Effect of the Spin on the I-V Characteristics of Thiophene Functionalized Metalla-Bis(Dicarbollide)

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Abstract

The conductance of thiophene functionalized metalla-bis(dicarbollide) is studied by forming a device in which the molecule is attached to bulk Au electrodes via linking atoms. The effect of the spin state on the I-V characteristics of the molecule is measured in order to determine the conductivity as a function of the spin state of the central transition metal atom. From the calculations present we observe a higher spin state leads to increased conductivity in Fe(III)-bis(dicarbollide).

Introduction

Thiophene functionalized metalla-bis(dicarbollide) consists of:

- **A central transition metal atom**
- **Two carborane cages**
- **Two thiophene rings**
- **Two linking atoms between the thiophene rings and the Au electrodes.**

Other research conducted that relates to our structure or motive includes:

- **Cobalt-bis(dicarbollide) can potentially act as a molecular rotor[1]**
- **Successfully synthetically produced thiophene functionalized metalla-bis(dicarbollide)[2]**
- **The spin state of $[Fe^{II}(bpp)_2]^{2+}$ can be manipulated by an external stimulus such as light, temperature, or an electric field.[3,4]**

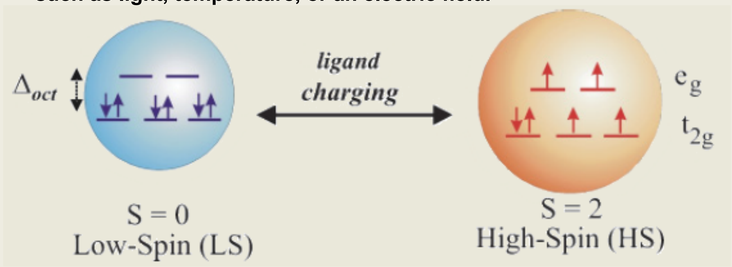

Figure 1: Schematic representation of the orbital population being manipulated by the charging of the ligand.[4]

Here we study the I-V characteristics for 3 different spin states of Fe(III)-bis(dicarbollide), employing sulfur atoms as the link between the thiophene rings and the bulk gold electrodes.

Methodology

Gaussian 09 software was employed to do the following:

- **Set the overall charge of the molecule**
- **Establish the spin of the central atom.**
- **Geometrically optimize the molecule to its lowest energy configuration using the B3LYP DFT functional**

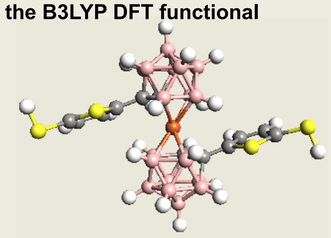

Figure 2: End result of geometric optimization for Fe(III)-bis(dicarbollide) in its low spin state with thiophene attached as determined by Gaussian 09.

The Atomistix Toolkit(ATK) software package was used for the subsequent tasks:

- **Situating the molecule between two Au electrodes**
- **Calculating the transmission spectrum according to the PBES DFT functional with a double zeta plus polarization basis set used on all atoms**
- **Determining the I-V characteristics with the use of Landauer-Büttiker formula.**

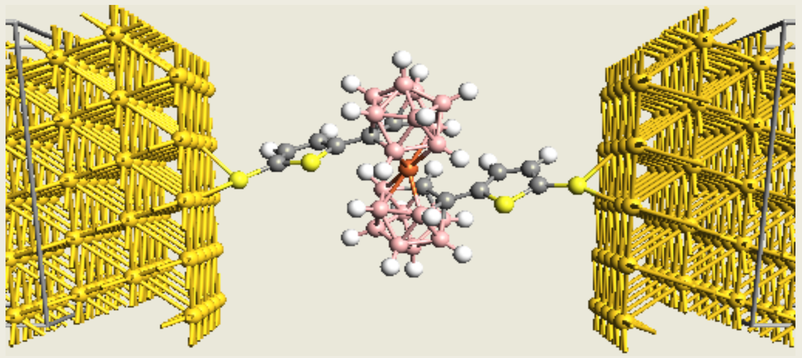

Figure 3: Schematic of the device created in ATK illustrating the thiophene functionalized Fe(III)-bis(dicarbollide) molecule in its low spin state attached to Au electrodes via S linking atoms.

Results

Figure 3 below shows an example of one of the transmission spectrums calculated by ATK. Once the transmission spectrum is calculated for each of the voltage biases, ATK translates each set of data into a value of current which goes into plotting the I-V curves describing the conductance. Results show an increase in conductivity with an increase in the spin polarization.

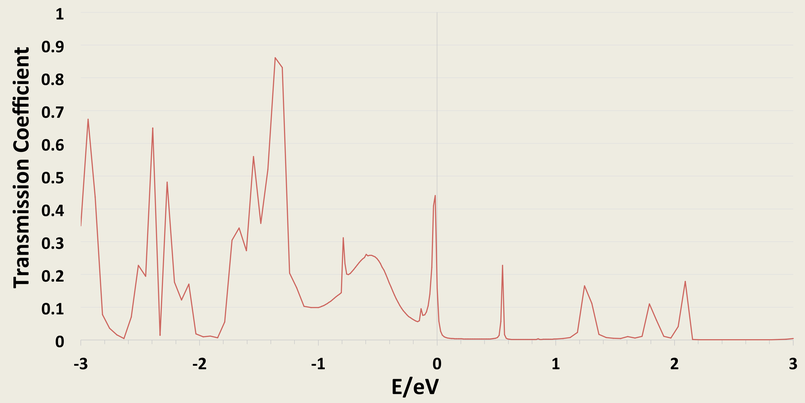

Figure 4: Zero bias transmission spectrum for thiophene functionalized Fe(III)-bis(dicarbollide) in its low spin state.

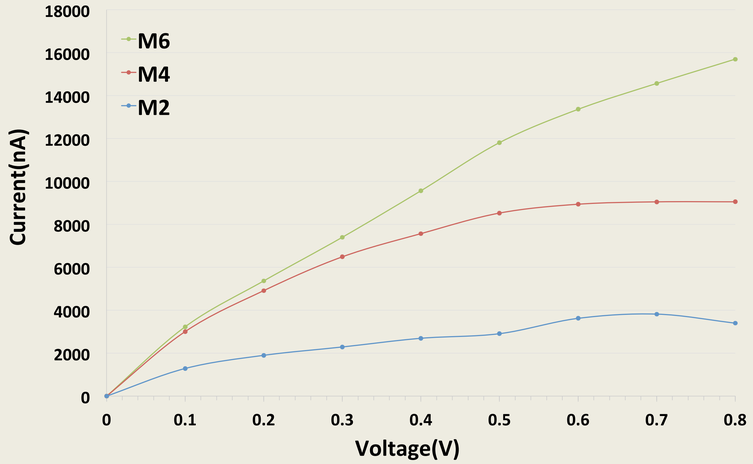

Figure 5: Current(nA) vs. voltage(V) as a function of spin state for thiophene functionalized Fe(III)-bis(dicarbollide)

Conclusions

- **We have shown that the different spin states of thiophene functionalized Fe(III)-bis(dicarbollide) exhibit significantly different levels of conductivity.**
- **Potentially we could indirectly control the conductivity of a molecule by using an external stimulus to manipulate its spin state, which would be very beneficial for the emerging field of molecular electronics**

Future work

Further studies of the same nature are planned to be performed with slight variations in order to determine the most suitable molecular configuration for this application. These variations include:

- **Repeating calculations for Fe(II)**
- **Employing different transition metals as the central atom such as cobalt**
- **Exploring alternative linking atoms such as gold, phosphorous, and selenium.**

References

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