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High-Performance Thermoelectricity in Ferrocene Molecular Wires

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***Abstract*— The transport characteristics of the ferrocene trimer molecule and its reaction to temperature changes were investigated theoretically Here, we have conducted a theoretical comparison of the thermoelectric and electrical characteristics of four distinct ferrocene trimer topologies. Our findings show that the bonding type and connectivity between ferrocene trimer units significantly affect the regulation of quantum interference (QI) and the enhancement of thermoelectric characteristics indicating that these structures are excellent candidates to serve as materials for numerous thermoelectric applications and as thermoelectric enhancers such as Cooling/heating, power generation, and heat flux sensors.**

***Keywords*— molecular junctions, ferrocene, Figure of merit, transmission coefficient, and Seebeck coefficient.**

I. INTRODUCTION

Thermoelectric (TE) materials possess unique capabilities to directly convert waste heat into electricity. This unique ability of TE makes them have enormous potential applications in different fields of energy conversion and thermal management. In recent years, organic thermoelectric (OTE) has attracted special attention because of many properties such as eco-friendliness, and high flexibility [1-6]. Numerous experimental and theoretical studies have been conducted to develop and control electronic molecules [7–14] for future nanoelectronics circuit applications such as molecular wires [15], electrodes [16]. wiring circuits [17] and switches [18]. Several approaches to building and studying molecular junctions have also been developed. These studies have gained a lot of interest recently

Because they have the potential to produce electrical gadgets that are more useful and perform better in the future [19–21] thermoelectricity principles. These devices are made of thermoelectric (TE) materials that have been chosen as a convenient solution to this ever-growing field due to the direct conversion of heat into electricity [22–25]. Due to the unique transport properties and thermoelectric properties some molecules have the potential to be utilized in next-generation of nanoelectronic circuits. Thus, the thermoelectric properties of this kind of molecular junctions have been investigated extensively. One of the most significant of these molecular junctions is ferrocene, it has garnered a lot of interest over the years because of its exceptional thermal and chemical stabilities as well as its perfectly symmetric geometric structure. [26-30]. Since there are just a few groups around the world that can measure the thermal conductance of single molecules. Thus, theoretical research is required to design, find, and investigate new thermoelectric materials. So the aim is to find and explore for new materials that can achieve these strategies in the lab. In this work, we present a comparative theoretical investigation of the electrical and thermometric properties of four different configurations of ferrocene trimmers, as shown in Fig.1 where changing the bonding type between ferrocene units means that the electron will take multipath in turn, new pattern of quantum interference (QI) will appear that quantum interference (QI) has a strong influence on the electrical and thermometric properties, three examples of QI in single-molecule settings Mach-Zehnder interferometry, Breit-Wigner resonances, and Fano resonances are examined [31-37].

II. METHOD

The structures of all ferrocence trimers in this work shown in Fig.1a do not optimize the properties of nature or naturally occurring systems, like atom-to-atom angles or chemical bond lengths. So the geometries of all ferrocene trimers were firstly relaxed until the total atomic force was equal to $0.04\ eV/A^{\circ}$. The optimization was performed using DFT package SIESTA [38]. In addition, we have implemented a double-zeta polarized base set (DZP), generalized gradient approximation with the Perdew–Burke–Ernzerhof parameterization for exchange and correlation [39], norm-conserving pseudopotentials and the real space grid is defined with energy cutoff of 200 Rydberg. Then, each ferrocence trimers were attached to two gold electrodes via a thiol anchor group to calculate the quantum transport properties. The Hamiltonian of the whole structure (molecule and electrodes) was obtained, via SIESTA, and then implemented in a non-equilibrium Green's function code, Gollum [40]. Gollum calculates the transmission coefficient of the electrons passing from the

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left electrode to the right electrode through the molecule. After compute the transmission coefficient $T_{el}(E)$. The electrical conductance was computed by using the Landauer formula. We compute the thermopower S by using $S(E) = -\frac{1}{eT}\frac{L_1}{L_o}$ where T is the temperature, e is the electron charge and L_i can be calculated as $L_i = \int_{-\infty}^{\infty}(E - E_F)^i \; T_{el}(E)\frac{\delta f(E,T)}{\delta E}\, dE$ where $f(E,T)$ is the Fermi-Dirac probability distribution function.

