High Thermoelectric Performance of Metallophthalocyanine Molecular Junctions with *cis* and *trans* Configuration

Asala R. Lafta [1] ,

[1,2]Department of Physics, Collage of Sciences, University of Thi-Qar, Thi-Qar, Iraq
asalaramadhan@gmail.com

Mohammed Deia Noori [2]

[1,2]Department of Physics, Collage of Sciences, University of Thi-Qar, Thi-Qar, Iraq
2. mdn.noori_phy@sci.utq.edu.iq

ABSTRACT

A theoretical comparative study of electrical and thermoelectric properties of metallophthalocyanine (MPc) molecule sandwiched between two gold leads have been studied. Metallophthalocyanine (MPc) with different transition metal ions at the center of phthalocyanine (Fe, Co, and Cu) have been investigated in two different molecular configurations, *cis* and *trans*. The results show that the electrical conductance and thermopower are changed by varying the transition metal-center and both of them show higher values around Fermi energy in *trans* configuration than *cis* one. Higher value of figure of merit ZT has been computed in Fe-Pc in *cis* configuration ~ 3.3. High (ZT) values demonstrated that these molecular junctions are efficient thermoelectric applications.

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

Introduction

Over the past twenty years, single- molecule electronic systems have matured into a platform that enables the study of fundamental properties of materials at the molecular or atomic level, in particular the charge transport, molecular spintronic, and thermoelectric performance. Several approaches to building and studying molecular junctions have been developed [1-4] in addition to many experimental and theoretical studies have been carried out to develop and control electronic molecules[5-9] for future nanoelectronics circuits applications such as molecular wires[10], electrodes[11], wiring circuit[12], and switches[13]. These studies have attracted a great deal of attention in recent years since it holds promise for the next generation of electronic devices with enhanced functionality and improved performance.[14-16]. A phenomenon that can directly convert between heat and electric power to make heat engines or refrigerators possible is known as thermoelectricity. Though the effect has long been known, since the early 19th century[17-19]. Seebeck effect which measures the possibility of generating a voltage difference form a heat gradient. This effect is intended to enhance the generation of electric current by investing waste heat. Recently, much attention has been given to tune the parameters that control the thermoelectric properties, especially in molecular scale[5, 19-22]. The efficiency of thermoelectric materials is mainly determined by thermoelectric figure of merit (ZT), which is given by ($ZT=S^2GT/\kappa$), where S is the Seebeck coefficient, G is the electrical conductance, T is the temperate and κ is the electronic thermal conductivity. Molecular electronics is an extremely interesting and fundamental research field of nanotechnology, which tends to develop new high performance thermoelectric and nano-electronic devices working based on the single molecule level in which organic molecules are used as active elements[6, 7]. Phthalocyanine (Pc) is one of the most important organic molecules which has attracted huge attention for many years due to its distinguished high chemical and thermal stabilities in addition to ideal symmetric geometrical structure [23-25]. Phthalocyanine characteristics such as electronic, structure, magnetic, chemical, as well as transport can be tuned by inserting host central metallic ion in the center, in this case phthalocyanine (Pc) is known as metallophthalocyanines (MPc)[26, 27] . However, metallophthalocyanines have been considered in many applications from organic thin film transistors[28], chemical sensors[29], to optoelectronic and photovoltaic devices[30-33]. Metallophthalocyanines (MPc) have been investigated with techniques such as scanning tunneling spectroscopy (STS)[34], photoemission spectroscopy[35], gas phase electron diffraction[36], nuclear magnetic resonance[37],etc. Therefore, in MPc if the core metal ion varies, it can tune the molecular energy levels relative to the Fermi energy E_F of the electrodes, and if energy levels become close enough to E_F, then this should lead to transport resonances, which should lead to transport resonances improve the thermopower[38]. Moreover, using different structural configuration can change the pathway of charge transport[39], and this will lead to show new features of quantum interference QI in transport curve. In this work, we introduced a comparative theoretical study of electrical and thermometric properties of metallophthalocyanine (MPc) as shown in Fig. 1 the single (MPc) molecule is sandwiched between couple gold electrodes in two different configurations *cis* and *trans*, with a variety of different metal ions (Fe , CO, and Cu) are embedded in the center of (Pc) molecule to present the comparison.

