encompassing **D1**($C \equiv C$), **D2** ($C - N$), and **D3** ($N - N$), connected between gold electrodes [31].

III. RESULTS AND DISCUSSION

Despite all these structures being constructed, from ZnP, this research highlights the crucial role of molecular design. Figure 1 illustrates various structures of zinc porphyrin (ZnP) examined in this study all these structures have been optimized Four Zn-triphenylporphyrin (TriPP) complexes meso–meso linked by two-atom bridges , namely, C2H2 , C2, CH=N, and N2, were investigated, for comparison of electrical and thermoelectric properties . The initial structure represents a ZnP monomer **M**. Also, we explore Zinc porphyrin dimers in two families, one exhibiting strong inter-porphyrin coupling and the other demonstrating moderate coupling. Stronger coupling is achieved through the direct connection of the dimer porphyrin units, creating structure **D0**, while moderate coupling is attained using double triple-bond linkers in structure **D1**. Modifications to the linker type C-N in D2 and C-N in **D3** are also investigated.

For a comprehensive and clear comparison, Figure 2a shows transmission curves for all structures (monomer and dimers), plotting the transmission coefficient as a function of energy. Notably, Clearly D0 has a far higher transmission coefficient than the other structures. In Figure 3b, we observe that **D0** and **M** exhibit distinct electrical conductivity values in the vicinity of the Fermi energy, with **D0** displaying higher values. While, **D2** exhibits the lowest electrical conductance values among the structures.

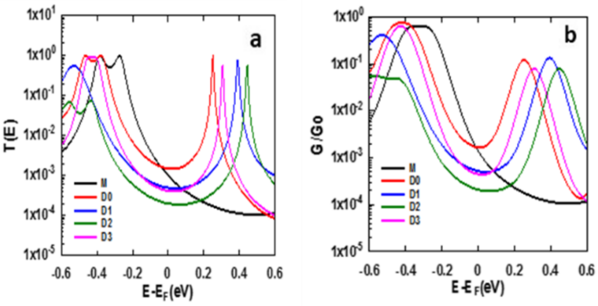

Fig: 2 display two plots: (a) illustrates the total transmission coefficient as a function of energy, while (b) presents the electrical conductivity of every structure under examination at room temperature.

To explore the thermoelectric properties of these structures, we calculated the Seebeck coefficient (S). Our results revealed that both the magnitude and sign of (S) exhibit sensitivity to the linker of the junction. In Figure 3a, we observe that the **M, D2, and D3** structures exhibit higher thermopower values compared to the other structures. Figure **3b** shows the relationship between thermal conductivity and energy. Notably, there is a substantial variation in the thermal conductivity across the five configurations, with the **M** and **D0** structures displaying the highest values, particularly around the Fermi energy.

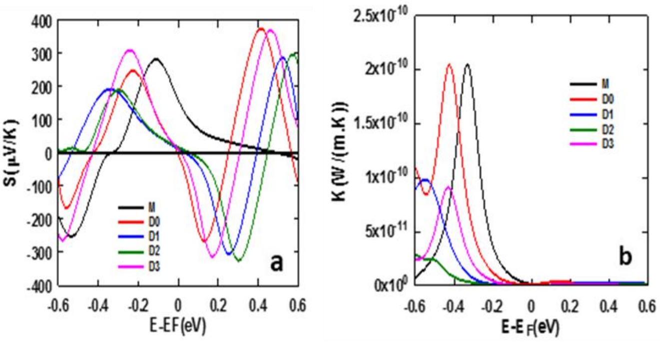

Fig: 3 shows the, Seebeck coefficient (thermopower) S (a), and the electronic contribution to thermal conductance for all structures (b).

In Figure 3a, the structure **M** exhibits a notably higher Seebeck coefficient, resulting in a greater ZT value (approximately ZT≈ 0.4). In Figure 4b inset figure shows closer view of the differences in the ZT values However, Fig. 4 demonstrated that the variations of linker lead to significant differences in the figure of merit. Among the dimer structures, **D2** demonstrates the highest ZT value, follow by **D1**. On the other hand, the **D0** structure shows the lower value of ZT around Fermi energy. This is due to the fact that electrical conductance and electronic thermal conductance, being interrelated, effectively negate each other in the ZT equation.

