Edelweiss Applied Science and Technology
ISSN: 2576-8484
Vol. 9, No. 2, 1830-1838
2025
Publisher: Learning Gate
DOI: 10.55214/25768484.v9i2.4936

Theoretical investigation of the impact of zinc ion in the center of trimer porphyrins on the electrical and thermoelectric properties

Ghofran Zamel Hassan[1*], Mohammed Deia Noori[2]
[1,2]Department of Physics, College of Sciences, University of Thi-Qar, Thi-Qar, Iraq; ghufran.hassan@utq.edu.iq (G.Z.H.).

Abstract: Thermoelectrics as a way to use waste heat is essential in many electronic applications. In this work, the effect of the appearance of zinc ions in the center of trimer porphyrins on the electronic and thermoelectric properties of zinc porphyrin trimer molecular junctions was investigated theoretically using a combination of density functional theory (DFT) methods. Our results show that all electronic and thermoelectric properties have been affected by the appearance of zinc ions in the center of porphyrin trimer units. However, the findings indicate that the presence of a zinc metal ion in the center of the porphyrin trimers with one, two, or three zinc ions significantly affects their electronic and thermal conductance, particularly in the vicinity of the Fermi energy.

Keywords: *Molecular junctions, Thermoelectrics, Zinc ions.*

1. Introduction

The performance of thermoelectric materials has been greatly improved by recent developments, allowing for effective waste heat recovery and the production of renewable energy. This helps to meet the pressing need for sustainable energy solutions and reduce greenhouse gas emissions in line with efforts to mitigate climate change [1]. The concept of generating a voltage disparity due to a temperature gradient, known as the Seebeck effect, was initially introduced during the early 19th century[2]. Nowadays, a significant focus has been on enhancing this phenomenon's effectiveness by examining the variables governing thermoelectrical properties, specifically molecular materials and devices. The thermoelectric figure of merit (ZT) is the primary metric for evaluating thermoelectrical materials' effectiveness. It is computed using the formula $ZT = S^2GT/\kappa$, where S represents the Seebeck coefficient, G denotes the electrical conductance, T signifies the temperature, and κ stands for the electronic thermal conductivity. This equation allows researchers to quantitatively assess the efficiency of thermoelectrical materials by considering their unique properties, such as the Seebeck coefficient, electrical conductance, temperature, and electronic thermal conductivity. Using the ZT value, scientists can compare and contrast different materials and determine their potential for thermoelectrical applications. This metric comprehensively evaluates a material's thermoelectric performance, enabling researchers to make informed decisions regarding developing and optimizing thermoelectrical materials[3-9].

However, a large number of theoretical and experimental investigations have been conducted to produce and manipulate electronic molecules [4, 10-12]. They have been adjusted for future applications in molecular wires and other nanoelectronics circuits [13], biological systems[14, 15], quantum dots [16, 17], electrodes [18, 19] and switches [20, 21].

Porphyrins are characterized by their highly conjugated structure, rigid planar geometry, and remarkable chemical stability, which enable them to form metalloporphyrins through the coordination of metal ions within their macrocyclic framework [22-24]. Of the metalloporphyrin families, zinc

History: Received: 20 December 2024; Revised: 28 January 2025; Accepted: 28 January 2025; Published: 20 February 2025
* Correspondence: ghufran.hassan@utq.edu.iq

porphyrin is one of the most well-known and prevalent. Their complexes' intriguing photochemical and photophysical properties have recently drawn increased attention[25-34].

Specifically, zinc porphyrin derivatives are important because of their distinct structural characteristics and possible uses in a number of industries, such as spintronics, thermoelectric materials, and catalysis [35]. Our previous studies have been done to investigate the thermoelectric characteristics of zinc porphyrins connected to gold electrodes with promising results[10-12, 35-38].

These significant results increase the appeal of zinc porphyrins for molecular-scale thermoelectric devices. Therefore, we believe that more adjustments and changes in zinc porphyrins configurations can impact the thermoelectric properties of zinc porphyrins. Thus, in this work we have introduced a comprehensive investigation of transport properties, electrical and thermoelectric properties of six zinc porphyrin trimers as shown in Fig. 1. The aim of this investigation is to enhance our knowledge and understand how the presence of a zinc atom in the center of porphyrin trimer units impact charge transport, electronic properties, and thermoelectric performance. These factors are critical for advancing the development of molecular-scale devices and applications in nanotechnology [39].