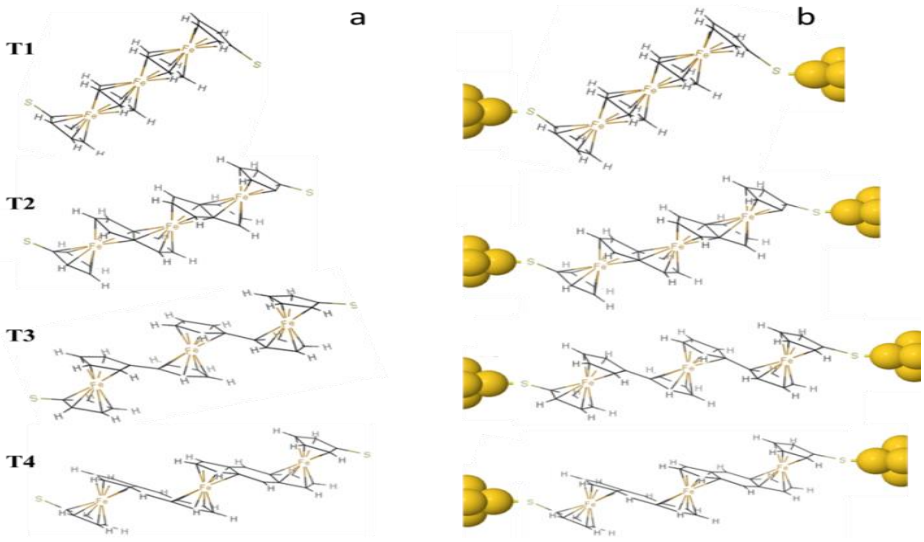

Fig.1 (a) Schematic illustration of the configuration of four trimer ferrocene structures. (b) all molecular junctions consist of ferrocene trimmers sandwiched between two gold electrodes.

III. RESULTS AND DISCUSSION

For examining the thermoelectric and electrical properties of the trimer ferrocene, we start by determining the fundamental transmission coefficient T(E) for all four presumed junctions as shown in Fig. 1b. Altering the bond type between ferrocene trimer units which means changing in structural arrangement this can modify the charge transport pathway, this in turn, results in the presence of novel quantum interference (QI) patterns in the transport curve. Fig. 2 shows the transmission probability of the four ferrocene trimers as a function of energy. Fig. 2 shows the transmission probability of the four ferrocne trimers as a function of energy. It is clear from Fig. 2 that the transmission coefficient T3 (dashed red lines) is more flat and smooth without any features compared with T1, T2, and T4 which show noticeable features near Fermi energy EF = 0 eV. We can attribute that to changing the bonding type between ferrocene units will push electron to take multipath which means a new pattern of quantum interference (QI) will occur. These features (resonances) of T1,T2, and T4 are significant in the next calculations and that because they are very close to Fermi energy.

The room temperature electrical conductance is shown in Fig.3a. Reflecting on the peaks in the transmission coefficient curve around Fermi energy Fig.2. The new pattern of quantum interference (QI) that is produced due to altering the bonding type between ferrocene units leads to distractive quantum interference (DQI) with low conductivity and constructive quantum interference (CQI) with high conductivity. Fig. 3 illustrates that T1, T2, and T4 show high electrical conductance than T3. Fig.3b shows the electronic thermal conductivity as a function of energy.

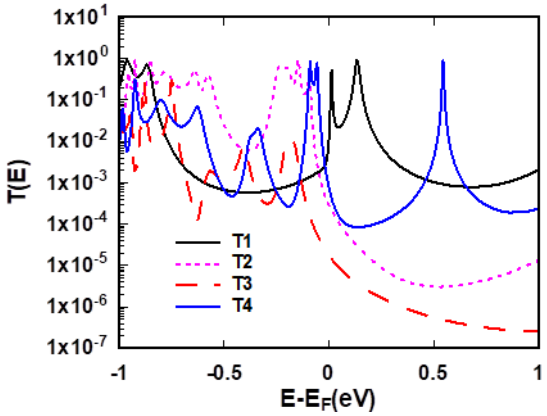

Fig.2: DFT-transmission probability, T(E), as a function of energy for T1, T2, T3, and T4 ferrocene molecular junctions appeared in Fig.1.

It is clear that all systems have the same attitude where T1 and T2 show a higher value of electronic thermal conductivity than T3 and T4 near Fermi energy. Fig.3b shows that the thermal conductivity as a function of energy is clearly we can see that it's affected by the changing the bonding between ferrocene trimers. We can see that T1 shows a slightly higher value in the thermal conductivity in energy window ≈ 0 to +0.3 eV.

