



Electronic transmission stability in Pyrene Derivatives

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ABSTRACT

In this study the electronic properties of pyrene molecules are investigated. The study includes single and multiple pyrene molecules. The effect of some radicals has been also studied. The electronic transmission curves are shown to be symmetric around Fermi level and the energy gap of the molecule decreases as the length of the molecule increases. The additives cause some fano peaks that having positions can be modified by tuning the on-site energy of the heteroatoms. However, changing the on-site energy does not change the transmission value at Fermi level.

Key words : Pyrene derivatives, electronic transmission.

1. INTRODUCTION

Single-molecule junction represents the main part of future electronic circuits. The molecular junction mainly consists of electrode, anchor molecule, core (main) molecule, anchor molecule, and electrode. The electrons are allowed to pass from one electrode to the other through the main molecule. In general, the dimensions of the electrodes are much greater than the molecule so that the energy levels can be regarded as continuous spectra. In contrast, the energy levels of the core molecule are very discrete and fragile. In other words, the energy of the passing electrons should coincide with the energy of one of the molecular levels to let the electrical current flow (closed circuit). Furthermore, these molecular energy levels are extremely sensitive to a number of variables such as impurities, deformations, substituents, torsion angle of the molecule. Therefore, understanding the electronic structure of the molecule is a fundamental task to understand and develop sophisticated nanoscale junctions.

Organic molecules represent the main candidates for future single-molecule junctions. These molecules are abundant, cheap, easy to fabricate and control, and convenient for environment. In this study we have chosen pyrene to be investigated and analyzed by using tight binding method and density function theory. This molecule is well known to be used in photovoltaic cells and light emitting diodes [1].

2. THEORETICAL METHODS

2.1 Tight binding

To characterize the electronic properties Green's function code Olife [2] has been used. In this method tight binding Hamiltonians (TBH) with Green's function (GF) are combined to produce the results. This combination significantly reduce the time required for the calculations and results in trusted results [3-7] This is facilitated because Olife depends on TBH and this basically consists of two parameters. The onsite energy of the orbitals is the first parameter and the coupling energy between two successive orbitals (off diagonal elements). The off-diagonal elements of the Hamiltonian represent the hopping elements. The hopping elements represent the strength of the bonds. This can represent the length of the bond. This means that we have used a single value for the similar bond lengths of the molecules and stronger coupling elements for shorter bonds. In addition, TBH scales the energy units by one parameter for convention.

As a result, Olife is a friendly code to calculate the

conductance,
$$\sigma = (2e^2/h) \int dE T(E) (-\partial f_E),$$
 by applying Landauer formula [8]. Where e is the electron

charge, h is Planck's constant, E is the energy, $T(E) = |t|^2$ is the transmission coefficient, $f(E)$ is the Fermi-Dirac

distribution function $= [1 + \exp^{-\beta(E-E_F)}]^{-1}$, E_F is the Fermi energy, $\beta = k_B T$, k_B is Boltzmann's constant, T is the temperature, and t is transmission amplitude for one allowed channel since we allocated a single energy for each site. The formula of the transmission amplitude is

$G_{\delta,\mu} = (1/i\hbar v) t e^{ik}$. Where $G_{\delta,\mu}$ is the Green's function [9].

2.2 Density Functional Theory

Density functional theory (DFT) is a quantum mechanical method used to characterize the electronic structure molecular systems. DFT used for investigating the ground state properties of different materials [10]. DFT has started with Thomas-Fermi model, in 1927. They depended on

representing the kinetic energy of an atom as a function of the electron density and using classical expressions for the nuclear-electron and electron-electron interactions to calculate the energy of the atom [11 and 12]. The DFT depends on the electron density $\rho(r)$. It is also dependent on the ground state energy of the systems and all other ground state electronic properties are uniquely determined by the electron density. The exact ground state of the system corresponds to the electronic density of minimal total energy.