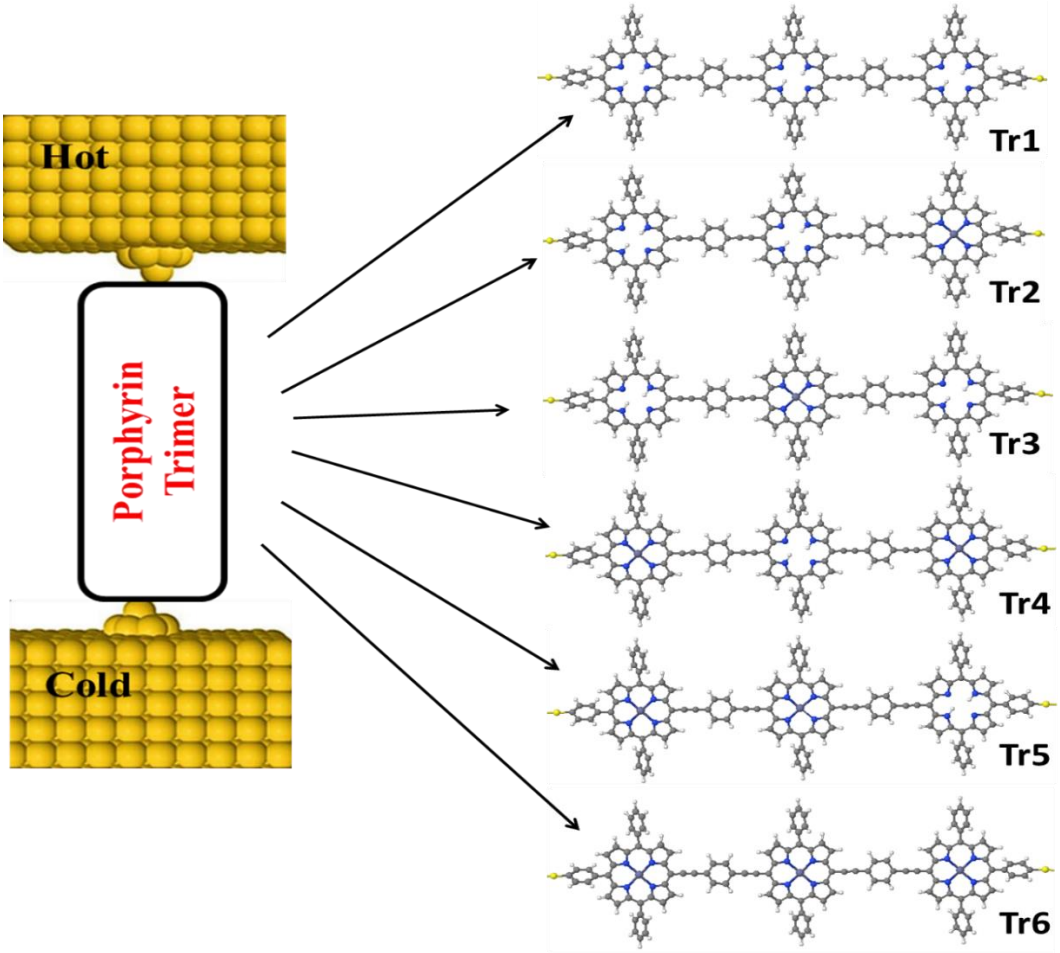

Figure 1.
Schematic illustration of the molecular structure junctions investigated consists of the zinc porphyrin trimers: free-based porphyrin trimer (Tr1), porphyrin trimer with one zinc ion in the edge unit of porphyrin trimer (Tr2), porphyrin trimer with one zinc ion in the middle unit of porphyrin trimer (Tr3), porphyrin trimer with two zinc ions in the terminal units of porphyrin trimer (Tr4), porphyrin trimer with two zinc ions in middle and terminal units of porphyrin trimer (Tr5), porphyrin trimer with three zinc ions in all units of porphyrin trimer (Tr6).

Edelweiss Applied Science and Technology
ISSN: 2576-8484
Vol. 9, No. 2: 1830-1838, 2025
DOI: 10.55214/25768484.v9i2.4936

2. Methods

Density Functional Theory (DFT) is a quantum computational technique that employs complex algorithms to achieve geometrical structure in a variety of molecular systems using quantum physics and quantum chemistry. DFT is used to compute the electronic characteristics of systems with several molecules, where the wave function determines the electron density [40].

All molecular structures of the porphyrin trimers that are shown in Fig.2 were optimized. Using the generalized gradient functional approximation (GGA-PBE), a double-polarized basis set (DZP) for exchange and correlation [41, 42], norm-conserving pseudopotentials, the density functional theory (DFT) package SIESTA code [43], and a real space grid defined with an energy cutoff of 200 Rydberg, the optimization was carried out. Next, we integrate the GOLLUM quantum transport code with the mean-field Hamiltonian H. The transmission coefficient, Tel(E), is found by combining the mean-field Hamiltonian H with the GOLLUM quantum transport code [44].