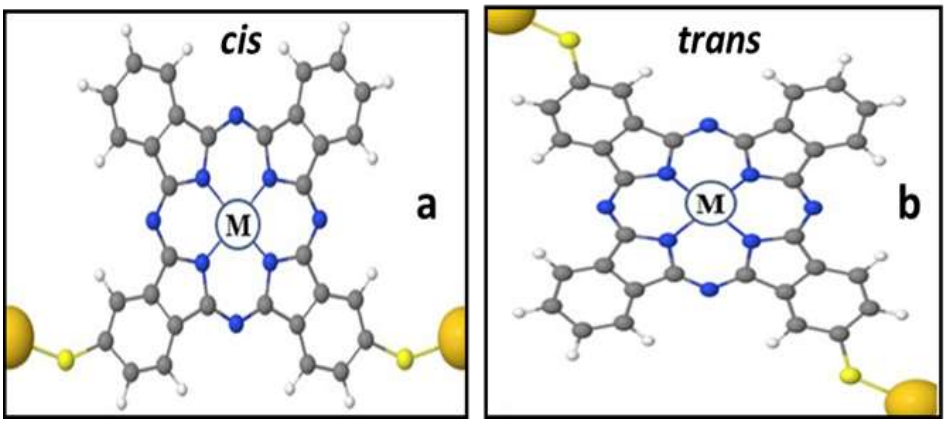

Figure 1. Metallophthalocyanine (M-Pc) molecule structure sandwiched between two gold electrodes in two different configurations (a) *cis*, and (b) *trans.*

Results and Discussion

To investigate the transmission properties and electrical conductance of metallo-phthalocyanine (MPc), different transition central metals such as: Fe, Co, and Cu have been used. The system connected in two different molecular configurations *cis* and *trans* as shown in Fig. 1. The transmission function for both spin up T↑ and spin down T↓ were calculated. Then, the total transmission function is found according to the formula T(E) = (T↑ + T↓). Fig. 2 shows the transmission coefficient of (MPc), where (M= Fe Co, and Cu), in two different configurations *cis* (left column) and *trans* (right column). In all of them, different line styles and colors are presented to represent spin up, spin down, and total transmission coefficient.

