The Effect of Different Anchor Groups on Spectral and Electronic Properties of Single Molecule Junctions

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Abstract

Understanding charge transport of single molecules sandwiched between electrodes is of fundamental importance for molecular electronics. The structural properties of oligo (phenylene-ethynylene) (OPE) with five different anchor groups (thiol (SH), pyridine (PY), methyl sulfide (SMe), tetramethylsilane (TMS) and dibenzothiophene (DBT)). The optimized molecular junction geometries conform well to a description of the SH, SMe and BDT contacted compounds forming an angle of 52° contact between anchor groups and the under coordinated gold atoms of the gold electrodes. In addition, it shows that PY and TMS contact groups create an angle of 160°.Undoubtedly, these structural aspects will affect the junction formation probability and all other properties (electronic and spectral) of these molecules. On the other hand, The transmission coefficient value of all molecules was high. This can understand in terms of the quantum interference is a constructive interference and there is not a destructive interference signature and that (OPE-1) introduces a high value of transmission coefficient (5.8×10^{-4}), while the lowest value of the transmission (3.12×10^{-6}) is presented by molecule (OPE-4). The molecule OPE-4 with TMS anchor groups produces the highest f_{em} (2.4), while the molecule (OPE-2) with PY contact groups shows the lowest f_{em} (1.8).

Keywords: Density functional theory, Anchor Groups, Transmission Coefficient T(E).

1. Introduction

Quantum theory physics has made tremendous strides in the previous two decades in terms of theoretical approaches. These advancements have enabled scientists to produce novel materials [1, 2], reduce the structural complexity of electronic circuits [3, 4], and construct sophisticated simulation tools [5-7]. Molecular electronics has emerged as a novel topic with ever-expanding possibilities since 1974, when Aviram and Ratner offered the first prediction [8]. However, shrinking the size of an organometallic devices to near or below 10 nm [9] necessitates the creation of new theories to describe and study the behavior of molecules in such domains, as well as the prediction of their features and phenomena [10]. For instance, DFT calculations characterize the ground state properties, whereas the GF (Green's Function) relies heavily on DFT for transmission calculations, as it requires the system's DFT Hamiltonian [11]. The state of the field of molecular electronics from a quantum transport perspective is addressed in this technical review, with a particular focus on recent theoretical results obtained using single-molecule junction devices and electrically conductive gold junctions [12]. To get a better knowledge of electronic transport events at the atomic and molecular scales, as well as the practical use of a single-molecule junction for molecular electronics, a reliable electronic and structural characterization approach for single-molecule junctions is required. Recent improvements in characterization techniques enable the elucidation of the unique electronic properties of a quasi-one-dimensional conductor used in a single-molecule junction. The potential uses of single-molecule junctions in electronic devices such as molecular switches, diodes and transistors have been explored [1,13-15].

2. Computational Methods

Initially, the electronic structures of all molecules were computed at B3LYP level of theory with a (6-31G) basis set. Plots of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) are shown in Figure 4. To elucidate the experimentally observed trends, and to better evaluate the transport properties of these molecular junctions, Calculations by using a combination of DFT (the SIESTA code) [16] and a non-equilibrium green's function formalism were also carried out. This DFT-Landauer approach used in the modeling assumes that on the time scale taken by an electron to traverse the molecule, inelastic scattering is negligible. This is known to be an accurate assumption for molecules up to several nanometers in length. For the transport calculations, each molecule was attached to opposing 35-atom (111) directed pyramidal gold electrodes, then geometrically optimization was carried out by using the DFT code SIESTA, with a generalized gradient approximation [16,17] These layers were then further repeated to yield infinitely long current-carrying gold electrodes. From these model junctions the transmission coefficient, T(E), was calculated using the Gollum code.[18] The use of DFT to compute the ground

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state energy of various molecular junctions, allows binding energies and optimal geometries to be computed. However, these calculations are subject to errors, due to the employing of localized basis sets, which are concentrated on the nuclei. At the point when atoms are sufficiently close to each other so that their basis functions overlap, can cause an artificial strengthening of the atomic interaction and an artificial shortening of the atomic distances. To avoid this kind of error the basis set superposition error correction (BSSE) [19] or the counterpoise correction [20] were used.

