# Effect of metal electrodes and transport properties of 2,5-divinylthiophene molecular nanowire under external electric field: A DFT study

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## ABSTRACT

The Au and thiol substituted 2,5-divinylthiophene molecule has been studied for the zero field and various levels of applied external electric fields (EFs) using quantum chemical calculations coupled with AIM theory. The variation in geometrical parameters due to the various external EFs and the corresponding transport properties of the molecule has been analyzed. The variation in MPA and NPA charges, the reduction of HOMO-LUMO gap (from 2.34 to 1.08 eV) and the increase of electric dipole moment (from 0.98 to 13.21 D) with the increase of external EFs (from zero to $0.26 \text{ V\AA}^{-1}$) of the molecule reveals that using thiol as linker and Au as electrodes, 2,5-divinylthiophene molecule can be act as an efficient molecular nanowire.

## Introduction

Recent progress in nanotechnology and nanoscience has facilitated both experimental and theoretical study of Molecular electronics [1]. Nanoelectronics refer to the use of nanotechnology in electronic components. The term 'Nanoelectronics' covers a various set of devices and materials, with the common characteristic that they are so small that quantum mechanical properties need to be studied extensively[1,2]. Recently, several new molecular-electronic systems, analytical tools, and device architectures have been introduced and explored [3]. The sole intention of molecular wires is to electrically connect different parts of a molecular electrical circuit. Molecular wire is a molecule in which, a set of overlapping delocalized electronic states across the entire molecule is necessary for electronic conduction. In recent years, enhancing the electrical conduction of molecular wires by using conjugated molecules has been a key focus in molecular electronics [3,4]. The term conjugated means an alternation of multiple and single bonds linking a sequence of bonded-atoms, such that there is an extended series of overlapping p orbitals, and the electrons involved are π electrons [4,5]. The first measurement of the conductance of a single molecule was realized in 1994 by C. Joachim and J. K. Gimzewski and published in 1995 [6]. To understand the charge transport mechanism of a metal-molecule junction by experiment is a challenging one, hence, nowadays, numerous theoretical ideas have been used in an attempt to understand the conductivity of molecular wires [7,8].
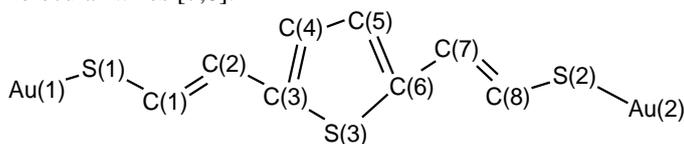


**Fig. 1 Au and S substituted 2,5-divinylthiophene (DVT) molecule.**

Thiophene, also commonly called thiofuran, is a heterocyclic compound which exhibits charge transfer property. The present study provides, the electrical characteristics of Au and thiol substituted 2,5-divinylthiophene (DVT) molecular

nanowire (Fig.1) under various levels of applied electric field (EFs) using quantum chemical calculations.

## Computational details

The Au and thiol substituted 2,5-divinylthiophene (DVT) molecule has been optimized for the zero field and applied field of four biasing steps (0.05, 0.15, 0.21 and $0.26 \text{ V\AA}^{-1}$) by Density Functional Theory (DFT) method using Gaussian09 program package [9-12]. A combination of Becke's three parameters exchange function and Lee, Yang and Parr gradient-corrected correlation function (B3LYP hybrid function) is applied for whole DFT calculation along with LANL2DZ (Los Alamos National Laboratory of Double Zeta) basis set, which provide effective core potential and the detailed description of the effect of heavy metal atoms in the molecule [13,14]. All geometry optimizations were performed via Berny algorithm in redundant internal co-ordinates. The threshold convergence for maximum force, root mean square (RMS) force, maximum displacement and root mean square (RMS) displacement are 0.00045, 0.0003, 0.001 and 0.0012 au respectively. The self consistency of non-interactive wave function was performed with a requested convergence on the density matrix of $10^{-8}$ and $10^{-6}$ for the RMS and maximum density matrix error between the iterations. As a part of Hamiltonian an external dipolar field is set to compute the effect of voltage. The GaussSum program has been used to determine the density of states (DOS) at various levels of applied EF [15]. The variation of bond lengths, variation of atomic charges has been plotted by using Origin software.

## Results and discussion

### Structural aspects

The conductivity has been assessed from electron transfer rates as a function of the distance between the donor and acceptor sites of a molecule [16]. Recent reports show that the nature of the carbon bonds of a molecule affects the electrical properties [17]. The electrons of carbon nanowires present a quasi-free electron behavior and this enhances qualitatively the high electrical conduction. The electric conduction dependence with the number of atoms and the wire size; however, the nature of bonds plays a major role in the electrical conduction through

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molecule [17, 18]. Generally, the conducting molecules are very sensitive to the applied external electric field. Hence, to understand the structural stability of the molecules over the range of applied field, it is essential to compare its zero field geometry with the applied fields.