To calculate electrical conductance, the Landauer formula was employed. Additionally, a thermoelectric material's ability to convert heat into electricity is described by the Seebeck coefficient. Over a large range of Fermi energies, we calculate the thermopower S energies by using the equation

$$S = -\Delta V/\Delta T = -\frac{1}{eT}\frac{L1}{L0} \quad (1)$$

where ΔT is established between them ΔV is the voltage difference generated between the two ends of the junction when temperature difference, e is the electron charge and L_n can be calculated as

$$L_n = \int_{-\infty}^{\infty}(E - E_F)^n T(E)\left(\frac{\partial f(E,T)}{\partial E}\right) dE \quad (2)$$

where $f(E, T)$ is the Fermi distribution function defined *as*

$$f(E, T) = [e^{(E-E_F)/K_BT} + 1]^{-1}$$

where K_B is *Boltzmann's constant*. From Equation (1) it can also be obtained G and K:

$G = G_0 L_0$ (3)

where ($G_0 = 2e^2/h$) is the quantum of conductance,

$K = 1/hT\,(L_2 - L_1^2/L_0)$ (4)

This leads to the final evaluation of the figure of merit values (ZT).

3. Results and Discussion

To investigate the impact of the presence zinc metal ions in the different centers of the units of porphyrin trimer on the electronic and thermoelectric properties, as shown in Fig. 1. The calculations starting by computing the key quantity which is transmission coefficient T(E) for all configurations that shown in Fig.1. Fig. 2 shows the essential change in transmission coefficient T(E) when moving from free-based porphyrin trimer Tr1 to zinc porphyrin trimer Tr6, passing through Tr2, Tr3, Tr4, and Tr5. Fig.2 reveals that the transmission coefficient T(E) is strongly affected by the presence of a zinc ion in the center porphyrin trimer. The gradual appearance of zinc ions in the center of porphyrin trimer units leads to shifting peaks on the both side of around Fermi energy (comparing black line with green line).

Edelweiss Applied Science and Technology
ISSN: 2576-8484
Vol. 9, No. 2: 1830-1838, 2025
DOI: 10.55214/25768484.v9i2.4936

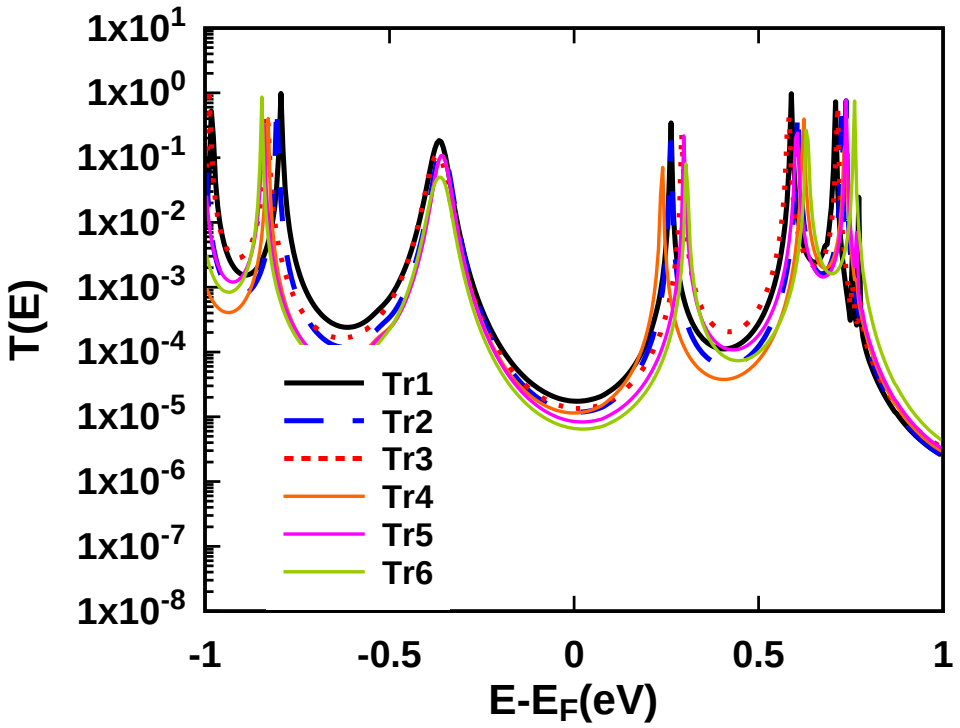

Figure 2.
The electronic transmission coefficients as a function of energy for all the porphyrin trimers structures are shown in Figure 1.