3. Results and Discussion

3-1 Structural Properties

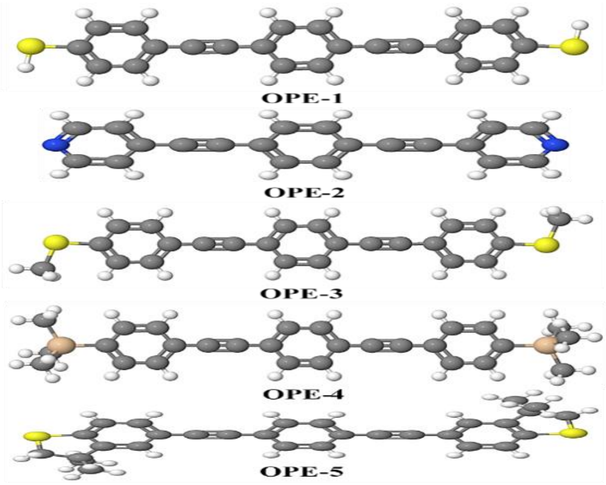

Figure 1: The relaxed geometries of all molecules

The oligo(phenyleneethynylene) (OPE) molecules are shown in Figure1, with five different anchor groups. The first molecule (OPE-1) possess thiol (SH) contact groups, while the second molecule (OPE-2) have pyridine (PY) anchor groups. The third, fourth and fivth molecules (OPE-3, OPE-4 and OPE-5) have methyl sulfide (SMe), tetramethylsilane (TMS) and dibenzothiophene (DBT) respectively. Furthermore, there are various angles between carbon atom, anchor atom (N or S or Si) and gold atom for contact groups. Undoubtedly, these structural aspects will affect the junction formation probability and all other properties (electronic and spectral) of these molecules.

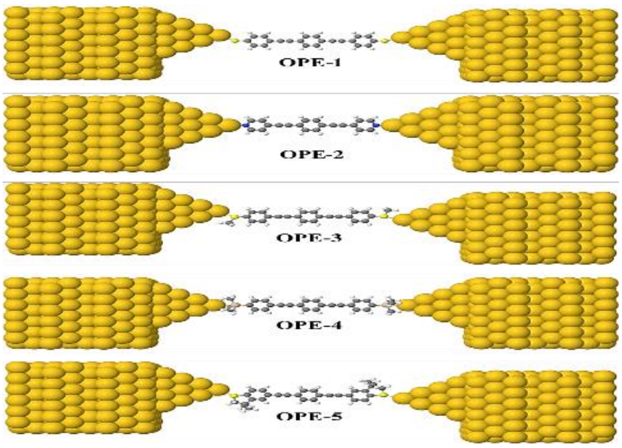

Figure 2: The relaxed geometries of all molecular junctions.

3-2. Electronic Properties

Designing highly conductive single-molecule junctions is critical for their potential application to components of small electronic devices. Charge transport through a single-molecule junction can be explained using the tunneling barrier model.

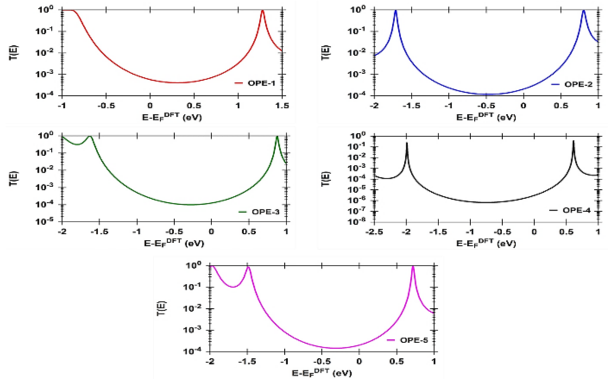

Figure 3: Represents the transmission coefficient T(E) as a function of electrons energy of all molecules.

