University of Thi-Qar Journal

ISSN (print): 2706- 6908, ISSN (online): 2706-6894

Vol. 20 No.4 Dec 2025

Investigation the effect of linkers in Zinc Porphyrin dimer Molecular Junctions on the Electrical and Thermoelectric Properties

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Abstract

The development of higher oligomeric porphyrin arrays represents a promising pathway toward next-generation molecular electronics. In this study, the thermoelectric properties of five zinc porphyrin dimers (ZnP) were theoretically investigated by analyzing electron transport through Zn-porphyrin dimers connected between gold electrodes via five distinct configurations. The impact of the presence, type, position, and number of linkers on the electrical and thermoelectric properties was systematically examined. The results demonstrate that transitioning from direct to linker-mediated contacts significantly alters both electrical and thermal conductance. Moreover, variations in linker position and number strongly influence electrical conductivity, thermal conductivity, and thermopower (S). These findings underscore the critical role of linker engineering in controlling the electrical and thermoelectric performance of zinc porphyrin dimers for molecular electronic applications.

Keywords: Zinc porphyrin; transmission coefficient; Seebeck coefficient; figure of merit; molecular junctions.

Introduction:

More than 10% of the global electricity consumed by computers and the internet is dissipated as waste heat, which can be exploited for cost-effective power generation through high-efficiency thermoelectric materials [1]. Thermoelectric energy conversion is based on the **Seebeck effect**, discovered in the early 19th century, where a temperature gradient induces a voltage difference, enabling electricity generation from waste heat sources such as automobile exhausts and industrial equipment [2].

Recent research has focused on improving thermoelectric performance by understanding the parameters governing thermoelectric properties, particularly in molecular materials and devices [3–7]. The efficiency of thermoelectric materials is quantified by the **figure of merit (ZT)**, defined as $ZT = (S^2GT)/k$ where S is the Seebeck coefficient, G is the electrical conductance, T is the temperature, and κ is the electronic thermal conductivity [8]. The ZT value enables direct comparison of different materials and guides the optimization of thermoelectric performance [9]. Although inorganic materials dominate thermoelectric applications, organic materials have gained increasing attention due to their lower toxicity, greater availability, and reduced cost [10,11]. Additionally, the thermoelectric properties of inorganic systems can be tuned through nanostructural engineering [12,13], motivating extensive studies of single-molecule junctions connected to nanogap electrodes for nanoscale devices [4,14–27]

Porphyrins and their metal complexes exhibit exceptional optical and electronic properties, making them attractive for applications in catalysis, electronics, photonics, and beyond. Their planar aromatic structure contains a central cavity capable of hosting various metals, such as Zn, Fe, and Co, forming metalloporphyrins with enhanced functionality [28,29]. Studies on metalloporphyrins coupled to gold electrodes have demonstrated that modifying the linker position and structure shifts molecular energy levels relative to the electrode Fermi energy, thereby significantly affecting thermoelectric properties [30,31]. This tunability highlights the potential of metalloporphyrins in molecular-scale thermoelectric devices.

In this work, we present a systematic investigation of the electrical and thermoelectric properties of fused zinc porphyrin dimers. The study examines (i) the presence and bonding type of the linker, (ii) the effect of linker position, and (iii) the influence of increasing the number of linkers between dimer units [32]. The results demonstrate that the linker plays a crucial role in governing charge transport and thermoelectric performance, underscoring its importance in the design of efficient molecular thermoelectric systems.

The manuscript is organized as follows: Section 2 describes the computational methods, Section 3 presents the results and discussion, and Section 4 summarizes the conclusions.

Method

Before constructing the junction model, optimising the molecular geometry of the zinc porphyrin was imperative. This step was crucial in ensuring the accuracy and reliability of the subsequent analysis. The optimisation process involved refining the geometry of each structure, comprising two gold electrodes and a singular zinc porphyrin molecule. The highly sophisticated SIESTA code,[33] which utilised advanced algorithms and computational techniques to optimise the geometries above, was employed to achieve this. By rigorously optimising the molecular geometry, the resulting junction model would possess enhanced stability and facilitate a more comprehensive understanding of the system under investigation. [34]. the implementation of density functional theory (DFT) This approach employs a double-polarized (DZP) basis set in combination with the generalized gradient approximation (GGA-PBE) for the exchange-correlation functional.The DFT Hamiltonian, a mathematical representation of the system's total energy, is merged with our quantum transport algorithm, GOLLUM.This combination enables the investigation and analysis of various electronic properties and phenomena within the system, providing a deeper understanding of its behavior and characteristics. [35] to calculate the transmission coefficient , one must evaluate the probability of electrons with energy traversing from the left to the right gold electrode via the single molecule. The electrical conductance is subsequently obtained by combining with the Landauer formula [36,37].The said formula is expressed as $G = G_0 \int_{-\infty}^{\infty} dE\, T(E)[-\frac{\partial f(E,T)}{\partial E}]$,In this expression, f(E,T) represents the Fermi–Dirac distribution function, defined as $f(E,T) = [e^{(E-E_f)/K_BT} + 1]^{-1}$. It is important to note that K_B represents Boltzmann's constant and G_0 is equal to $2e^2/h$, representing the quantum of conductance.