The corresponding room temperature electrical conductance versus energy is presented in Fig. 3. As expected, and reflected in the transmission coefficient in Fig. 2, the electrical conductance decreased with the appearance of zinc ions in the center of porphyrin trimer units. Fig. 3 shows that moving from a free-based porphyrin trimer (black line Tr1) to a zinc porphyrin trimer with three zinc ions in the center of the porphyrin (green line Tr6) leads to a noticeable decrease in electrical conductance around Fermi energy.

Edelweiss Applied Science and Technology
ISSN: 2576-8484
Vol. 9, No. 2: 1830-1838, 2025
DOI: 10.55214/25768484.v9i2.4936

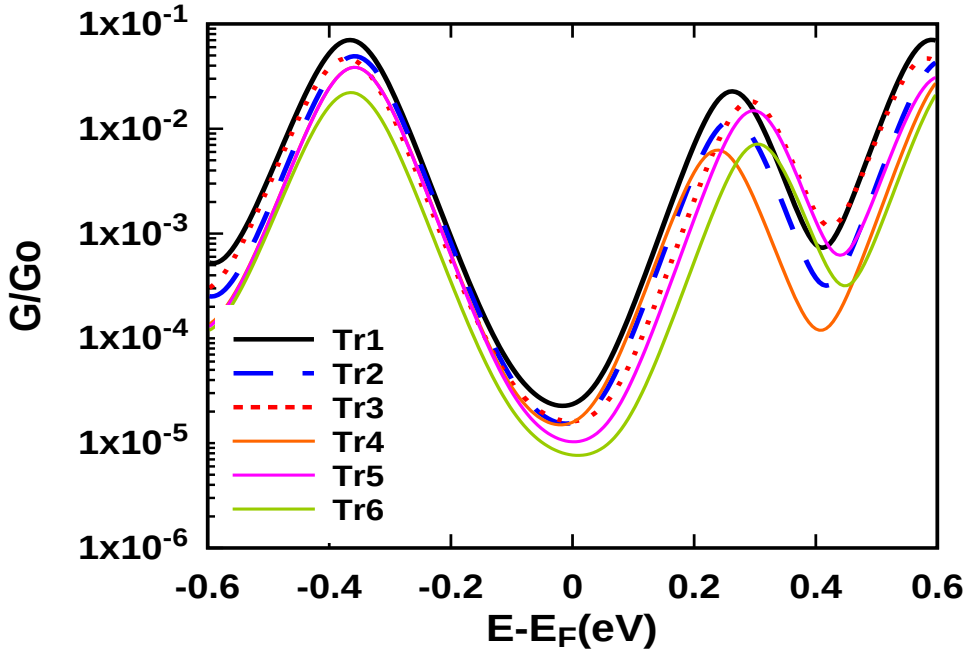

Figure 3.
The electrical conductance (G) as a function of energy for all the ethynyl and phenyl-linked porphyrin trimers molecular structures are presented in Figure 1.

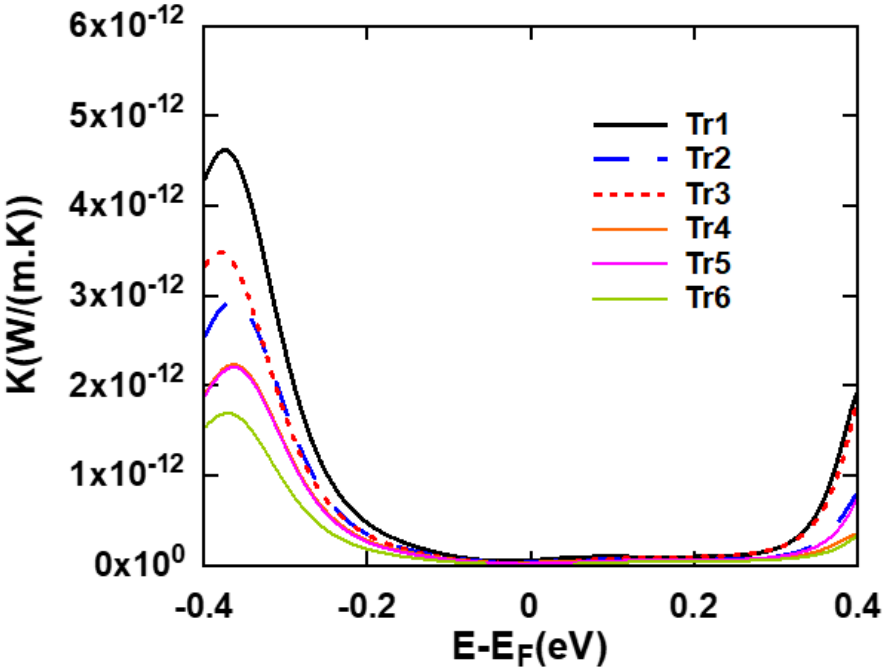

Figure 4.
The electronic thermal conductivity κ as a function of energy for all the porphyrin trimers structures are presented in Figure 1.