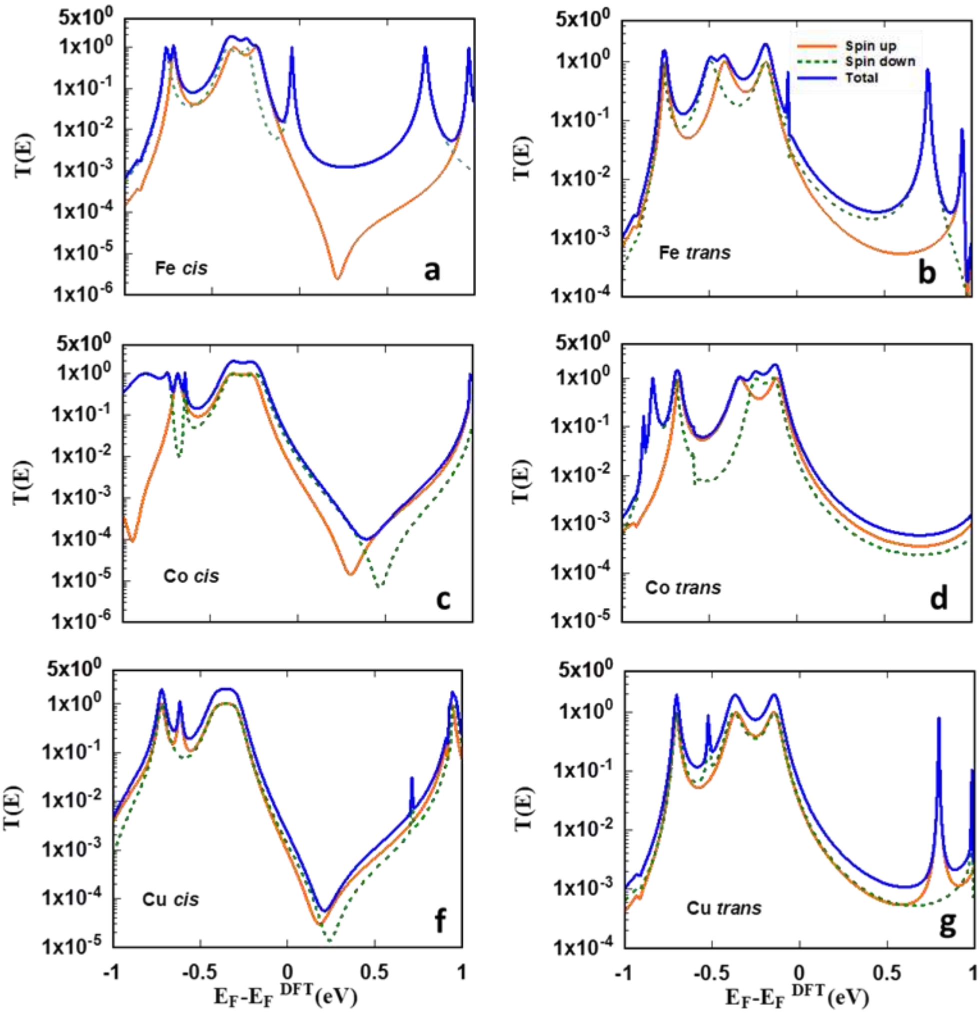

Figure 2. Electron transmission coefficient of metallophthalocyanine (MPc) (a, c, and f) *cis*, and (b, d, and g) *trans* configurations.

From the transmission curves, in Fig. 2 we can explore the spin state. In Fig. 2, the transmission curves of all systems in both configurations *cis* (a) and *trans* (b) show spintronic properties since the spin up and spin down curves are not identical. In *cis* configurations (Fig. 2a) the transmission curves of Fe-(Pc) shows a huge difference between spin up (red line) and spin down (green dotted line) transmission curves while in *trans* (Fig. 2d) the difference is much less than *cis* case. Fig. 2c-g show *cis* and *trans* configuration of Co-(Pc) and Cu-(Pc) show lower spintronic properties than Fe-Pc. This can be explained by referring to the square planar molecular geometry of metallophthalocyanine (MPc) that used in this work, and orbital diagram of transition metal according to crystal field theory[40] in which in all cases (Fe, Co and Cu) metals have unpaired electrons in the last d-orbital. However, Fe-(Pc) show higher spintronic properties in both cases *cis* and *trans* as shown in Fig 2. (a-b, and i-j), because iron atom has two unpaired electrons in the last d-orbital (e_g). In all other cases (Co) and (Cu) metals have just a single unpaired electron in the last d orbital (e_g). These spintronic results have a very good agreement with the electronic structure diagram in[41]. The corresponding room-temperature conductance versus Fermi energy E_F are shown in Fig. 3 for Fe-(Pc), CoPc, and CuPc. It is shown that almost in all cases electrical conductance is higher in *trans* cases than in *cis* connection around Fermi energy. This is highly expected since the previous transmission calculations shown in Fig. 2 stated that molecular junctions connected in *trans* showed enhanced transmission curves compared to *cis* connection, and it is well known that electrical conductance is proportional to transmission values.

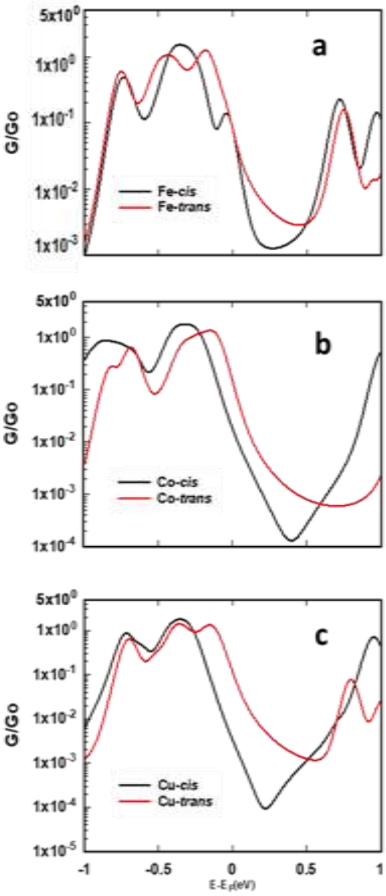

Figure 3. Room temperature electrical conductance of metallophthalocyanine (MPc) in *cis,* and *trans* configurations.

To investigate the thermoelectric properties of all structures in both configurations, we have computed the Seebeck coefficient (S) as described in the method section and shown in Fig. (4) as a function of Fermi energy E_F. It states that both the magnitude and sign of (S) are sensitive to configuration of the junction and shows that *cis* configuration Fig. 4a has a large positive fluctuation values comparing to *trans* configuration Fig. 4b.