The zero field bond distance of the C-C single bonds and C-C double bonds in the molecule are found as ~1.45 and ~1.36 Å respectively. When the applied field increases, these distances are slightly modified, the maximum observed variation is 0.011 Å. However, the zero field bond distances of the C−H bond remains same (~1.086 Å) for various applied EFs. The zero field distance of S(3)−C(3) bond of the thiophene ring attached with Left part of the wire is 1.826 Å and the S(3)−C(6) bond of the thiophene ring attached with right part of the wire is 1.784 Å. When the applied filed increased to 0.26 VÅ⁻¹, the S(3)−C(3) bond distance increases to 1.835 Å, whereas S(3)−C(6) bond distance decreases to 1.774 Å and the maximum observed variation is 0.01 Å. For the zero field, the terminal S−C bond distances is the same (1.816 Å) at either ends of the molecule. As the field increases, the distance in the left-end (L) decreases, whereas the value of the same bond in the right-end (R) increases. The variation in the L-end (0.018 Å) is more than the R-end (0.015 Å).
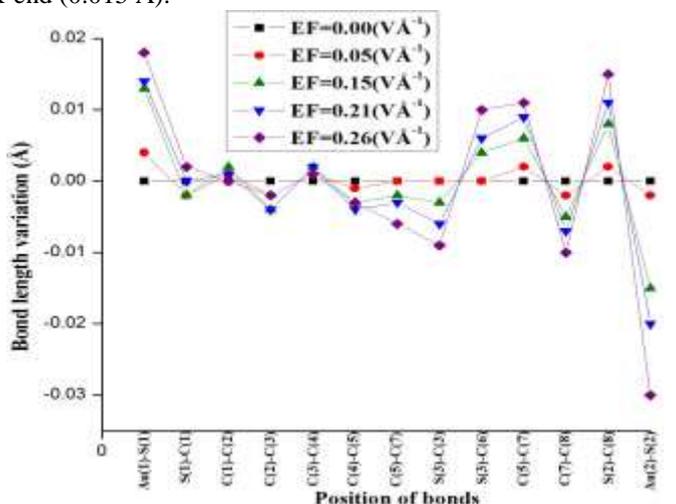


**Fig. 2 Variation of bond lengths for various applied EFs with reference to zero field.**

The zero field bond distances of Au−S bonds at either are found to be equal (~2.4 Å), which are matched with reported theoretical and experimental values [7,19,20]. When the applied field increases, the bond distance in the L-end decreases, whereas, the value of the same bond in the R-end increases; also the variations in both ends are unequal. And, for the maximum applied field (0.26 VÅ⁻¹), the distance at L- and R-end are 2.393 and 2.437 Å respectively. The large variation (Fig.2) is attributed to the applied field lengthening the Au−S bond through by shrinking the S−C bond distance in the R-end, whereas, opposite trend is observed in the L-end. Further, it is found that the terminal bonds [Au−S & S−C] at both ends, S−C bonds of thiophene ring are very sensitive on comparing C-C bonds of the molecule due to the application of external EFs (Table 1).

**Atomic charges**

Atomic charges are created due to the asymmetric distribution of electrons in chemical bonds of a molecule. Generally, the shared electron of a chemical bond of a molecule oscillates between the bonded atoms [21]. When an electrically neutral atom and another neutral atom with more electronegative are bonded together chemically, its electrons are partially drawn away. This leaves the region about that atom's nucleus with a

partial positive charge; hence, it causes a partial negative charge on the atom to which it is bonded [21,22]. Hence, the partial atomic charges of a molecule may either be positive or negative. To determine the atomic charges, various methods are available, the most frequently used are Mulliken population analysis, Natural population analysis, Chelpg scheme and Merz-kollman (MK) schemes [23,24]. The present study reports, variation of atomic charges of the DVT molecular nanowire under various external EFs by MPA and NPA methods.

The MPA charges of all C-atoms for zero field vary from -0.049e to -0.724e. When the applied field increases, the charges are also varied. For the zero field, the charge of S3 in the thiophene ring is equal (0.294e). As the field increases, the charge of S3 atom also increases (0.313e). The linker atoms on either ends S(1) and S(2) possess the MPA charge of 0.055 and 0.062e respectively for zero field; as the field increases this value decreases to 0.001e for S(1) and 0.045e for S(2). For the zero field, the charge of Au atom at either ends are the same (~ -0.041). As the field increases, the charge of Au(1) atom in the L-end increases to 0.126e, whereas at the R-end, the charge of Au(2) increases to -0.208e. The maximum observed variation of MPA charges of Au(1) and Au(2) atoms are 0.16 and 0.14e respectively. The MPA charges for the zero and various applied EFs of the molecule are presented in Table 2. Fig. 3 illustrates the variations of MPA charges for various EFs with reference to zero feld of the molecule.