Edelweiss Applied Science and Technology
ISSN: 2576-8484
Vol. 9, No. 2: 1830-1838, 2025
DOI: 10.55214/25768484.v9i2.4936

The electronic thermal conductivity of these junctions is shown in Fig.4. This figure shows that the electronic thermal conductivity of free-based porphyrin trimer Tr1 is higher than other structures Tr2, Tr3, Tr4, Tr5, and Tr6. This means that the electronic thermal conductance also decreased with the appearance of zinc ion in porphyrin trimer units.

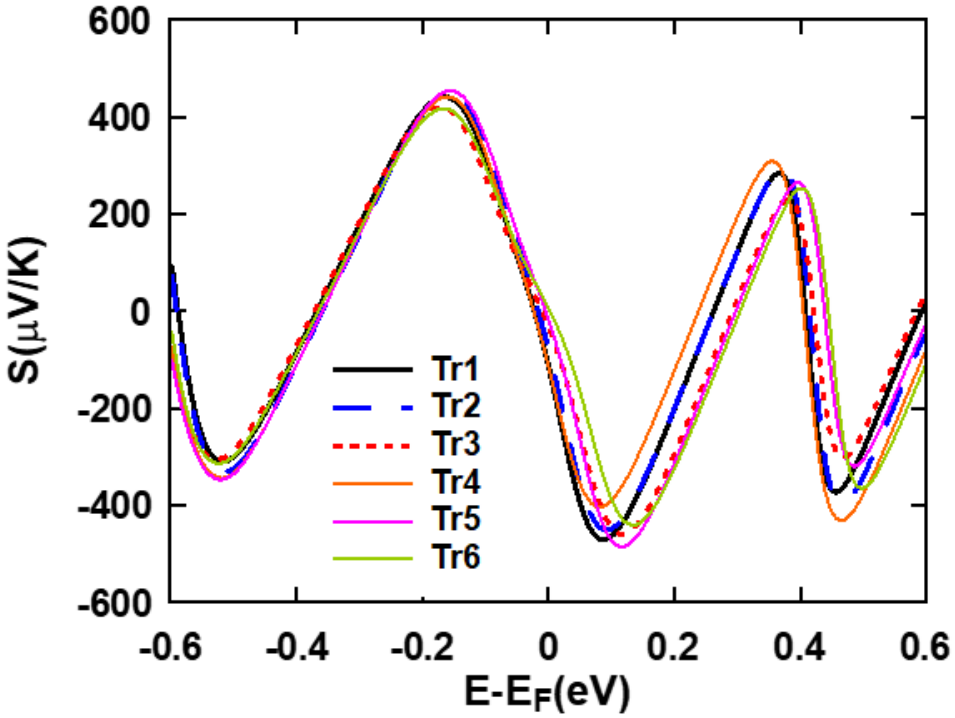

Figure 5.
The Seebeck coefficient S (thermopower) for all the porphyrin trimers molecular structures are presented in Figure 1.

Figure 5 shows the Seebeck coefficient S over a range of Fermi energies at room temperature for each porphyrin trimers' molecular structures. Fig. 5 demonstrates that both the magnitude and sign of S are sensitive to the appearance of zinc ions at the center of the porphyrin trimers. Structure Tr6 porphyrin with three zinc and Tr5 with two zinc atoms has the highest values, (green line and pink line) around Fermi energy.

Figure of merit ZT is the crucial factor that establishes the thermoelectric efficiency. ZT, is inversely proportional to the thermal conductance κ and proportional to the electric conductance G and the square of the Seebeck coefficient S. for all the porphyrin trimers molecular structures, Fig. 6 shows the thermoelectric figure of merit ZT over a range of Fermi energies at room temperature for all the porphyrin trimers molecular structures are shown in Figure 1. Due to the highest value of the Seebeck coefficient S and the low value of electronic thermal conductance κ, Fig. 6 shows that the highest thermoelectric figure of merit ZT value is achieved at **Tr1** and **Tr4** around EF=0eV but outside this window of energy (-0.1 to 0.1) almost all structures have a good value of ZT.