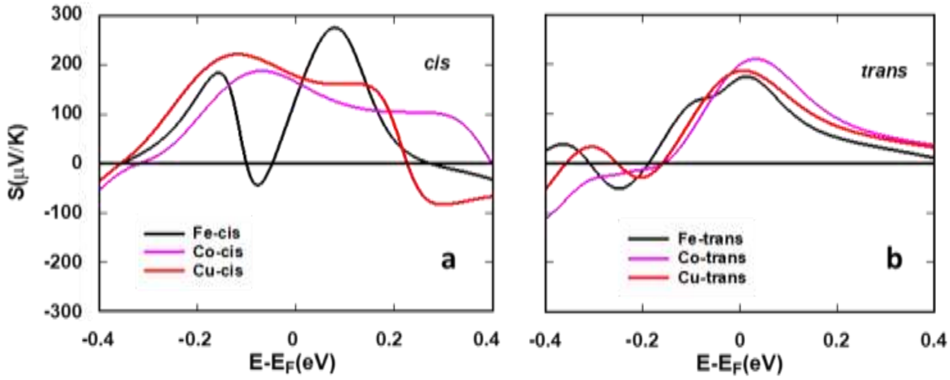

Figure 4. (a) Seebeck coefficient (S) curves of metallophthalocyanine (MPc) in *cis* (b) *trans* configurations.

To compare the electrical conductance and thermopower in all systems, Fe, Co, and Cu we have plotted them in Fig. 5 in both *cis* and *trans* configurations as a function of metallic atoms at

E_F=0.0 eV. Fig. 5a reveals that the electrical conductance in *trans* is higher than *cis* configurations in both Co-Pc, and Cu-Pc, while its almost equal in Fe-Pc. However, the variation in electrical conductance across this family of molecules increases in *trans* case takes the order Co > Cu > Fe. The lowest electrical conductance in *cis* case is in Cu-(Pc) while in *trans* case is in Fe-(Pc). Fig. 5b shows that the thermopower in *trans* is higher than *cis* in all cases, and the highest thermopower value is recorded in Co-Pc ~ 200 μV/K.

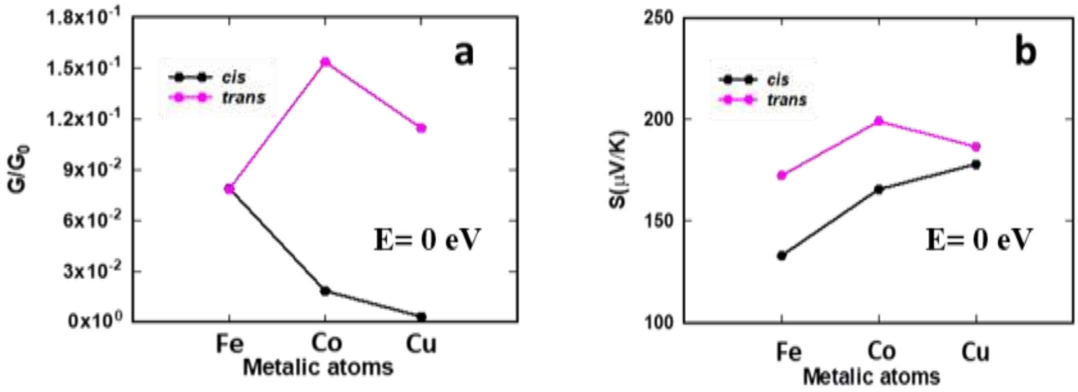

Figure 5. Comparison of (a) electrical conductance and (b) thermopower (S) values for all structures of metallophthalocyanine (MPc) in *cis*, and *trans* configurations.

Fig. 6 shows the thermal conductivity k as a function of energy. From this figure, the thermal conductivity k found to be higher in *trans* than *cis* configuration in the vicinity of Fermi energy for Fe-(Pc), Co-(Pc), and Cu-(Pc). In Fig. 6a the lowest value of k in *cis* case recorded in Cu-(Pc) while, the lowest value of k in *trans* case is in Fe-(Pc) as shown in Fig. 6b.