3. RESULTS AND DISCUSSION

Firstly, we have investigated the optimization properties of the pure pyrene molecules and the pyrene molecules with the dopants using the Gaussian 09 code with hybrid function B3LYP with basis set 6-31G [13]. Next, the electronic transmission curves of pyrene are calculated by using Olife code. A single value of energy is used for the C-C bond. The values of the other bonds, with the heteroatoms, are used depending on the strength of the bonds. Throughout the study we have not change the locations of the dopants and the electrodes.

The electronic transmission curves show symmetry around the Fermi level, as shown in figure 1. The symmetry is also common for multiple pyrene chain.

The energy gap is calculated as the separation between the higher occupied molecular orbital (HOMO) and the lower unoccupied molecular orbital (LUMO). The results show that, as the length of pyrene chain increases the energy gap of the molecules decreases and thus the conductance of the molecules increases. This can be attributed to the increment in the density of the energy levels around Fermi level.

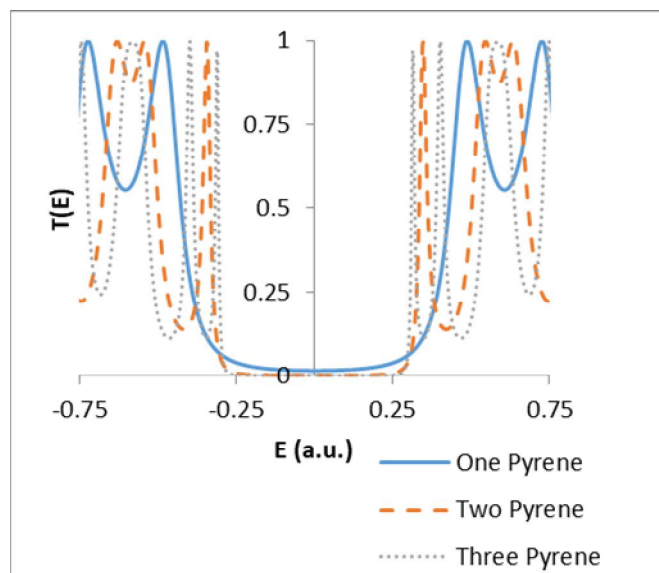


Figure 1: The electronic transmission as a function of energy for pyrene molecules

This result is also confirmed by using density function theory (DFT) method. This result suggests a new method for tuning the conductivity of the pyrene molecules. Gap tuning via changing the length of the molecules is fundamental for some applications such as solar cells.

In addition, the DFT method shows that the electron negativity increases as the chain length increases. The relationship between the energy gap and the length of the pyrene molecules stays the same even when pyrene molecules is not pure. The impurities that have been examined in this subject are OH, NH₂, OCH₃, and COOH.

The electronic transmission of pyrene seems to be very stable when adding heteroatoms (or molecules) in unsymmetrical positions. This means that pyrene is useful in electronic circuits in terms of stable conductivity.

Adding impurities to pyrene results in the appearance of Fano-resonance. In order to investigate the effect of the additives on the fano-peaks we used different values for the on-site energy of the heteroatoms. The results show that the position of the fano peaks can be controlled by changing the on-site energy of the heteroatoms. This behavior is common in pyrene chains regardless the length of the chains. Figures 2 and 3 show the electronic transmission of one pyrene and two pyrene in the case of impurities in the positions shown in figure 4.