Furthermore, the Seebeck coefficient, which quantifies a thermoelectric material’s capability to convert heat into electrical energy, is calculated and defined as follows.$S = -\Delta V/\Delta T$, Here, denotes the voltage difference produced across the junction when a temperature gradient is applied between its two ends. This necessitates the evaluation of the figure of merit values, denoted as ZT, which are calculated using the formula $ZT = (S^2GT)/k$. In this equation, T represents the temperature, and κ represents the thermal conductivity, with only the electronic component being considered. The phonon contribution is omitted in this calculation, a common practice owing to the lack of direct measurement techniques **.**

Results and discussion

In this work, we present a comparison study of zinc porphyrin dimers' electric and thermoelectric properties. The Results and Discussion section is structured as follows: In Section I, we examine the impact of transforming a zinc porphyrin dimer from a configuration without any linker between the dimer units (Structure D) to a configuration containing a single triple bond. (ethyne) linker **D0 structure** and **D1** structure with the double, triple bond linker. In section II, we investigated the effect of both the position and number of linkers (bridges) of this dimer on the electric and thermoelectric properties.

Section I: Firstly, we investigate the effect of the presence of the linker between units of zinc porphyrin dimers. Starting by comparing the direct contact zinc porphyrin dimer (without any linkers) structure **D** with the zinc porphyrin dimer of the linker with one triple bond (ethyne) structure **D0** and then with the double, triple bond (1,3-butadiyne) linker structure **D1** as shown in Fig. 1

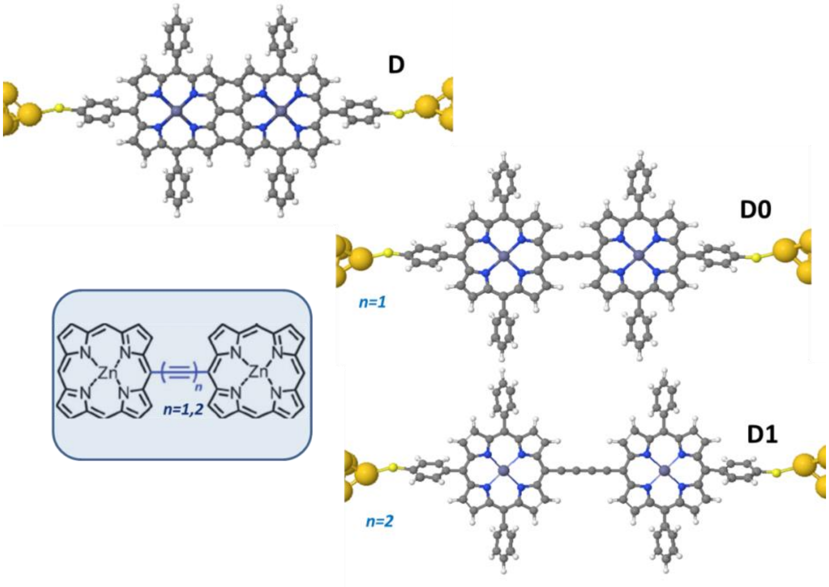


Fig. 1 The zinc porphyrin dimer (**D**) direct contact (**D0**) zinc porphyrin dimer with one triple bond (ethyne), and (**D1**) zinc porphyrin dimer with a double triple bond (1,3-butadiyne)

The room temperature electrical conductance has been shown in Fig.2a. This figure highlights a significant variation in electrical conductance near the Fermi energy among D, D0, and D1, with D showing the highest conductance values. This result demonstrates that the conductance in the presence of linker **D0** and **D1**decreases significantly. Fig2b shows that thermal conductivity also there is a slight decrease around Fermi energy between $\approx -0.2\ to\ 0.2\ eV$. This decrease is due to the alteration in the electronic structure of the zinc porphyrin dimer, leading to a shift in the energy level and transmission peaks.

