Theoretical investigation of bonding type effect in ferrocene dimers on electric and thermoelctric proteprties

Rasha Talal Jasim[1*], Mohammed Deia Noori[2]
[1,2]Department of Physics, College of Sciences, University of Thi-Qar, Thi-Qar, Iraq; rasha.talal@utq.edu.iq (R.T.J.).

Abstract: Thermoelectric materials possess the capacity to significantly impact worldwide energy usage by virtue of their capability to transform heat into electrical energy. However, the majority of these materials exhibit low efficiency. Currently, there are ongoing studies exploring the thermoelectric properties of molecular junctions and low-dimensional structures. These investigations aim to identify and evaluate new nanostructure systems that can overcome the existing limits. In this study, we have conducted a theoretical comparison of the electrical and thermoelectric properties of four distinct topologies of ferrocene dimers. The findings of our study indicate that the connectivity and bonding type between ferrocene dimer units play a crucial role in controlling the quantum interference (QI) and enhancing the thermoelectric properties of these molecular junctions. These structures are highly promising for use as thermoelectric enhancers and are well-suited for many thermoelectric applications.

Keywords: Ferrocene, Figure of merit, Molecular junctions, Seebeck coefficient, Transmission coefficient.

1. Introduction

In the last two decades, there has been substantial advancement in the domain of single-molecule electronic systems. These systems currently offer a platform for investigating fundamental characteristics of materials at the molecular or atomic level. This encompasses the examination of charge transport, molecular spintronics, and thermoelectric performance, as indicated by references [1-6]. Various empirical and theoretical studies have been conducted to enhance and control electronic molecules [7–14] for potential utilization in nanoelectronics circuits, such as molecular wires [15], electrodes [16], wiring circuits [17], and switches [18]. Various methodologies for constructing and analyzing molecular junctions have also been devised. These studies have garnered significant attention in recent times because of their potential to develop electrical devices that are more practical and exhibit superior performance in the future [19–21]. Thermoelectricity is the phenomenon of directly converting heat into electric power. Numerous devices operate on the principles of thermoelectricity [22–24]. These devices consist of thermoelectric (TE) materials, which have been selected as a practical solution in this rapidly expanding industry since they directly convert heat into electricity [25]. Several experimental studies have been conducted to examine the molecular heat transport of these junctions. However, the ultrasmall scale of these junctions presents significant challenges. Most of the measurements are plagued by uncertainties, and many of the transport mechanisms still require further explanation and understanding. Therefore, a theoretical examination provides a solution to these challenges. Theoretical simulation allows us to improve our understanding and gain more detailed knowledge about electron transport pathways in different models of molecular junctions. Furthermore, it enables us to clarify the experimental measurements. The text provided by the user is [26]. Certain molecules possess distinctive transport capabilities and thermoelectric qualities that make them promising candidates for utilization in the development of nanoelectronic circuits in the future. Therefore, there has been substantial investigation into the thermoelectric properties of these specific