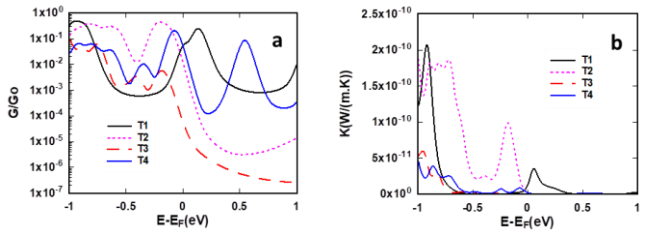

Fig.3:(a) Room temperature electrical conductance, and (b) Thermal conductivity as function of energy of all four ferrocene trimmers.

Fig.4 shows the thermopower S as a function of energy. Fig.4 shows that T2, T3, and T4 have a higher thermopower value than T1 at Fermi energy EF = 0 eV, this can be explained by the transmission coefficient curve's peaks near the Fermi level. The highest values of thermopower occur in T2 is about +390 μV/K (pink line) and +350μV/K in T3 (dashed red line).

The efficiency of thermoelectric materlials is determined by the dimensionless Fig. of merit ZT, $ZT = \frac{S^2 G}{\kappa} T$ which is proportional to the electric conductance G and the Seebeck squared coefficient, and inversely proportional to the thermal conductance κ.

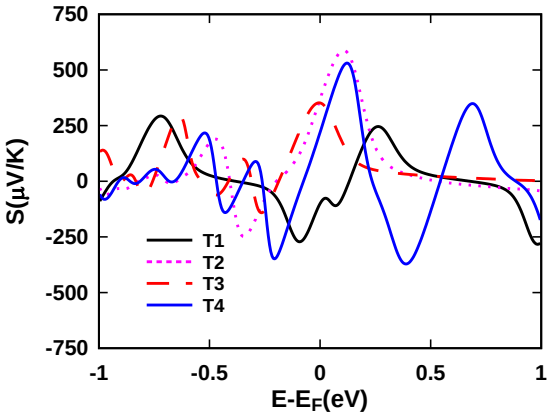

Fig.4 : Seebeck coefficient S as a function of Fermi energy for all ferroce trimer junctions

Thermal conductance κ in this relation has two parts $\kappa = \kappa_{el} + \kappa_{ph}$ thermal conductance due to electrons (κ_{el}) and phonons (κ_{ph}), in this work we will deal with the electronic part only. Generally, to achieve a large value of merit ZT, it is appropriate to get a high value of thermopower S and electric conductance G around the Fermi level. Fig. 5 shows ZT for all four ferrocene trimers as a function of energy. Since T4 has a high value of electrical conductance and thermopower S near the Fermi level shows that T4 shows a great value of ZT with ≈ 16 at 0.0 eV, also T2 achieved ZT ≈10 at 0.0 eV. The large values of S and ZT can occur in the case that the resonances are at energy close to the Fermi level.

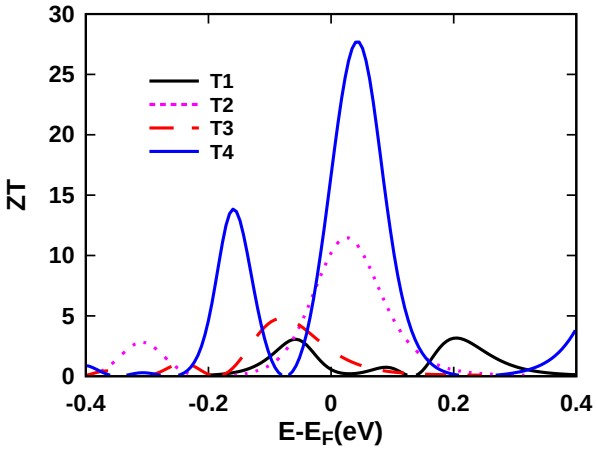

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Fig.5 Thermoelectric figure of merit ZT as a function of Fermi energy for all ferroce trimer junction.

IV. Conclusion

In this work, we examined the thermoelectric characteristics of four distinct ferrocene trimer topologies sandwiched between two gold electrodes and linked via thiol atoms. The findings showed that by altering the bonding between ferrocene units, these systems' electronic transport and thermoelectric characteristics may be effectively controlled. The S and ZT are strongly supported by the resonances, T4 has the highest electronic figure of merit ZT value, which is ≈16. T2 also has a promising electronic figure of merit ZT value, which is ≈10. These results, in our opinion, are important because they provide new opportunities for thermoelectric energy exchange in functionalized organic molecules. The thermoelectric material's performance is assessed by the value of ZT, so a high ZT value means the maximum efficiency of the thermoelectric material.

Conflict of Interest

Authors declare that they have no conflict of interest.

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