Influence of Central-Metallic Atoms of Molecular Junction on Electrical and Thermal Transport

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Abstract

Molecular structures of a series of metal-complexes molecules of bipyrimdine have interesting features in various applications such as industrial and scientific. The transition through metal complexes at molecular structures has a significant role in the metal-bridges interactions. Hence, the bipyrimdine's complex molecules were used to show the effect of the metal atoms on the electronics, electrical, and thermoelectric properties and to identify the π-conjugated system in all attempts before/ or after replaced one carbon with nitrogen atoms in one or two the pyridine rings. SIESTA code, and GOLLUM code programs were used in our calculations. The results showed that the energy gap decreased significantly with the type of metal atoms, which appear in electronic applications at various LUMO-HOMO energy gaps. The electrical and thermal results have confirmed the effect of metal-complexes center atoms in the transmission and Seebeck coefficients. From the position of the Fermi energy (E-EF=0 eV), the conductance and the thermopower values are determined, and thus the specificity figure of merit ZTe was computed. Therefore, we found the ZTe be a high value for bipyridine molecule about 1.7, which is several order of magnitude higher than of the set molecules. Whereas a low value of ZTe for Cr-metal-molecule.

Key Words: Electrical-thermal Transport, Metal-complexes Bipyrimdine, SIESATA Code, ZT_e Merit.

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Introduction

The thermoelectric of single molecules linked to metallic electrodes is being studied to learn more about the basics of quantum transport and to design future molecular-scale devices and circuits (Manrique et al., 2015; Chen, 1999; Reed et al 1997; Smit et al, 2002; Jia & Guo, 2013; Xiang et al, 2013). Quantum interference (QI), that can be destructive or constructive, causes molecules to deviate from regular electrical circuit principles, opening up new possibilities for exploiting their electrical properties. It has been achieved in a variety of molecules as multi-or monolayer films layered between pairs of conductors or as single molecules bridging through nanoelectrode leads (Naghibi et al, 2019; Ismael et al, 2017). A great deal of work is now being put into improving the effectiveness of these effects and determining the factors that influence the thermoelectric performance of materials and devices. Although inorganic thermoelectric materials are the most prevalent, organic thermoelectric materials are gaining interest, mainly because many frequently used inorganic thermoelectric elements are toxic, costly to produce, and have limited worldwide supply (Al-Galiby et al, 2019).

Designing and construction of organometallic molecules is an active field of research due to their possible application to information technology, in particular, the form of molecular-scale electronics devices, the biological environment, and complementing all views of the transition of metal complexes applications as in medicine.

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The study of molecular-scale electronics has been driven by fundamental interest and by potential practical applications the highly interdisciplinary subject is a meeting place for synthetic chemists, physical chemists, and experimental physicists (Ballhausen & Gray, 1980). In this work, the Bipyridine (Bpy) and metal-complexes bipyrimdine (Bpyrim) molecules were studied due to intensely observes their wavelengths in the visible part of the spectrum. Therefore, the thermoelectric transport is attributed to metal-ligand charge transport. As well as, these components of molecular electronics and metal complexes were having electrochemically switchable characteristics are of interest (Ie et al, 2011; Kamenetska et al, 2010).

Computational Method

To calculate the electrical and thermal properties of the molecular structures under study, the relaxed molecules were found by using SIESATA code (Li et al, 2006). DFT-based SIESTA code was carried out to get completely optimized structures of the gas phase molecules. In addition, it has been used a double-zeta polarized (DZP) which is the basis set for all molecules, and also the generalized gradient approximation (GGA) for the exchange and correlation functional (Tan et al 2011). As well as, on a real-space grid formed by a plane-wave cutoff of 250 Ry, the Hamiltonian and overlap matrices were computed. The transmission coefficient of electrons passing through the molecule from the left lead to the right lead is then calculated by using GOLLUM code (Ferrer et al, 2014). The electrical conductance G was computed from the Landauer formula (Sert et al, 2016; Oftadeh, Naseh & Hamadanian, 2011).

$$G = G_0 \int_{-\infty}^{\infty} dE\, T(E) \left(-\frac{df(E)}{dE}\right) \qquad (1)$$