types of molecular junctions. Ferrocene is considered one of the most important molecular junctions due to its remarkable thermal and chemical stabilities, as well as its flawlessly symmetrical geometric structure. This has led to a great deal of attention in ferrocene throughout the years. The range of values is from 27 to 30. Due to the limited number of organizations worldwide with the capability to quantify the thermal conductivity of individual molecules. Hence, it is imperative to do theoretical study in order to develop, discover, and explore novel thermoelectric materials. The objective is to discover and investigate novel materials that can successfully implement these tactics in a laboratory setting. This work presents a comparative theoretical analysis of the electrical and thermometric properties of four distinct configurations of ferrocene dimers. The first structure is the TM(FeCp2) structure D1, the second is the bisferrocenylpentalenyl structure D2, the third is the biferrocene structure D3, and the last is the bisferrocenylindacenyl dithiolates structure D4 [30-35], as illustrated in Figure 1a.
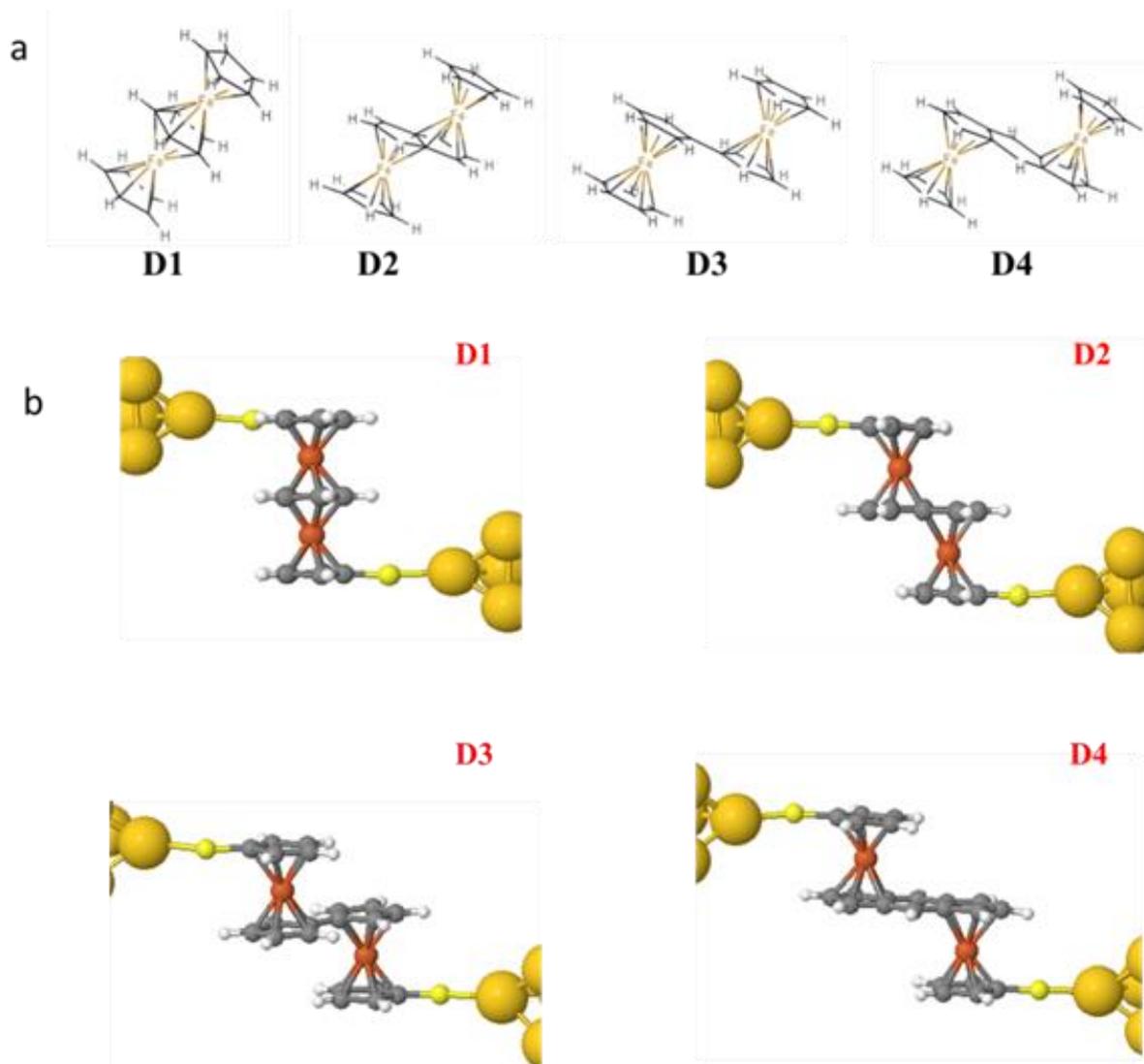

Figure 1.
(a) Schematic illustration of the configuration of four dimer ferrocene structure D1 is TM(FeCp2), structure D2 is bisferrocenylpentalenyl, structure D3 is biferrocene, structure D4 is bisferrocenylindacenyl dithiolates (b) Molecular junction gold electrode- ferrocene dimer-gold electrode of all dimer ferrocene.