Edelweiss Applied Science and Technology
ISSN: 2576-8484
Vol. 9, No. 2: 1830-1838, 2025
DOI: 10.55214/25768484.v9i2.4936

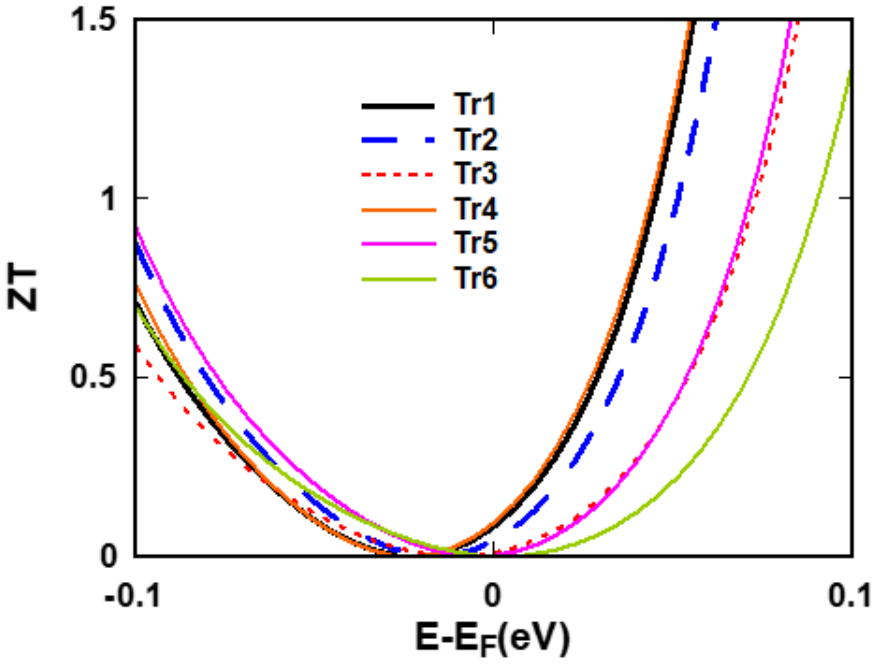

Figure 6.
The electronic figure of merit ZT for all the porphyrin trimers molecular structures are presented in Figure 1.

4. Conclusion

This work has explored the potential of porphyrin trimer structures for high efficiency thermoelectricity. Our calculations perfectly focused on the correlation between the presence of zinc metal ions in the center of the porphyrin trimer units and electronic and thermoelectric properties. The result demonstrates that in the in all zinc porphyrin trimers, all electrical and thermoelectric properties transmission coefficient, electrical conductance G, thermal conductivity K, thermopower S, and figure of merit ZT have been affected by the appearance of zinc ion in the center of porphyrin trimers. The result demonstrates that the electrical and thermal conductance are decrease by the presence of a zinc metal ion in the center of these trimers. where a noticeable drop in electrical and thermal conductance occurs when a zinc atom appears. Moreover, the thermopower of structures has a noticeable change particularly in the vicinity of Fermi energy leading to varied in ZT values.

Transparency:

The authors confirm that the manuscript is an honest, accurate, and transparent account of the study; that no vital features of the study have been omitted; and that any discrepancies from the study as planned have been explained. This study followed all ethical practices during writing.

References

[1] R. Singh *et al.*, "Advancements in thermoelectric materials for efficient waste heat recovery and renewable energy generation," *Hybrid Advances*, p. 100176, 2024. https://doi.org/10.1016/j.hybrid.2024.100176

[2] T. J. Seebeck, *Magnetische polarisation der metalle und erze durch temperatur-differenz* (no. 70). W. Engelmann, 1895.

[3] A. A. Al-Jobory and M. D. Noori, "Thermoelectric properties of metallocene derivative single-molecule junctions," *Journal of Electronic Materials*, vol. 49, no. 9, pp. 5455-5459, 2020. https://doi.org/10.1007/s11664-020-08279-4

[4] M. Noori, H. Sadeghi, and C. J. Lambert, "Stable-radicals increase the conductance and seebeck coefficient of graphene nanoconstrictions," *Nanoscale*, vol. 10, no. 40, pp. 19220-19223, 2018. https://doi.org/10.1039/C8NR04869J

[5] 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. https://doi.org/10.1140/epjd/e2019-100033-8

[6] 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, vol. 2457, no. 1.

[7] T. A. Hussein and M. D. Noori, "Investigation electrical and thermoelectrical properties of Ferrocene in staggered and eclipsed conformations," in *Journal of Physics: Conference Series*, 2021, vol. 1973, no. 1, p. 012055.

[8] M. D. Noori and A. A. Al-Jobory, "Tuning the thermoelectric properties of ferrocene molecular junctions," in *IOP Conference Series: Materials Science and Engineering*, 2018, vol. 454, no. 1, p. 012143.

[9] R. T. Jasim and M. D. Noori, "Theoretical investigation of bonding type effect in ferrocene dimers on electric and thermoelctric proteprties," *Edelweiss Applied Science and Technology*, vol. 8, no. 6, pp. 2836-2842, 2024.