Where f(E) is the Fermi function:

$$f(\mathrm{E}) = [e^{\beta(E-E_F^{DFT})} + 1]^{-1} \qquad (2)$$

E_F is the Fermi energy and $\beta=1/k_BT$,

Seebeck coefficient of a material is calculated from equation (Al-Khaykanee et al, 2018)

$$S = \frac{-\pi k_B^2 \tau}{3|e|} \frac{d ln \mathrm{T(E)}}{dE}\Big|_{E=E_F} \qquad (3)$$

Geometry of Studied Molecules

To study the electrical and thermoelectric properties for set molecular structures, and after relaxing all isolated molecules, they were attached through two gold leads as shown in figure 1. As in the experimental results the angle of bipyridine molecule approximates between the two rings to be around was 34° (Venkataraman et al, 2006; Artacho et al, 2008). In our DFT calculations, the torsion angle was found about 40°. However, the torsion angle of bipyrimdine molecule is 0° due to the overlap between the pi-orbitals which increases when the rings are rotated perpendicular to each other as shown in table 1, and the electrical transport follows a cos2θ (Landauer, 1957). For X(CO)4-bipyrimdine molecules, the angle between the two rings was found 0° because a metal linked atom (W, Mo, and W) via two pyridine rings in those structures.

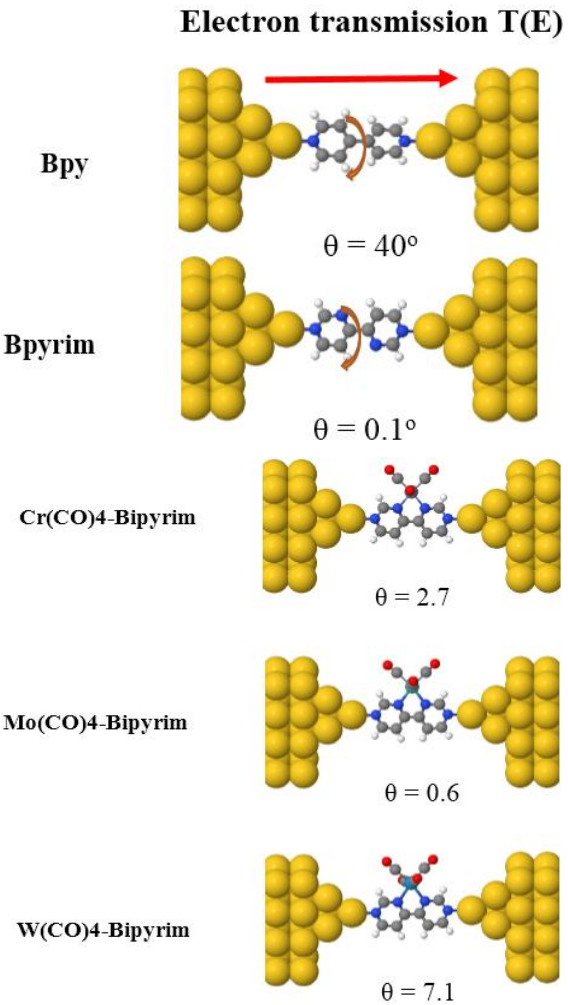

Figure 1. Molecular structures of a set of Bpy, Bpyrim, and X(CO)4-Bipyrimdine molecules between two gold leads at different metal centre (Cr, Mo, W) complexes

The possible path of the electron is designated as a cross-plane path either through the backbone of molecule and this is clear shown in the transmission curve for Bpy and Bpyrim molecules or through metal(CO) group to the end of molecule, and then to the electrodes leads as shown in Figure 2.