2. Method

The molecular geometry of all the ferrocone dimers depicted in Figure 1 was optimized before the junction model was constructed. The thiol anchor group was employed in Fig. 1b to secure ferrocone units to gold leads. The SIESTA [36] algorithm was utilized to conduct the geometrical optimization of all systems by incorporating Density Functional Theory (DFT). The generalized gradient approximation (GGA) was employed to calculate the exchange and correlation functions with a double-z polarized (DZP) basis set [37]. The GOLLUM algorithm was used to integrate the mean-field Hamiltonian that was derived from the converged DFT computations [38]. Quantum transport theory has been employed by the GOLLUM software to calculate the thermoelastic and electrical properties of a variety of junctions.

3. Results and Discussion

To analyze the electrical and thermoelectric properties of the dimer ferrocene, the initial step is determining the transmission coefficient T(E) for each junction. These junctions are composed of a dimer of ferrocene positioned between two gold electrodes, as depicted in Figure 1b. Modifying the bond type between ferrocene dimer units leads to a change in their structural arrangement, which in turn modifies the channel for charge transport. This alteration results in the emergence of new quantum interference (QI) patterns in the transport curve. Figure 2 displays the transmission probability of the four ferrocene dimers as it varies with energy. Figure 2 clearly demonstrates that the transmission coefficients of D1 and D3, represented by the black and dashed red lines, exhibit a more uniform and consistent behavior without any distinct characteristics. In contrast, D2 and D4 display visible features in close proximity to the Fermi energy EF = 0 eV. The proximity of the resonances of D2 and D4 to the Fermi energy makes them crucial for the upcoming calculations.
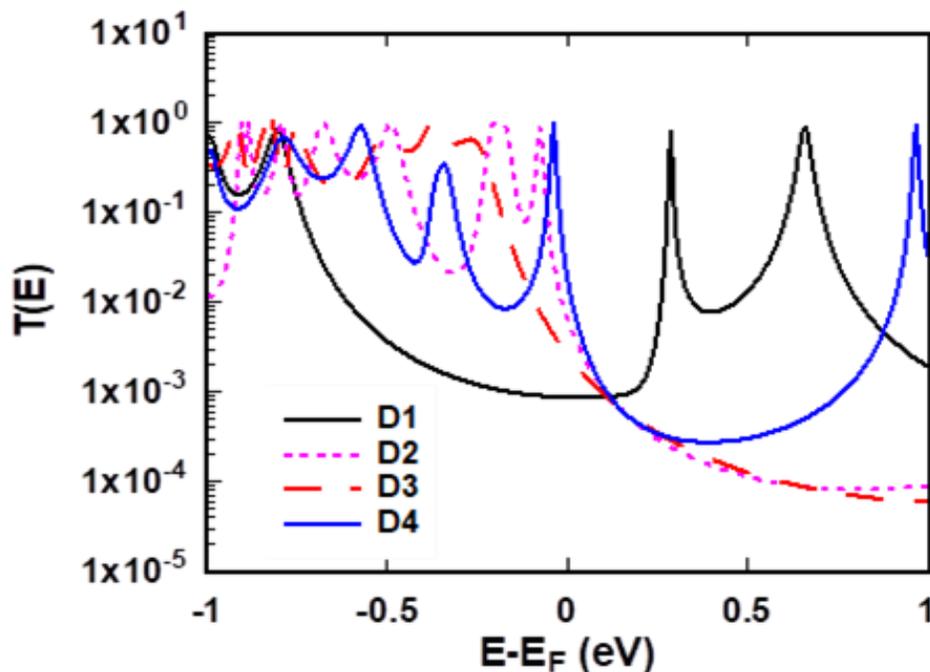

Figure 2.
The DFT-transmission probability T(E) as a function of energy for all molecular junctions.