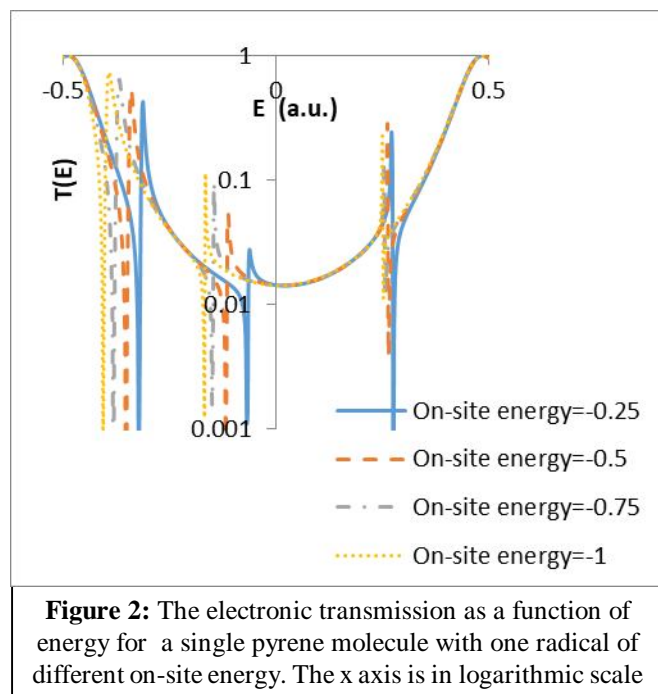


Figure 2: The electronic transmission as a function of energy for a single pyrene molecule with one radical of different on-site energy. The x axis is in logarithmic scale

It is clear from figures 2 and 3 that the value of the electronic transmission of the system at the Fermi level does not change by changing the on-site energy of the heteroatoms.

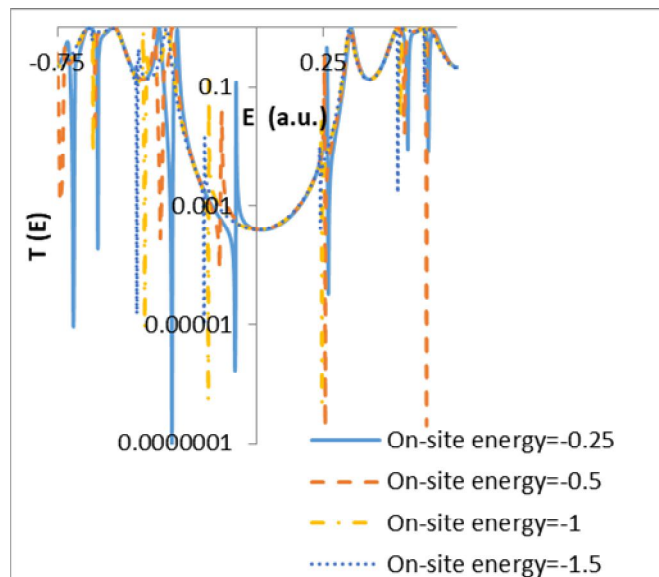


Figure 3: The electronic transmission as a function of energy for two pyrene molecules with radicals of different on-site energy. The x axis is in logarithmic scale

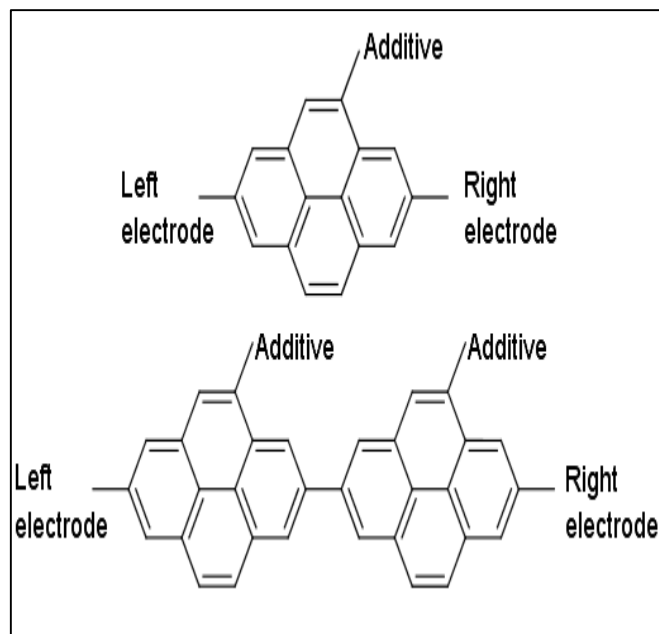


Figure 4: Pyrene molecules with additives

4. CONCLUSION

The electric conductivity of pyrene molecules is investigated. The electric transmission curves of the molecules are symmetric and the band gap decreases as the length of the molecule increases. However, electron negativity increases as the chain length increases. The conductivity of pyrene does not affected by the addition of radicals. However, the addition of the dopants creates some fano peaks on the transmission

curves. The position these peaks can be changed by tuning the on-site energy of the dopant.

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