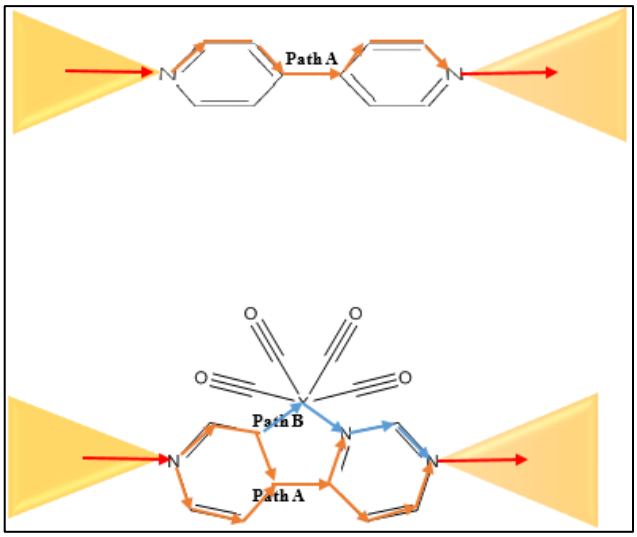

Figure 2. Simple carton shows for (a) the electrons path through bpy structure and (b) there are more electrons path through X(CO)4-bpyrim structure

Results and Discussion

The electrical characteristics were calculated of a family of bipyridine, bipyrimdine, and X(CO)4-bipyrimdine molecules using DFT-based GOLLUM code to compute T(E). Geometrical optimizations have carried out using DFT SIESTA code. All molecules studied in this chapter were freely relaxed in isolation to yield optimized geometries. For each molecular structure, the transmission coefficient of electrons T(E), which describes the propagation of energy of electrons from one electrode to the other was calculated by first calculating the Hamiltonian from SIESTA code, and then using GOLLUM code to compute T(E), electrical conductance was calculated at room temperature using the equation 1. The optimized distance between anchor group N and the gold electrodes was 0.23 nm. The transport coefficient, T(E) is characterizing the passage of electrons with energy E from the left to the right electrode for two gold leads, the transmission coefficient was computed for each relaxed junction structure by first deriving the relevant Hamiltonian and overlap matrices using the DFT-based SIESATA and GOLLUM codes.

To understand more about the thermoelectric devices, DFT simulations were performed to see how the electrical conductance of molecular structures changes with the type of each molecule under study. As mentioned previously, the gold lead/molecule/gold lead were linked perpendicularly to the plane of the molecules, and the planar geometries of the molecules were studied. The mechanics of the transport calculations was represented the transmission coefficients of bipyridine and X(CO)4 bipyrimdine molecules that were appeared various results around Fermi energy EF as shown: for bipyridine and bipyrimdine molecules without metal complexes, the findings exhibited bipyridine molecule was lower than bipyrimdine about twice as shown in figure (3-a). This difference is due to the chemical structure between molecules, as well as the effect of the molecular conformation.

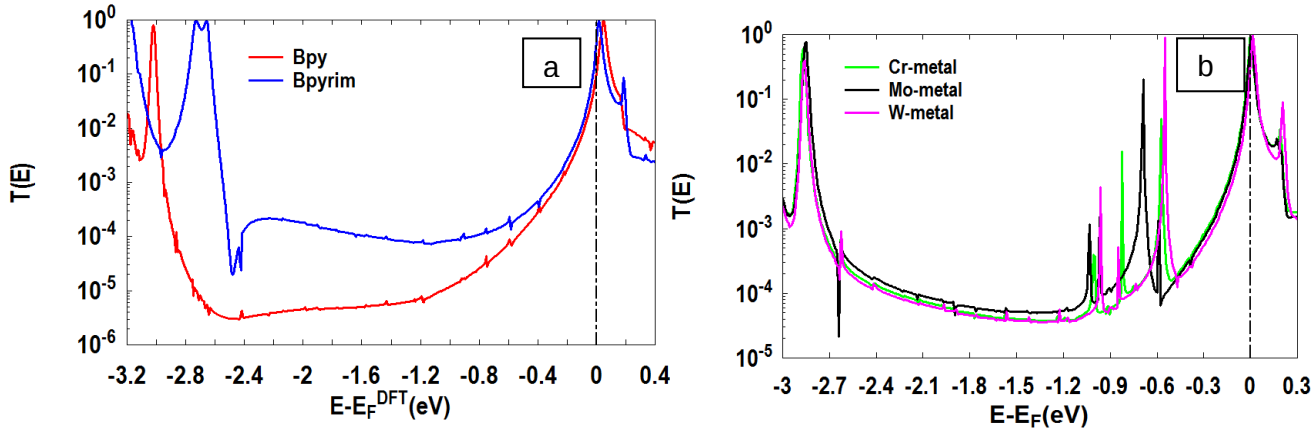

Figure 3. Theoretical calculation of transport coefficient as a function of the Fermi energy for a) Bpy and Bpyrimdine b) X(CO)4-bipyrimdine molecular junctions

From figure 4, it is clearly seen that the electrical conductance of five molecules was various values at Fermi energy (E_F), which leads to appear the resonances are close to Fermi energy for Cr, Mo, and W central metal atoms to show the important role of those complexes, in particular the quantum interference concept in single-molecule junctions.