The corresponding electrical conductance is shown in Figure 3a. Reflecting on the peaks in the transmission coefficient curve around Fermi energy Figure 2, both D4 and D2 show higher electrical conductance than D1 and D3. Figure 3b illustrates the relationship between thermal conductivity and energy. It is evident that all systems exhibit a similar disposition, with D4 and D2 displaying a slightly greater thermal conductivity value than D1 and D3 in the vicinity of the Fermi energy.
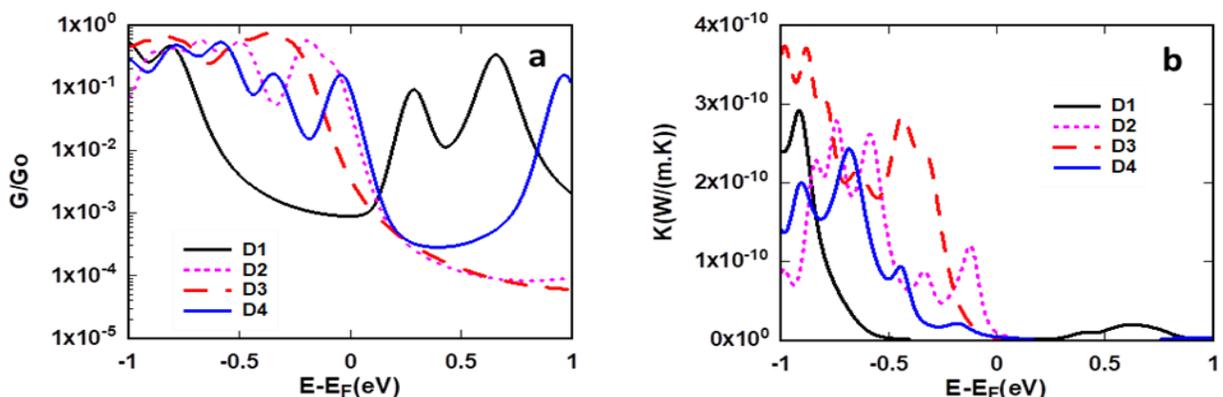

Figure 3.
(a) Room temperature electrical conductance (b) Thermal conductivity as function of energy of all four ferrocene dimers.

Figure 4 shows the thermopower S as a function of energy. Fig.4 shows that **D2, D3,** and **D4** have a higher thermopower value than **D1** at Fermi energy EF = 0 eV, this can be attributed to peaks around the Fermi level in the transmission coefficient curve. The highest values of thermopower occur in **D2** varied between +265 μV/K (pink line) and +155μV/K in **D3** (dashed red line).
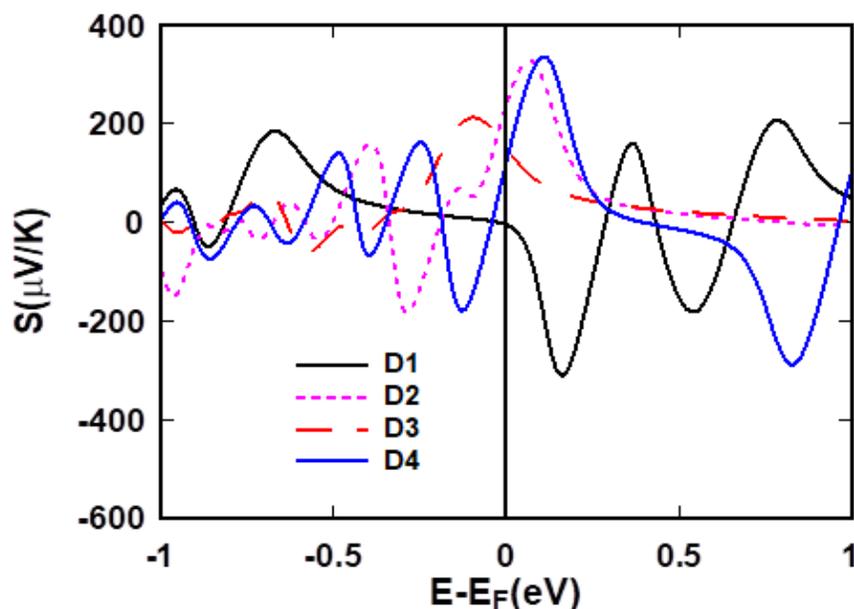

Figure 4.
Seebeck coefficient S as a function of Fermi energy for all ferroce dimer junctions.