Fig. 3 shows thermopower S and the figure of merits ZT versus energy. Fig. 3 demonstrates that changing the linker type significantly affects thermopower S and ZT. For thermopower, Fig. 3a shows that moving from direct contact **D** to linker contact **D0** and **D1** changes the attitude of thermopower. In contrast, in Fig.3a, the thermopower curves in **D0** and **D1** more smoothly change around Fermi energy. This behavior is attributed to the change in the slope of ln T(E). The figure of merit, , as a function of energy is presented in Fig. 3b. Owing to the high thermopower of D0 near the Fermi energy, Fig. 3b shows that D0 exhibits the highest values around the Fermi energy compared to the other structures, D and D1.

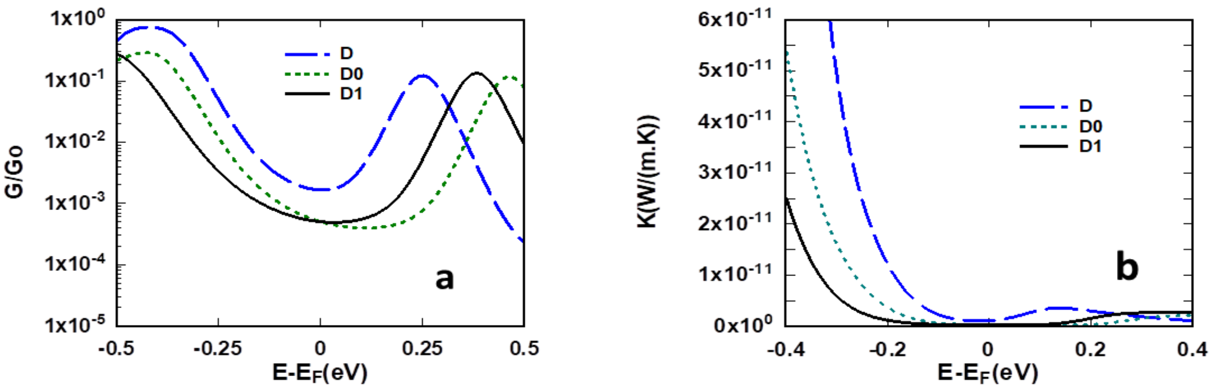


Figure 2 displays two plots: (a) the variation of electrical conductance with energy, and (b) the thermal conductivity of each analyzed structure at room temperature**.**

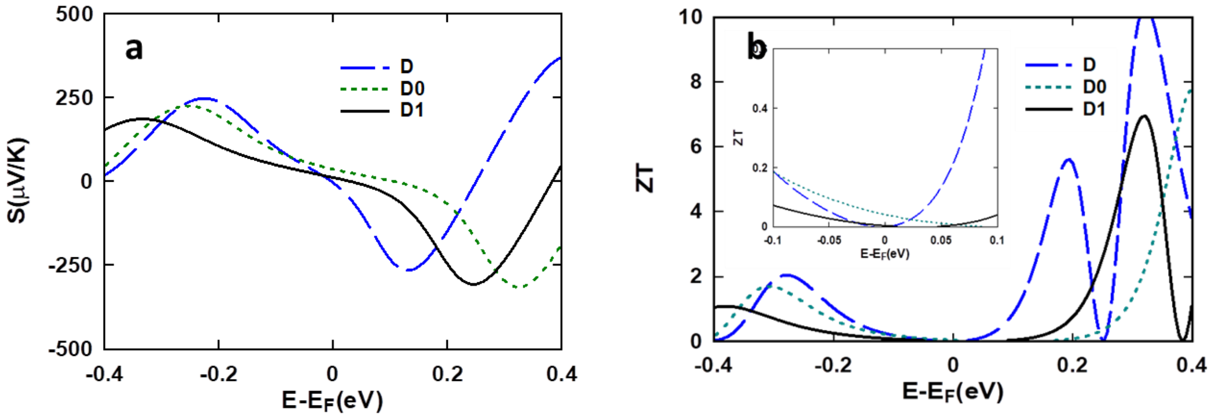


Fig. 3 Illustrates two plots: (a) shows the Seebeck coefficient as a function of energy, while (b) shows the merit (*ZT*) of each structure being examined at room temperature