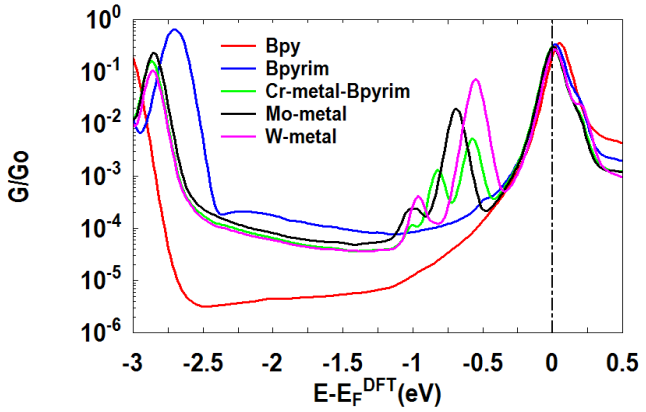

Figure 4. Electrical conductance values at room temperature as a function of energy for Bpy (red), Bpyrim (blue), Cr-metal (green), Mo-metal (black), and W-metal (pink)

Theoretical investigation into the Seebeck coefficient S of molecular junctions using a quantum transport method using Bpy, Bpyrim, Cr-metal, Mo-metal, and W-metal. For the thermoelectric coefficient, the thermoelectric structures will later be used to construct molecular structures. Several molecules have been investigated to understand more about the factors that could the effect the sign and magnitude of their thermopower. Therefore, when a temperature is differential *T* and a voltage variation *V* through a system, the thermoelectric effect might be characterized as a conversion between thermoelectric and electric energy. This occurs in the passing of an electrical *I* and a heat Q current via a molecular device. The Seebeck coefficient S was calculated from the relation (3). The results were demonstrated in Figure 5.

It can be shown that quantum interference produces resonances in the gap between the HOMO and LUMO resonances. The shifting of this resonance leads to an enhancement of the thermopower *S*. This behavior is dependent on the connectivity of the molecule as a para-connected molecule produces a constructive feature that dominates and reduces the sensitivity to destructive interference through the pi-orbital geometry.

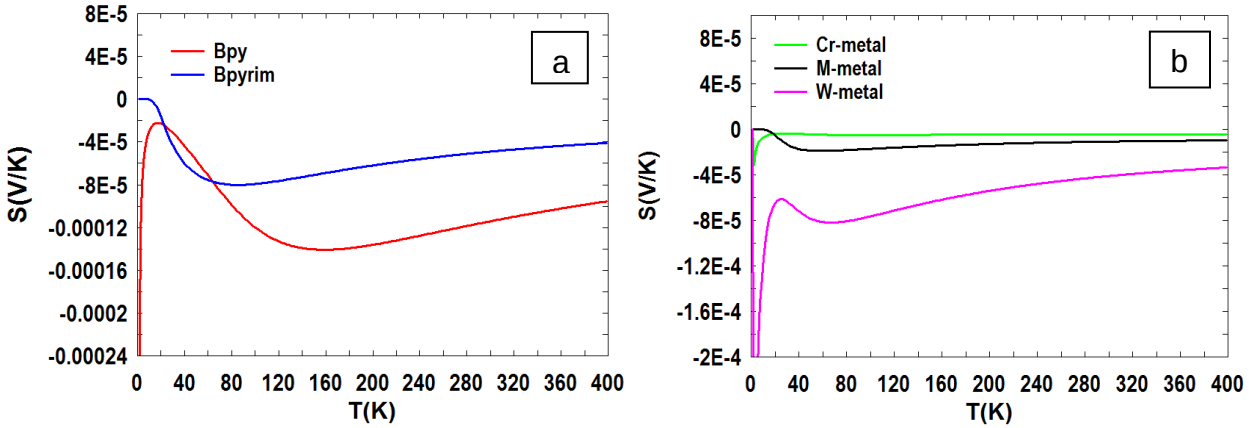

Figure 5. Seebeck coefficient S as a function of the temperature for a) Bpy and Bpyrim b) X(CO)4-bipyrimdine molecular junctions at Fermi energy