The most important quantity calculated is the thermoelectric efficiency ZT. The ZT is a dimensionless parameter that serves as a measure of performance [20]. The equation ZT = S^2 * G * T / κ represents the correlation between the figure of merit ZT and the electric conductance G, the square of the Seebeck coefficient S, and the thermal conductance κ. The variable ZT is directly proportional to the variables G and S squared and inversely proportional to the variable κ. Generally, to achieve a high thermopower S and ZT figure of merit, it is recommended to have properties at the Fermi level. Figure 5 illustrates the energy-related merit of the four ferrocene dimes. Due to its high electrical conductance and the presence of thermopower S near the Fermi level, D4 exhibits significant conductivity. Furthermore, D4 exhibits a high ZT value of approximately 6 at 0.0 eV, while D2 has attained a ZT value of approximately 4 at 0.0 eV. The high values of S and ZT can arise when the resonances are located near the Fermi level.
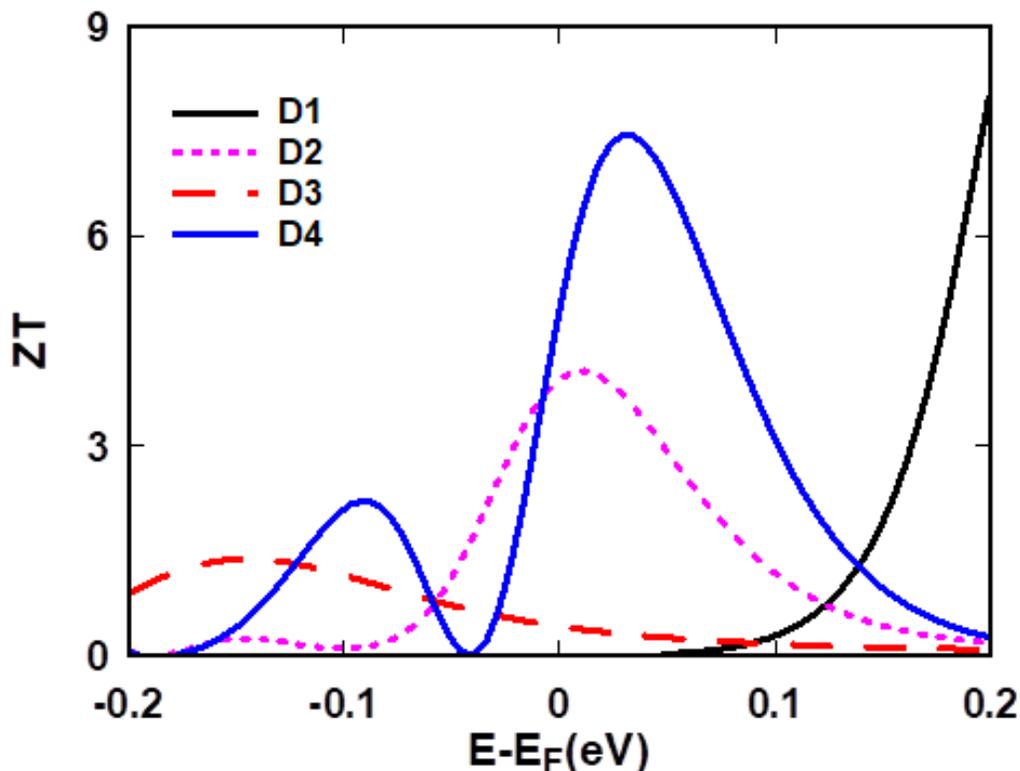

Figure 5.
Thermoelectric figure of merit ZT as a function of Fermi energy for all ferroce dimer junctions.