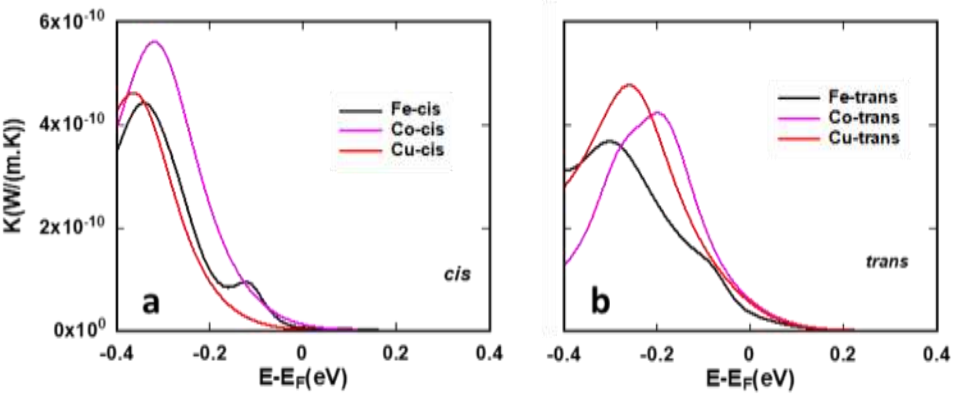

Figure 6. (a) Thermal conductance k as a function of energy of metallophthalocyanine (MPc) in *cis*, (b) *trans* configurations.

As a result, the figure of merit (ZT) can be obtained from the formula $ZT=S^2GT/\kappa$ and as shown in Fig. (7), which shows that (ZT) in *trans* connection is higher than *cis* connection except Fe-Pc, where Fe-Pc in *cis* configuration shows the highest value of ZT with low values for Co-Pc, and Cu-Pc. Otherwise, in *trans* case Co-Pc, and Cu-Pc have the higher values of (ZT) than Fe-Pc. Fig. 7 also demonstrated that Fe-Pc in *cis* case, and Co-Pc in *trans* case these structures are promising for efficient conversion of the heat to electricity.

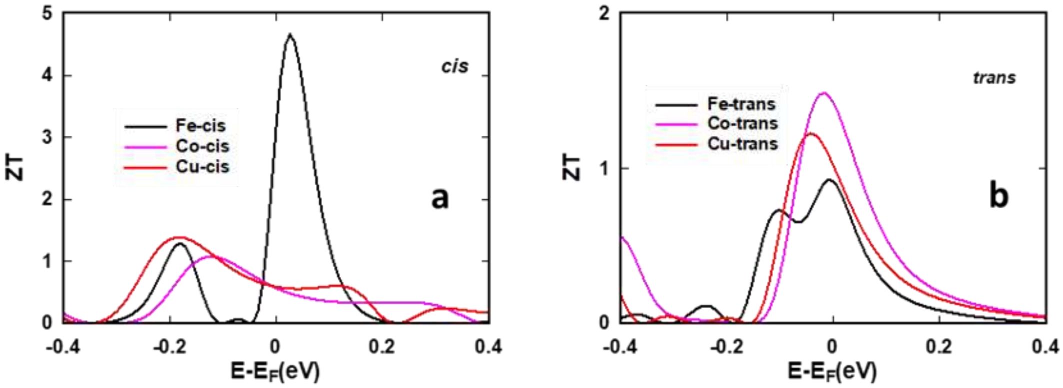

Figure 7. (a) Room temperature figure of merit ZT of phthalocyanine (MPc) in *cis* (b) *trans* configurations.

Conclusion

Overall, we have compared theoretically the electrical and thermoelectric properties of three metallophthalocyanine (MPc) molecule sandwiched between two gold electrodes in two different molecular configurations, *cis* and *trans* with different metals in the center of metallophthalocyanine (MPc), where M=Fe, Co, and Cu. The results show that in *cis* case the Fe-Pc shows a highest ZT value around Fermi energy ≈ 3.3. While in *trans* case the higher value is recorded by Co-Pc ≈ 1.5. Consequently, enhanced (ZT) values demonstrated that these systems have a very high thermoelectric performance and promising candidates for many applications in thermoelectric field.

Method

At the beginning, all the structures of *cis* and *trans* molecular geometry that shown in Fig. 1 was optimized before building the junction model. Then, the geometry of each structure that consist of two gold electrodes and metallophthalocyanine (MPc) molecule was optimized again, the thiol anchor group was used to bind ferrocene units to gold leads as shown in Fig.1. We used the spin density functional theory (DFT) code SIESTA[42], with a double-ζ polarized basis set (DZP) and generalized gradient functional approximation (GGA-PBE) [43, 44]. After we obtain the mean-field Hamiltonian H then combined it with the quantum transport code, GOLLUM[45] to calculate the transmission coefficient Tel(E). The electrical conductance was computed by using Landauer formula. We compute the thermopower S over a wide range of Fermi energies by using equation $S= -\frac{1}{eT}\frac{L1}{L0}$ where T is the temperature, e is electron charge and Ln can be calculated as $L_n=\int_{-\infty}^{\infty}(E - E_F)^n\ T(E)\ (\frac{\partial f(E,T)}{\partial E})$ where f(E,T) is the Fermi-Dirac probability distribution function[46].

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