A more thorough comprehension of thermoelectric properties can be represented by the Seebeck coefficient that clearly shows its behavior at passing the heat current from the hot side to another colder nanowires (organic and organometallic materials) in the presence of complex metals. In the fact, the change of the sign of thermopower depends on either the connection between the molecular and the electrodes or on the pi-conjugated molecules. Therefore, the transmission coefficient T(E) at the Fermi level E_F provided by DFT is closest to the LUMO resonance, with a positive slope due to the existence of pyridine anchors; however, the Seebeck coefficient is negative, indicating that the LUMO is moving closer to the Fermi energy.

Figure 6 shows the value of *S* is proportional to the slope of the transmission at the Fermi Energy. The oscillator of Seebeck coefficient with electron energy of the set molecules that were studied in this thesis. The HUMO-dominated at the DFT Fermi energy leads to the negative Seebeck coefficient. In addition, to demonstrate the oscillated sign of thermopower of metal-complexes molecules (green, black, and pink lines) in Figure (6-b), hence appears the role of these metals, but all these results are various position and so far from Fermi energy E_F between (-1.173 to-0.28 eV).

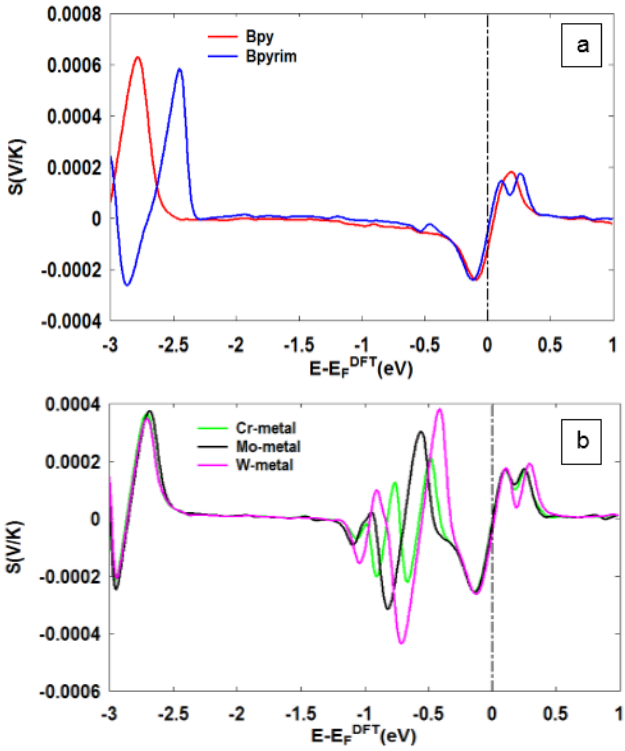

Figure 6. Thermopower *S* as a function of electron energy for a) bpy and bpyrim and b) Cr-Mo-W(CO)4 bipyrimdine molecules, respectively

The electronic contribution to the figure of merit ZT_e at over a range of temperatures has been calculated at Fermi energy E_F as shown in Figures 7.