4. Conclusion

In conclusion, it was investigated that the thermoelectric properties of four different configurations of ferrocene dimers placed between two gold electrodes. The results indicate that the electrical transport and thermoelectric properties of these systems can be effectively controlled by altering the bonding type between ferrocene dimer units. The resonances greatly support the S and ZT, especially when they are close to the Fermi level. The maximum value of ZT≈6 is archived in **D4,** and **D2** shows a good ZT value with≈4. It is believed these discoveries are significant because they provide new opportunities for the transfer of thermoelectric energy in functionalized organic molecules.

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References

[1]   M. M. Waldrop, "The chips are down for Moore's law," Nat. News, vol. 530, no. 7589, p. 144, 2016.

[2]   S. K. Saxena, U. M. Tefashe, and R. L. McCreery, "Photostimulated near-resonant charge transport over 60 nm in carbon-based molecular junctions," J. Am. Chem. Soc., vol. 142, no. 36, pp. 15420–15430, 2020.

[3]   Sakban, Raunaq H., Mohammed D. Noori, and Samar M. Abdulalmohsin. "Radical Enhancement Electric and Thermoelectric Efficiency of Graphene Nano constrictions." *Solid State Technology* 63.1 (2020): 1788-1793.

[4]   M. Tian et al., "A three-dimensional carbon nano-network for high performance lithium ion batteries," Nano Energy, vol. 11, pp. 500–509, 2015.

[5]   Al-mebir, Alaa Ayad K., Mohammed D. Noori, and Bahjat B. Kadhim. "Tuning the Electrical and Thermoelectric Properties of Phthalocyanine and Metallo-Phthalocyanine Molecular Junction." *Journal of Physics: Conference Series.* Vol. 1999. No. 1. IOP Publishing, 2021.

[6]   D. Stefani et al., "Large conductance variations in a mechanosensitive single-molecule junction," Nano Lett., vol. 18, no. 9, pp. 5981–5988, 2018.

[7]   K. Nakada, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, "Edge state in graphene ribbons: Nanometer size effect and edge shape dependence," Phys. Rev. B, vol. 54, no. 24, p. 17954, 1996.

[8]   Noori, Mohammed Deia. *Quantum Theory of Electron Transport Through Photo-Synthetic Porphyrins.* Lancaster University (United Kingdom), 2017.

[9]   J. S. Junias and J. Clement, "Predictive analytics of conductance and HOMO-LUMO gaps with topological descriptors of porphyrin nanosheets," Phys. Scr., vol. 99, no. 1, p. 15208, 2023.

[10]   M. Noori et al., "Tuning the electrical conductance of metalloporphyrin supramolecular wires," Sci. Rep., vol. 6, no. 1, p. 37352, 2016.

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

[12]   Hussein, Thoalfkar Ali, and Mohammed D. Noori. "Investigation Electrical and Thermoelectrical properties of Ferrocene in staggered and eclipsed conformations." *Journal of Physics: Conference Series.* Vol. 1973. No. 1. IOP Publishing, 2021.

[13]   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," Biosens. Bioelectron., vol. 181, p. 113158, 2021.

[14]   Noori, Mohammed D., and Alaa A. Al-Jobory. "Tuning the Thermoelectric Properties of Ferrocene Molecular Junctions." *IOP Conference Series: Materials Science and Engineering.* Vol. 454. No. 1. IOP Publishing, 2018.

[15]   J. C. Scott, "Metal–organic interface and charge injection in organic electronic devices," J. Vac. Sci. Technol. A Vacuum, Surfaces, Film., vol. 21, no. 3, pp. 521–531, 2003.

[16]   N. Darwish, I. Díez-Pérez, S. Guo, N. Tao, J. J. Gooding, and M. N. Paddon-Row, "Single molecular switches: Electrochemical gating of a single anthraquinone-based norbornylogous bridge molecule," J. Phys. Chem. C, vol. 116, no. 39, pp. 21093–21097, 2012.

[17]   M. A. Rampi and G. M. Whitesides, "A versatile experimental approach for understanding electron transport through organic materials," Chem. Phys., vol. 281, no. 2–3, pp. 373–391, 2002.

[18]   G. Bhatt, A. Ghatak, and R. Murugavel, "Futuristic storage devices: Single molecular magnets of rare earths versus spin crossover systems of earth-abundant metals," J. Chem. Sci., vol. 135, no. 2, p. 40, 2023.