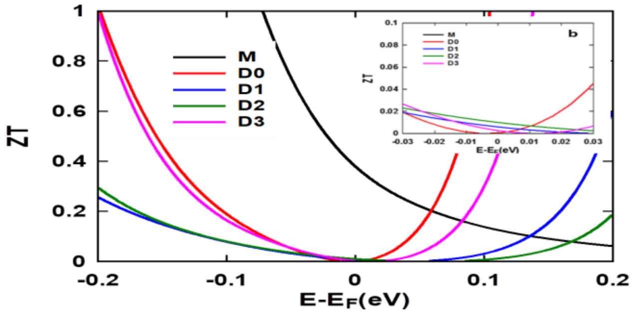

Fig: 4a shows five zinc porphyrin structures of merit (ZT) at different Fermi energies. b: ZT around window (-0.03 to 0.03).

IV. CONCLUSION

Overall, our study involved a comparison of the electrical and thermal characteristics of five distinct zinc porphyrin structures placed between pair of gold. The results demonstrated that the zinc monomer consistently exhibited the highest ZT value when compared to the dimer, In dimer case the results show that the changing of the linker between zinc dimer units has an essential effect on the room temperature electrical conductance G and thermopower S values of these structures. Which in turn the figure of merit ZT will change which means changing in the thermoelectric efficiency of these structures.

CONFLICT OF INTEREST

Authors declare that they have no conflict of interest.

REFERENCES

[1] M. D. Noori, S. Sangtarash, and H. Sadeghi, "The effect of anchor group on the phonon thermal conductance of single molecule junctions," *Applied Sciences*, vol. 11, p. 1066, 2021.

[2] A. A. K. Al-mebir, M. D. Noori, and B. B. Kadhim, "Tuning the Electrical and Thermoelectric Properties of Phthalocyanine and Metallo-Phthalocyanine Molecular Junction," in *Journal of Physics: Conference Series*, 2021, p. 012036.

[3] T. J. Seebeck, "Ueber die magnetische Polarisation der Metalle und Erze durch Temperaturdifferenz," *Annalen der Physik*, vol. 82, pp. 253-286, 1826.

[4] T. L. R. Bennett, "Synthesis and characterisation of novel molecular wires for studies of thermoelectricity," 2022.

[5] O. Albeydani, "Theoretical study of vertical van der Walls metal-porphyrin and metal free-porphyrin junctions," *Physica Scripta*, vol. 98, p. 085403, 2023.

[6] A. A. Al-Jobory and M. D. Noori, "Thermoelectric properties of metallocene derivative single-molecule junctions," *Journal of Electronic Materials*, vol. 49, pp. 5455-5459, 2020.

[7] D. Xiang, X. Wang, C. Jia, T. Lee, and X. Guo, "Molecular-scale electronics: from concept to function," *Chemical reviews*, vol. 116, pp. 4318-4440, 2016.

[8] A. Aviram and M. A. Ratner, "Molecular rectifiers," *Chemical physics letters*, vol. 29, pp. 277-283, 1974.

[9] A. A. Al-Jobory, Z. Y. Mijbil, and M. Noori, "Tuning electrical conductance of molecular junctions via multipath Ru-based metal complex wire," *Indian Journal of Physics*, vol. 94, pp. 1189-1194, 2020.

[10] A. A. Al-Jobory and M. D. Noori, "Electrical and thermal properties of GaAs 1− x P x 2D-nanostructures," *The European Physical Journal D*, vol. 73, pp. 1-4, 2019.

[11] D. Taherinia, C. E. Smith, S. Ghosh, S. O. Odoh, L. Balhorn, L. Gagliardi, *et al.*, "Charge transport in 4 nm molecular wires with interrupted conjugation: Combined experimental and computational evidence for thermally assisted polaron tunneling," *ACS nano*, vol. 10, pp. 4372-4383, 2016.

[12] J.-H. Zhu, Y.-G. Feng, A.-J. Wang, L.-P. Mei, X. Luo, and J.-J. Feng, "A signal-on photoelectrochemical aptasensor for chloramphenicol assay based on 3D self-supporting AgI/Ag/BiOI Z-scheme heterojunction arrays," *Biosensors and Bioelectronics*, vol. 181, p. 113158, 2021.

[13] E. Leary, B. Limburg, A. Alanazy, S. Sangtarash, I. Grace, K. Swada, *et al.*, "Bias-driven conductance increase with length in porphyrin tapes," *Journal of the American Chemical Society*, vol. 140, pp. 12877-12883, 2018.