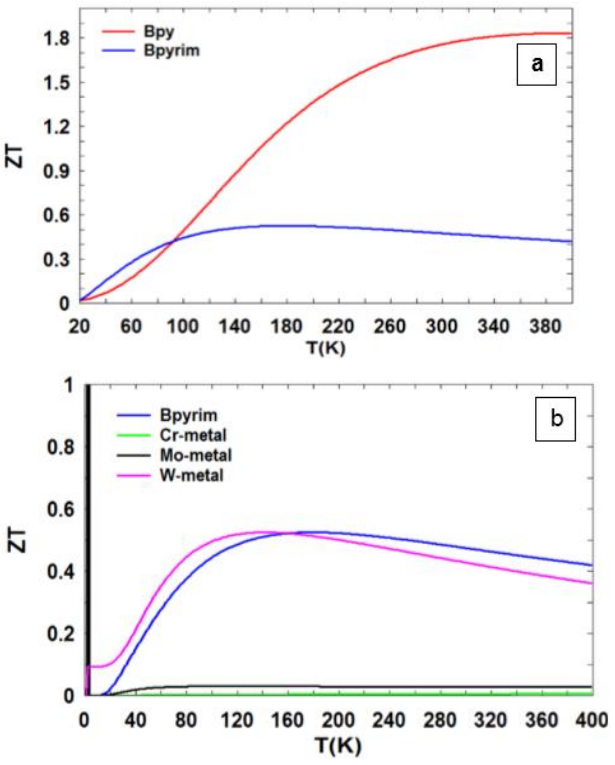

Figure 7. The electronic contribution to the figure of merit ZT_e at Fermi energy as a function of room temperature for a) Bpy and Bpyrim b) central atom (Cr, Mo, and W) metal complexes

At comparing bpy and bpyrim molecules, the findings were explained the ZT_e value at room temperature of bpy is about 1.75, whereas for bpyrim is 0.474 which means bpy is greater than bpyrim. For metal-complex molecules, it can be shown W metal has a high value compared with other metal complexes as Cr-Mo metal, which have a low value of ZT_e. On the other hand, all these results depend on the position of Fermi energy that limits the value of the figure of merit in all molecular structures used here in this thesis. From Figure 7, as mentioned the ZT_e depodes on the position of the Fermi energy, which determines the values of the electrical conductance and thermopower. Thus, the highest value of ZT_e was for Bpy, whereas the lowest value for Cr-metal-bpyrim molecule. The variation of the value of the figure of merit is due to as mentioned above the chemical structures of those molecules and the position of the Fermi energy.

Conclusion

In this work, it can be summarized all results of various structures as organic and organometallic molecules that have studied through our work to calculate the electrical and thermal properties of family molecules using Density Function Theory DFT. The metal-ligand chemical bond between metal complexes with CO group and backbone of a molecule plays more important due to change of the behavior of molecules before and after the addition of these structures, which led to change the value of the electronic properties, in particular when compared with the bipyridine molecule that used as a basics molecule and X(CO)4-bipyrimdine. The Seebeck coefficient of all molecules taking advantage of steep slopes depends in transmission coefficient, and the Seebeck coefficients are negative. The Seebeck coefficient is an observable magnitude that is affected by factors such structural conformation, where S in order to as bpy > bpyrim > W > Mo > Cr molecules.

References

Manrique, D.Z., Huang, C., Baghernejad, M., Zhao, X., Al-Owaedi, O.A., Sadeghi, H., Kaliginedi, V., Hong, W., Gulcur, M., Wandlowski, T., Bryce, M.R. and Lambert, C.J. (2015). A quantum circuit rule for interference effects in single-molecule electrical junctions. *Nature Communications*, 6(1).

Chen, J. (1999). Large On-Off Ratios and Negative Differential Resistance in a Molecular Electronic Device. *Science*, 286(5444), 1550–1552. https://www.eng.yale.edu/reedlab/publications/95%20Science%20NDR.pdf

Reed, M.A., Zhou, C., Muller, C.J., Burgin, T.P. and Tour, J.M. (1997). Conductance of a Molecular Junction. *Science,* 278(5336).

Smit, R.H.M., Noat, Y., Untiedt, C., Lang, N.D., van Hemert, M.C. and van Ruitenbeek, J.M. (2002). Measurement of the conductance of a hydrogen molecule. *Nature*, 419(6910).

Jia, C. and Guo, X. (2013). Molecule–electrode interfaces in molecular electronic devices. *Chemical Society Reviews*, 42(13).

Xiang, D., Jeong, H., Kim, D., Lee, T., Cheng, Y., Wang, Q. and Mayer, D. (2013). Three-Terminal Single-Molecule Junctions Formed by Mechanically Controllable Break Junctions with Side Gating. *Nano Letters*, 13(6).