[19]   J. Cirera and E. Ruiz, "Modeling Magnetic Properties with Density Functional Theory-Based Methods," Mol. Magn. Mater. Concepts Appl., pp. 419–446, 2017.

[20]   S. Sanvito, "Molecular spintronics," Chem. Soc. Rev., vol. 40, no. 6, pp. 3336–3355, 2011.

[21]   M. Elbing et al., "A single-molecule diode," Proc. Natl. Acad. Sci., vol. 102, no. 25, pp. 8815–8820, 2005.

[22]   M. Josefsson et al., "A quantum-dot heat engine operating close to the thermodynamic efficiency limits," Nat. Nanotechnol., vol. 13, no. 10, pp. 920–924, 2018.

[23]   H. Sadeghi, S. Sangtarash, and C. J. Lambert, "Oligoyne molecular junctions for efficient room temperature thermoelectric power generation," Nano Lett., vol. 15, no. 11, pp. 7467–7472, 2015.

[24]   A. A. Al-Jobory, Z. Y. Mijbil, and M. Noori, "Tuning electrical conductance of molecular junctions via multipath Ru-based metal complex wire," Indian J. Phys., vol. 94, no. 8, pp. 1189–1194, 2020.

[25]   Abbasi, Misbah Sehar, et al. "Contemporary advances in organic thermoelectric materials: Fundamentals, properties, optimization strategies, and applications." *Renewable and Sustainable Energy Reviews* 200 (2024): 114579.

[26]   Mosso, Nico, et al. "Thermal transport through single-molecule junctions." *Nano letters* 19.11 (2019): 7614-7622.

[27]   Noori, Mohammed D., and Alaa A. Al-Jobory. "Tuning the Thermoelectric Properties of Ferrocene Molecular Junctions." *IOP Conference Series: Materials Science and Engineering.* Vol. 454. No. 1. IOP Publishing, 2018.

[28]   Aragonès, Albert C., et al. "Control over near-ballistic electron transport through formation of parallel pathways in a single-molecule wire." *Journal of the American Chemical Society* 141.1 (2018): 240-250.

[29]   Noori, Mohammed D. "Electrical and thermoelectric properties investigation of oligomeric ferrocene: Staircase versus flatcase." *AIP Conference Proceedings.* Vol. 2404. No. 1. AIP Publishing, 2021.

[30]   Yuan, Shundong, et al. "Theoretical studies of the spin-dependent electronic transport properties in ethynyl-terminated ferrocene molecular junctions." *Micromachines* 9.3 (2018): 95.

[31]   Böhm, Michael C. "Electron correlation in weakly coupled transition metal dimers: Bimetallocenylenes and bimetallocenes." *Theoretica chimica acta* 60 (1981): 233-268.

[32]   Wu, Jian-Chun, et al. "Manipulating spin transport via vanadium− iron cyclopentadienyl multidecker sandwich molecules." *The Journal of Physical Chemistry C* 113.18 (2009): 7913-7916.

[33]   Zhou, Liping, et al. "One-dimensional iron− cyclopentadienyl sandwich molecular wire with half metallic, negative differential resistance and high-spin filter efficiency properties." *Journal of the American Chemical Society* 130.12 (2008): 4023-4027.

[34]   Matsuura, Yukihito. "Tunnel magnetoresistance of ferrocene molecules." *Chemical Physics Letters* 692 (2018): 174-177.

[35]   Welker, Mark E. "Ferrocenes as building blocks in molecular rectifiers and diodes." *Molecules* 23.7 (2018): 1551.

[36]   J. M. Soler et al., "The SIESTA method for ab initio order-N materials simulation," J. Phys. Condens. Matter, vol. 14, no. 11, p. 2745, 2002.

[37]   J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865

[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

[39]   L. M. Hancock and M. J. Hollamby, "Assessing the practical skills of undergraduates: The evolution of a station-based practical exam," J. Chem. Educ., vol. 97, no. 4, pp. 972–979, 2020.