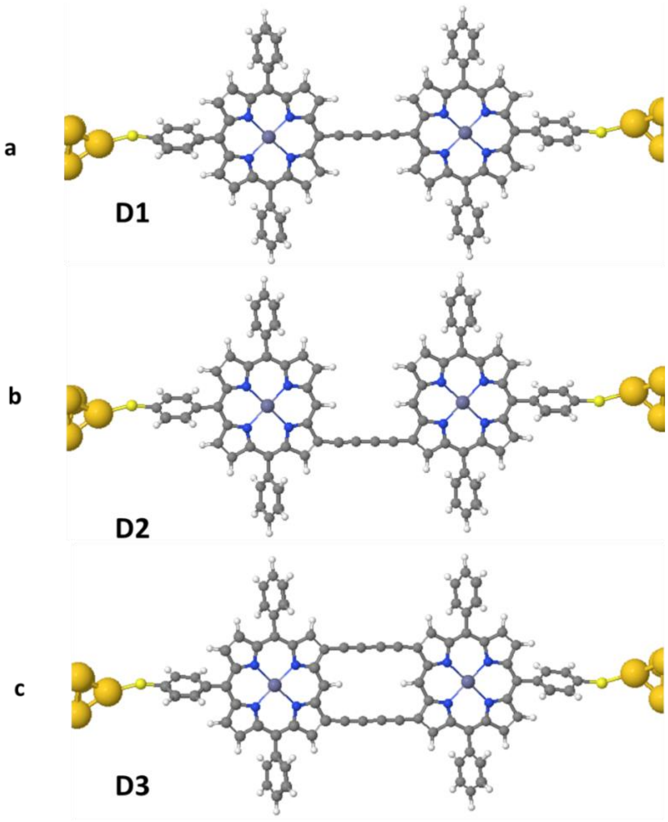
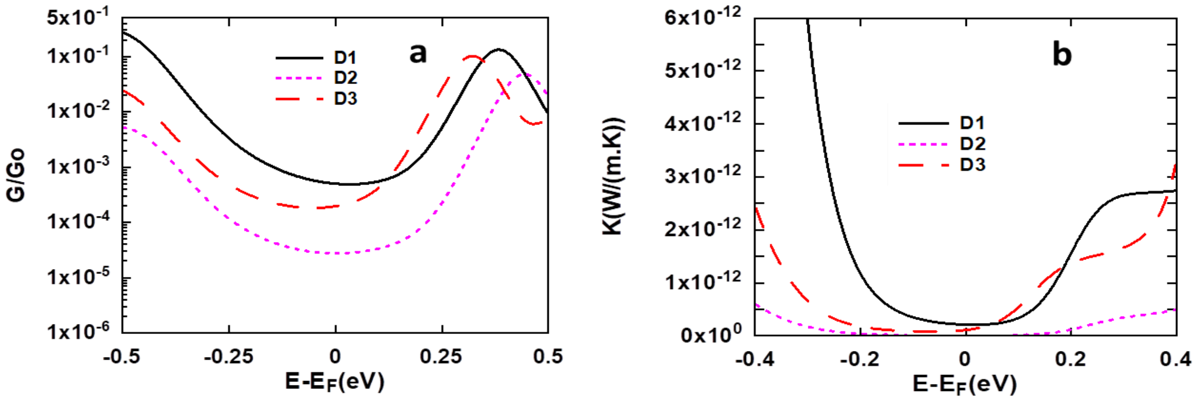


Fig 4. Illustrates the **dimer zinc porphyrin** structures (a) structure **D1**: 1,3-butadiyne holds in a central position, (b) structure **D2**:1,3-butadiyne hold in the edge position, and (c) structure **D3**:1,3-butadiyne double bridge between the **dimer zinc porphyrin**.

Section II: In this section, we will explore the effect of changing the molecule/linker contact point on the electric and thermoelectric properties as shown in Fig.4. In Fig.4a, the structure **D1** where the linker 1,3-butadiyne takes a central position, which one of the very popular configurations; otherwise, in Fig.4b, structure **D2** the linker 1,3-butadiyne holds in the edge position. Fig.4c shows the structure **D3, where the** number of linkers increases.