Naghibi, S., Ismael, A.K., Vezzoli, A., Al-Khaykanee, M.K., Zheng, X., Grace, I.M., Bethell, D., Higgins, S.J., Lambert, C.J. and Nichols, R.J. (2019). Synthetic Control of Quantum Interference by Regulating Charge on a Single Atom in Heteroaromatic Molecular Junctions. *The Journal of Physical Chemistry Letters*, 10(20).

Ismael, A.K., Wang, K., Vezzoli, A., Al-Khaykanee, M.K., Gallagher, H.E., Grace, I.M., Lambert, C.J., Xu, B., Nichols, R.J. and Higgins, S.J. (2017). Side-Group-Mediated Mechanical Conductance Switching in Molecular Junctions. *Angewandte Chemie International Edition*, 56(48).

Al-Galiby, Q.H., Sadeghi, H., Algharagholy, L.A., Grace, I. and Lambert, C. (2016). Tuning the thermoelectric properties of metallo-porphyrins. *Nanoscale*, 8(4).

Ballhausen, C.J. and Gray, H.B. (1980). *Molecular electronic structures: an introduction*. Benjamin/Cummings Publishing Company.

Ie, Y., Hirose, T., Nakamura, H., Kiguchi, M., Takagi, N., Kawai, M. and Aso, Y. (2011). Nature of Electron Transport by Pyridine-Based Tripodal Anchors: Potential for Robust and Conductive Single-Molecule Junctions with Gold Electrodes. *Journal of the American Chemical Society*, 133(9).

Kamenetska, M., Quek, S.Y., Whalley, A.C., Steigerwald, M.L., Choi, H.J., Louie, S.G., Nuckolls, C., Hybertsen, M.S., Neaton, J.B. and Venkataraman, L. (2010). Conductance and Geometry of Pyridine-Linked Single-Molecule Junctions. *Journal of the American Chemical Society*, 132(19).

Li, R., Hou, S., Zhang, J., Qian, Z., Shen, Z. and Zhao, X. (2006). Analysis on the contribution of molecular orbitals to the conductance of molecular electronic devices. *The Journal of Chemical Physics*, 125(19).

Tan, A., Balachandran, J., Sadat, S., Gavini, V., Dunietz, B.D., Jang, S.-Y. and Reddy, P. (2011). Effect of Length and Contact Chemistry on the Electronic Structure and Thermoelectric Properties of Molecular Junctions. *Journal of the American Chemical Society*, 133(23).

Ferrer, J., Lambert, C.J., García-Suárez, V.M., Manrique, D.Z., Visontai, D., Oroszlany, L., Rodríguez-Ferradás, R., Grace, I., Bailey, S.W.D., Gillemot, K., Sadeghi, H. and Algharagholy, L.A. (2014). GOLLUM: a next-generation simulation tool for electron, thermal and spin transport. *New Journal of Physics*, 16(9).

Sert, Y., Ucun, F., El-Hiti, G.A., Smith, K. and Hegazy, A.S. (2016). Spectroscopic Investigations and DFT Calculations on 3-(Diacetylamino)-2-ethyl-*3H*-quinazolin-4-one. *Journal of Spectroscopy*, 2016.

Oftadeh, M., Naseh, S. and Hamadanian, M. (2011). Electronic properties and dipole polarizability of thiophene and thiophenol derivatives via density functional theory. *Computational and Theoretical Chemistry*, *966*(1-3).

Al-Khaykanee, M.K., Ismael, A.K., Grace, I. and Lambert, C.J. (2018). Oscillating Seebeck coefficients in π-stacked molecular junctions. *RSC Advances*, 8(44).

Venkataraman, L., Klare, J.E., Nuckolls, C., Hybertsen, M.S. and Steigerwald, M.L. (2006). Dependence of single-molecule junction conductance on molecular conformation. *Nature*, 442(7105).

Artacho, E., Anglada, E., Diéguez, O., Gale, J.D., García, A., Junquera, J., Martin, R.M., Ordejón, P., Pruneda, J.M., Sánchez-Portal, D. and Soler, J.M. (2008). The SIESTA method; developments and applicability. *Journal of Physics: Condensed Matter*, 20(6).

Landauer, R. (1957). Spatial Variation of Currents and Fields Due to Localized Scatterers in Metallic Conduction. *IBM Journal of Research and Development*, 1(3).