[10] E. Leary *et al.*, "Bias-driven conductance increase with length in porphyrin tapes," *Journal of the American Chemical Society*, vol. 140, no. 40, pp. 12877-12883, 2018. https://doi.org/10.1021/jacs.8b06338

[11] E. Leary *et al.*, "Detecting mechanochemical atropisomerization within an STM break junction," *Journal of the American Chemical Society*, vol. 140, no. 2, pp. 710-718, 2018. https://doi.org/10.1021/jacs.7b10542

[12] M. D. Noori, *Quantum theory of electron transport through photo-synthetic porphyrins*. Lancaster University (United Kingdom), 2017.

[13] 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. https://doi.org/10.1007/978-981-10-0724-8_5

[14] A. A. K. Al-mebir and S. A. Al-Saidi, "Theoretical investigation of base Pairs-dependent electron transport in DNA system," in *Journal of Physics: Conference Series*, 2020, vol. 1530, no. 1, p. 012147.

[15] S. A. Al-Saidi and A. A. K. Al-mebir, "Electronic properties simulation of guanine molecule," in *Journal of Physics: Conference Series*, 2020, vol. 1530, no. 1, p. 012148.

[16] 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, no. 3, p. 1, 2021. https://doi.org/10.14704/nq.2021.19.3.NQ21021

[17] S. A. AL-Saidi and A. A. K. Al-mebir, "Asymmetric double quantum dot structure as nanoscale diode," *University of Thi-Qar Journal*, vol. 13, no. 4, pp. 1-17, 2018.

[18] S.-H. Ke, H. U. Baranger, and W. Yang, "Models of electrodes and contacts in molecular electronics," *The Journal of Chemical Physics*, vol. 123, no. 11, 2005. https://doi.org/10.1063/1.1993558

[19] 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, no. 1, pp. 23-27, 2011. https://doi.org/10.1038/nnano.2010.215

[20] Z. Liu, S. Ren, and X. Guo, "Switching effects in molecular electronic devices," *Molecular-Scale Electronics: Current Status and Perspectives*, pp. 173-205, 2019. https://doi.org/10.1007/978-3-030-03305-7_8

[21] S. A. AL-Saidi, A. A. K. Al-mebir, and M. Hallool, "Characteristics of thymine molecule system behave as molecular electronic device," *Misan Journal of Academic Studies (Humanities and Social Sciences)*, vol. 18, no. 35, pp. 130-143, 2019. https://doi.org/10.54633/2333-018-035-023

[22] M. Noori *et al.*, "Tuning the electrical conductance of metalloporphyrin supramolecular wires," *Scientific Reports*, vol. 6, no. 1, p. 37352, 2016. https://doi.org/10.1038/srep37352

[23] M. Mathius, *Synthesis of highly conjugated porphyrinoid systems*. Illinois State University, 2022.

[24] A. S. Estrada-Montaño, V. Gómez-Benítez, A. Camacho-Dávila, E. Rivera, D. Morales-Morales, and G. Zaragoza-Galán, "Metalloporphyrins: Ideal catalysts for olefin epoxidations," *Journal of Porphyrins and Phthalocyanines*, vol. 26, no. 12, pp. 821-836, 2022. https://doi.org/10.1142/S1088424622300051

[25] A. Yasin, V. S. Nair, M. H. Ab Rahim, Y. Yamaoka, C. S. Yelleswarapu, and R. Jose, "Structural parameters versus third-order optical susceptibility of zinc porphyrin molecules," *Journal of Materials Chemistry C*, vol. 9, no. 48, pp. 17461-17470, 2021. https://doi.org/10.1039/D1TC04777A

[26] V. Singh, P. S. Thakur, V. Ganesan, and M. Sankar, "Zn (II) porphyrin-based polymer facilitated electrochemical synthesis of green hydrogen peroxide," *Journal of Electroanalytical Chemistry*, vol. 919, p. 116536, 2022. https://doi.org/10.1016/j.jelechem.2022.116536

[27] C. Hahn da Silveira, O. A. Chaves, A. C. Marques, N. M. Rosa, L. A. S. Costa, and B. Almeida Iglesias, "Synthesis, photophysics, computational approaches, and biomolecule interactive studies of metalloporphyrins containing pyrenyl units: Influence of the metal center," *European Journal of Inorganic Chemistry*, vol. 2022, no. 12, p. e202200075, 2022. https://doi.org/10.1002/ejic.202200075

[28] N. C. M. Magdaong *et al.*, "Photophysical properties and electronic structure of zinc (II) porphyrins bearing 0–4 meso-phenyl substituents: Zinc porphine to zinc tetraphenylporphyrin (ZnTPP)," *The Journal of Physical Chemistry A*, vol. 124, no. 38, pp. 7776-7794, 2020. https://doi.org/10.1021/acs.jpca.0c06841