[14] A. C. Aragonès, N. Darwish, W. J. Saletra, L. Pérez-García, F. Sanz, J. Puigmartí-Luis, *et al.*, "Highly conductive single-molecule wires with controlled orientation by coordination of metalloporphyrins," *Nano letters*, vol. 14, pp. 4751-4756, 2014.

[15] M. Noori, H. Sadeghi, Q. Al-Galiby, S. W. Bailey, and C. J. Lambert, "High cross-plane thermoelectric performance of metallo-porphyrin molecular junctions," *Physical Chemistry Chemical Physics,* vol. 19, pp. 17356-17359, 2017.

[16] N. Algethami, H. Sadeghi, S. Sangtarash, and C. J. Lambert, "The conductance of porphyrin-based molecular nanowires increases with length," *Nano Letters,* vol. 18, pp. 4482-4486, 2018.

[17] M. D. Noori, *Quantum Theory of Electron Transport Through Photo-Synthetic Porphyrins*: Lancaster University (United Kingdom), 2017.

[18] A. A. K. Al-mebir, M. D. Noori, and B. B. Kadhim, "Investigation of the electric and thermoelectric properties of metallo-phthalocyanine molecular junctions with planar and axial configuration," in *AIP Conference Proceedings,* 2023.

[19] M. Noori, A. C. Aragonès, G. Di Palma, N. Darwish, S. W. Bailey, Q. Al-Galiby, *et al.*, "Tuning the electrical conductance of metalloporphyrin supramolecular wires," *Scientific reports,* vol. 6, p. 37352, 2016.

[20] P. J. Low and S. Marqués-González, "Molecular wires: an overview of the building blocks of molecular electronics," *Single-Molecule Electronics: An Introduction to Synthesis, Measurement and Theory,* pp. 87-116, 2016.

[21] S.-H. Ke, H. U. Baranger, and W. Yang, "Models of electrodes and contacts in molecular electronics," *The Journal of chemical physics,* vol. 123, 2005.

[22] G. Schull, T. Frederiksen, A. Arnau, D. Sánchez-Portal, and R. Berndt, "Atomic-scale engineering of electrodes for single-molecule contacts," *Nature nanotechnology,* vol. 6, pp. 23-27, 2011.

[23] E. Lörtscher, "Wiring molecules into circuits," *Nature nanotechnology,* vol. 8, pp. 381-384, 2013.

[24] A. A. K. Al-mebir and S. A. AL-Saidi, "Tuning Optoelectronic Properties of Double Quantum Dot Structure Using Tight-Binding Model for Photo-Electric Applications," *NeuroQuantology,* vol. 19, p. 1, 2021.

[25] Z. Liu, S. Ren, and X. Guo, "Switching effects in molecular electronic devices," *Molecular-Scale Electronics: Current Status and Perspectives,* pp. 173-205, 2019.

[26] J. Guo, Y. Wang, H. Zhang, and Y. Zhao, "Conductive materials with elaborate micro/nanostructures for bioelectronics," *Advanced Materials,* vol. 34, p. 2110024, 2022.

[27] Y. Zhao, L. Liu, F. Zhang, C. a. Di, and D. Zhu, "Advances in organic thermoelectric materials and devices for smart applications," *SmartMat,* vol. 2, pp. 426-445, 2021.

[28] R. K. Almughathawi, *Quantum Theory of Electronic and Thermal Transport through Nanostructures*: Lancaster University (United Kingdom), 2022.

[29] H. Sadeghi, S. Sangtarash, and C. J. Lambert, "Oligoyne molecular junctions for efficient room temperature thermoelectric power generation," *Nano letters*, vol. 15, pp. 7467-7472, 2015.

[30] J. Ferrer, C. J. Lambert, V. M. García-Suárez, D. Z. Manrique, D. Visontai, L. Oroszlany, *et al.*, "GOLLUM: a next-generation simulation tool for electron, thermal and spin transport," *New Journal of Physics,* vol. 16, p. 093029, 2014.

[31] S. R. Harper, M. C. Pfrunder, L. J. Esdaile, P. Jensen, J. C. McMurtrie, and D. P. Arnold, "Synthetic, Structural, and Spectroscopic Studies of Bis (porphyrinzinc) Complexes Linked by Two-Atom Conjugating Bridges," *European Journal of Organic Chemistry,* vol. 2015, pp. 2807-2825, 2015.