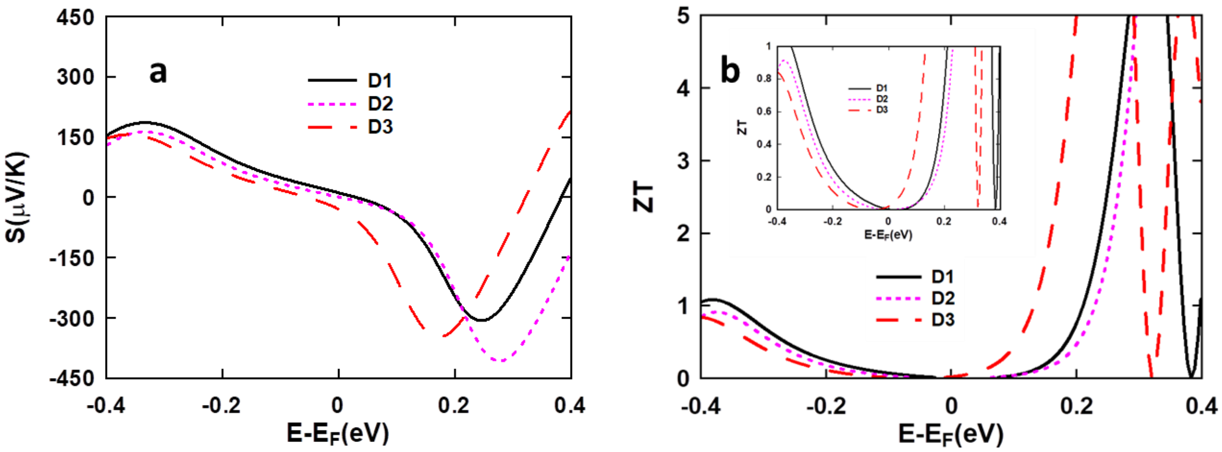
Fig.5 shows the electrical conductance and the thermal conductivity as a function of energy for structures **D1, D2,** and **D3.** Fig 5a,b reveal a significant difference in electrical conductance and the thermal conductivity values around Fermi energy.

Fig.5a shows the room temperature electrical conductance versus energy. It indicates that despite structure **D3** showing an increase in the number of linkers, structure **D1** still shows higher electrical conductance. At the same time, **D2** shows the lowest value in a wide range around Fermi energy. Fig.5b shows that the thermal conductivity is affected by the position and number of the linkers. We can see a slight difference in the thermal conductivity value in the energy window between $\approx -0.2\ to\ 0.2\ eV$ with a huge difference out of this window. In other words, Fig.5 demonstrates that the transfer of the position of the linker from the central **D1** to edge position **D2** leads to a significant decrease in electrical and thermal conductance. From all the above results, one can see that changing the contact linker point and the number of linkers between zinc porphyrin dimers play essential roles in electric and thermal properties. This can be an attitude that changing the contact point and the linker number will lead to an alteration in conducting pathways between dimer units, leading to changes in the quantum interference QI map.



“Figure 5 illustrates two graphs: (a) electrical conductance as a function of energy, and (b) the room-temperature thermal conductivity for each structure.”

Fig. 6 shows thermopower S and ZT versus energy. Fig. 6a demonstrates how changing the number and position of linkers affects thermopower S. This figure illustrates that changing the position of the linker has a very weak effect on the thermopower S values, especially around Fermi energy. So, changing the linker position to the edge led to a slight decrease in thermopower. Meanwhile, increasing the number of linkers will decrease the thermopower S, especially around Fermi energy and the negative part of energy. According to the above results and due to the very small change in thermopower values, S is the effective part of the ZT relation $ZT = (S^2GT)/k$. In addition to the corresponding change in both electrical conductance (numerator) and thermal conductivity (denominator), which almost means they cancelled each other. Fig.6b reveals that the values of the figure of merit ZT as a function of the energy of D1, D2, and D3 around Fermi energy show very close values.



“Figure 6 depicts two graphs: (a) the Seebeck coefficient versus energy, and (b) the thermoelectric figure of merit () for each structure at room temperature.”

Conclusion

In this work, we have systematically investigated how the type, position, and number of linkers between zinc porphyrin dimer units influence their electrical and thermoelectric properties.The result demonstrates that the electrical and thermal conductance in linkers **D0** and **D1** decreases significantly. In addition, moving from direct contact **D** to linker contact **D0** and **D1** changes the attitude of thermopower, where the thermopower curves in **D0** and **D1** become smoother in changes around Fermi energy. Because of the high thermopower value of **D0** near Fermi energy, this structure shows the highest *ZT* value around Fermi energy compared with other structures **D** and **D1**. Transferring the position of the linker from the central position **D1** to edge position **D2** leads to a significant decrease in electrical and thermal conductance. But for thermopower S, it has a very weak effect on the thermopower S values, especially around Fermi energy. On the other hand, increasing the number of linkers will decrease electrical and thermal conductivity and decrease the thermopower S. In summay, changing the contact linker point and the number of linkers between zinc porphyrin dimers play essential roles in electric and thermal properties.

Confect of Interest

The authors declare that they have no conflict of interest

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