[29] C. O. Paul-Roth, J. G. Williams, J. Letessier, and G. Simonneaux, "New tetra-aryl and bi-aryl porphyrins bearing 5, 15-related fluorenyl pendants: The influence of arylation on fluorescence," *Tetrahedron Letters*, vol. 48, no. 25, pp. 4317-4322, 2007. https://doi.org/10.1016/j.tetlet.2007.04.110

[30] C. O. Paul-Roth and G. Simonneaux, "Porphyrins with fluorenyl and fluorenone pendant arms," *Tetrahedron Letters*, vol. 47, no. 19, pp. 3275-3278, 2006. https://doi.org/10.1016/j.tetlet.2006.03.086

[31] C. O. Paul-Roth and G. Simonneaux, "Porphyrins with fluorenyl and fluorenone pendant arms as red-light-emitting devices," *Comptes Rendus Chimie*, vol. 9, no. 10, pp. 1277-1286, 2006. https://doi.org/10.1016/j.crci.2006.04.003

[32] Y. F. Liu *et al.*, "Computational investigation of acene-modified zinc-porphyrin based sensitizers for dye-sensitized solar cells," *The Journal of Physical Chemistry C*, vol. 119, no. 16, pp. 8417-8430, 2015. https://doi.org/10.1021/jp507746p

[33] D. Man, R. Słota, M. A. Broda, G. Mele, and J. Li, "Metalloporphyrin intercalation in liposome membranes: ESR study," *JBIC Journal of Biological Inorganic Chemistry*, vol. 16, pp. 173-181, 2011. https://doi.org/10.1007/s00775-010-0715-1

[34] R. Słota, M. A. Broda, G. Dyrda, K. Ejsmont, and G. Mele, "Structural and molecular characterization of meso-substituted zinc porphyrins: A DFT supported study," *Molecules*, vol. 16, no. 12, pp. 9957-9971, 2011. https://doi.org/10.3390/molecules16129957

[35] M. Noori, H. Sadeghi, and C. J. Lambert, "High-performance thermoelectricity in edge-over-edge zinc-porphyrin molecular wires," *Nanoscale*, vol. 9, no. 16, pp. 5299-5304, 2017. https://doi.org/10.1039/c6nr09598d

[36] 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, no. 26, pp. 17356-17359, 2017. https://doi.org/10.1039/c7cp02229h

[37] D. S. Preesam, H. Milani Moghaddam, and M. D. Noori, "Enhanced thermoelectric properties of zinc porphyrin dimers-based molecular devices," *The European Physical Journal D*, vol. 78, no. 11, pp. 1-5, 2024. https://doi.org/10.1140/epjd/s10053-024-00932-5

[38] D. Preesam, M. Noori, and H. Moghaddam, "The effect of linker group on thermoelectric properties of dimer zinc porphyrin-based molecular junctions," *University of Thi-Qar Journal of Science*, vol. 10, no. 2, pp. 177-180, 2023. https://doi.org/10.25130/j.v10i2.1133

[39] V. S. Tyurin, E. A. Mikhalitsyna, A. S. Semeikin, and I. P. Beletskaya, "Synthesis of new porphyrin trimers via buchwald-hartwig amination reaction," *Macroheterocycles*, vol. 8, pp. 358-365, 2015. https://doi.org/10.6060/mhc150358

[40] A. B. Ahmed, "Studying the electronic characteristics and physisorption of OTS on the pure silver surfaces (Ag10),(Ag15) and (Ag18)," *University of Thi-Qar Journal of Science*, vol. 10, no. 2, pp. 151-159, 2023. https://doi.org/10.32792/utq/utjsci/v10i2.1123

[41] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Physical Review Letters*, vol. 77, no. 18, p. 3865, 1996. https://doi.org/10.1103/PhysRevLett.77.3865

[42] B. Hammer, L. B. Hansen, and J. K. Nørskov, "Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals," *Physical Review B*, vol. 59, no. 11, p. 7413, 1999. https://doi.org/10.1103/PhysRevB.59.7413

[43] J. M. Soler *et al.*, "The SIESTA method for ab initio order-N materials simulation," *Journal of Physics: Condensed Matter*, vol. 14, no. 11, p. 2745, 2002. https://doi.org/10.1088/0953-8984/14/11/302

[44] J. Ferrer *et al.*, "GOLLUM: A next-generation simulation tool for electron, thermal and spin transport," *New Journal of Physics*, vol. 16, no. 9, p. 093029, 2014. https://doi.org/10.1088/1367-2630/16/9/093029