The transmission coefficient T(E) is a property of the whole system comprising the leads, the molecule and the contact between the leads and the molecule. In general, the transmission coefficient T(E) describing the propagation of electrons of energy E from the left to the right electrode. In this thesis, the transmission coefficient has been calculated by first obtaining the corresponding Hamiltonian and overlap matrices using SIESTA and then using the GOLLUM code. Figure 3.3 shows that OPE-1 introduces a high value of transmission coefficient (5.8×10-4), while the lowest value of the transmission (3.12×10-6) is presented by molecule (OPE-4). On the other hand, it can be seen that the transport mechanism for molecule OPE-1 is a HOMO-dominated transport, while for other molecules is an LUMO-dominated mechanism. In general, the transmission coefficient value of all molecules is high, and that can understand in terms of the quantum interference is a constructive interference and there is no a destructive interference signature within the gap. The order of the transmission is T(E)OPE-1 > T(E)OPE-2 > T(E)OPE-5 > T(E)OPE-3 > T(E)OPE-4.

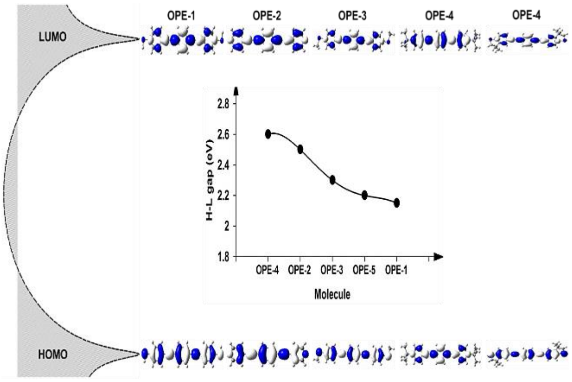

Figure 4: The iso-surfaces (±0.02 (e/bohr3)1/2) of the HOMOs and LUMOs for all molecules. The insert figure shows the trend of HOMO-LUMO gap of all molecules.

These results provide a convenient point to commence discussion and a basis for comparison between the highest occupied and lowest unoccupied molecular orbitals HOMO and LUMO, respectively. Unsurprisingly, the lowest and highest energy structures features arrangement the electronic structure with the frontier orbitals distributed almost evenly across the molecular backbone, making a linear, p-type conjugated pathway between the two anchor atoms. On the other hand, the lowest unoccupied molecular orbitals are localized on the (C≡C) bonds and shown more contribution than that of the highest occupied molecular orbitals, which are concentrated on the (C=C) bonds. It is worth to mention that the weight of the LUMO on the PY, TMS, DBT and SMe anchor groups is noticeable, and higher than that of the HOMO.

Table 1: T(E) is the transmission coefficient; H-L is HOMO-LUMO gap energy; B.E. is the binding energy; Γ is the number of transfer electrons from anchor atoms to electrodes

Molecule	T(E)	H-L gap(eV)	B.E. (eV)	Γ
OPE-1	5.87×10-4	2.15	0.67	7.13
OPE-2	2.13×10-4	2.5	0.52	6.78
OPE-3	1.26×10-4	2.3	0.45	6.12
OPE-4	4.12×10-6	2.6	0.23	2.18
OPE-5	2.05×10-4	2.2	0.41	6.03

that the hieghest binding energy is presented from molecule OPE-1, and this not only support the high value of transmission coefficient of this molecule as shown in Figure 3.3, but also it interprets the highest value of transfer electrons from this molecule to electrodes. Whereas the lowest binding energy and Γ are introduced by molecule OPE-4. These results prove the fact that there is a close relationship between the binding energy and the electronic transition, as the type of anchor group will determine the value of the binding energy, which in turn will determine the probability of the molecular junction formation, which in turn will determine the value of the transmission coefficient. In light of these results, it can be concluded that choosing the anchor group will greatly help researchers in improving the various properties of electronic devices based on single molecules, as well as in determining the appropriate application of those molecules.

2-3. Spectral Properties

In spectroscopy, oscillator strength is a dimensionless quantity that expresses the probability of absorption or emission of electromagnetic radiation in transitions between energy levels of an atom or molecule. For example, if an emissive state has a small oscillator strength, nonradiative decay will outpace radiative decay. Conversely, "bright" transitions will have large oscillator strengths.

The oscillator strength can be thought of as the ratio between the quantum mechanical transition rate and the classical absorption/emission rate of a single electron oscillator with the same frequency as the transition.

Figure 5 presents the absorption and emission results for all the molecules under study. Initially, it can be noticed that the emission intensity of the molecule (OPE-4), which characterized by TMS anchor groups is higher than those with other contact groups. Since its value was 3165 a.u. While, the emission intensity values for molecules with SH, PY, SMe and DBT are 2868 a.u., 2568 a.u., 2823 a.u., 2610 a.u. respectively.

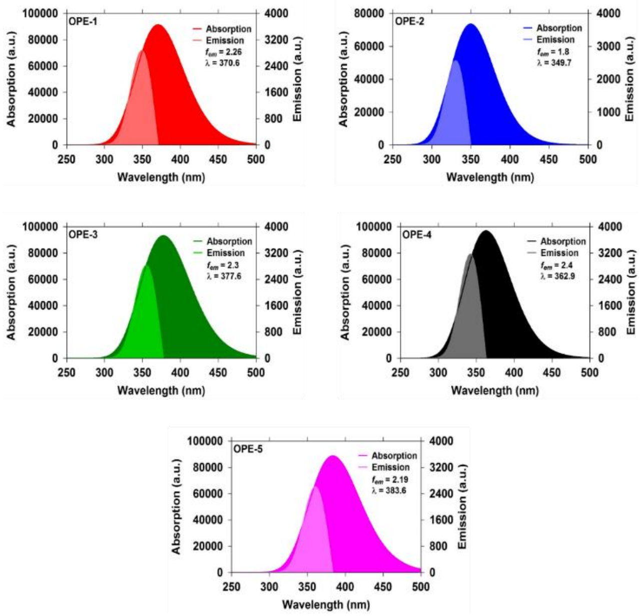

Figure 5: Represents the absorption, emission and emission oscillator strength (f_{em})of all molecules.

The molecule OPE-4 with TMS anchor gropus produces the highest fem (2.4), while the molecule (OPE-2) with PY contact groups shows the lowest fem (1.8). In addition, it could be observed that the maximum wavelength (λmax) for all molecules lies in the UV region, and there is also a fluctuation from 349.7 nm for OPE-2 to 383.6 nm for OPE-5. Based on these results, we can conclude that changing the anchor groups not only affects the intensity of the absorption, but also leads to a displacement in wavelengths.

Table 2: The emission and absorption intensities, and the emission oscillator strength (fem).

Molecule	f_{em}	Absorption (a.u.)	Emission (a.u.)
OPE-1	2.25	91372.9	2868
OPE-2	1.8	73532.3	2568
OPE-3	2.3	93160.5	2823
OPE-4	2.4	96874.4	3165
OPE-5	2.19	88747.3	2610

4. 5-Conclusion

In conclusion, this study using density functional theory methods have summarized systematic investigations on the effect of the anchoring group on electronic and spectral properties of single-molecule junctions of several families of oligo(phenyleneethynylene) (OPE), with five different anchor groups (SH, PY, SMe, TMS and DBT). The transmission coefficient value of all molecules is high. This can understand in terms of the quantum interference is a constructive interference and there is no a destructive interference signature. The order of the transmission is T(E)OPE-1 > T(E)OPE-2 > T(E)OPE-5 > T(E)OPE-3 > T(E)OPE-4.

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