For the zero field, the NPA charge for all C-atoms are found negative; the charges vary for the increase of field. When the applied field increases from 0 to 0.26 VÅ⁻¹, the NPA charge of S(3) atom gradually increases from 0.4 to 0.425e. The NPA charges of linker S(1) and S(2) atoms vary for various applied EFs, the maximum observed variation is ~0.016e.
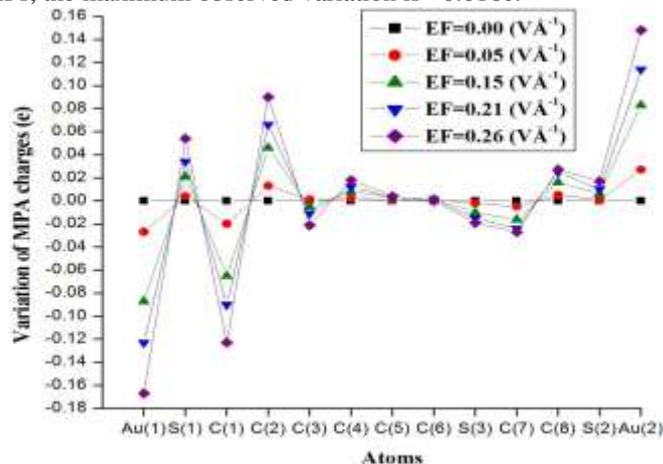


**Fig. 3 Variation of MPA charges of the molecule for the zero and various applied EFs.**
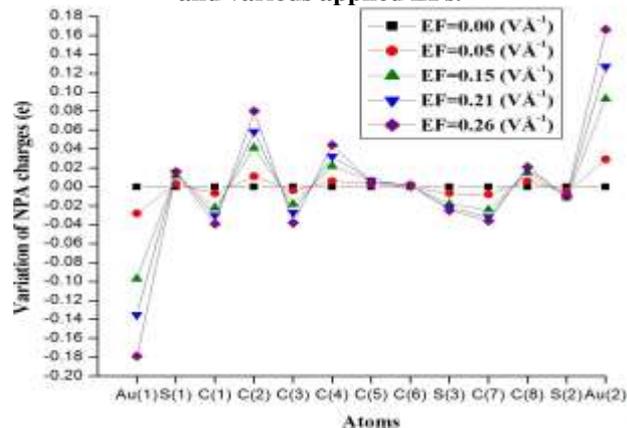


**Fig. 4 Variation of NPA charges of the molecule for the zero and various applied EFs.**

For the applied field, the charge of Au-atom at the L-end increases gradually from 0.227 to 0.406e, while at the R-end, the charge decreases from 0.206 to 0.04e. On the whole, the thiol atom in the thiophene ring, linker thiol atoms at both ends of the molecular wire and terminal Au atoms used as electrodes posses uniform and systematic variation for various applied EFs. The variations of NPA charges for various EFs with reference to zero feld are plotted as in Fig.4. The difference of NPA charge distribution for zero and various applied EF is listed in Table 2.

**Molecular orbital analysis**

Molecular orbitals (MOs) are created when atomic orbitals are brought together. Chemists sort the molecular orbitals by energy levels [25]. Each molecular orbital has a calculated energy level; it is assumed that the electrons will occupy the lowest energy level MOs first. The lowest unoccupied molecular orbital is known as LUMO and the highest occupied molecular orbital is known as HOMO. The difference of energy between these two energy levels is known as HOMO-LUMO gap (HLG), which provides an outline about the conducting properties of the molecule [25,26]. Hence, it is essential to study the variations in molecular orbital energy levels (HOMO-1, HOMO, LUMO and LUMO+1) for the various levels of external EFs. For the applied field (0 - 0.26 VÅ$^{-1}$), the HLG decreases from 2.34 to 1.08 eV. Fig. 5 illustrates the energy levels of the molecule for various applied EFs.

HOMO-LUMO gap can also be studied by using Density of states spectrum (DOS). Fig. 6, shows the density of states (DOS) for the zero and maximum applied field, in which the green lines indicate the HOMO and the blue is LUMO. Here, the distance between HOMO and LUMO (green and blue lines) for zero fields is 2.34 eV; when the field increases to 0.26 VÅ$^{-1}$, both HOMO and LUMO levels approach each other and their gap decreases to 1.08eV. The energy level variations of the molecule are almost symmetric for both positive as well as negative bias. Hence the charge transfer of the molecule does not depend on the direction of external EF. The decrease of HLG due to increase of EFs facilitates large electron conduction through the molecule [8], hence, the Au substituted DVT molecule can act as an efficient molecular nanowire.
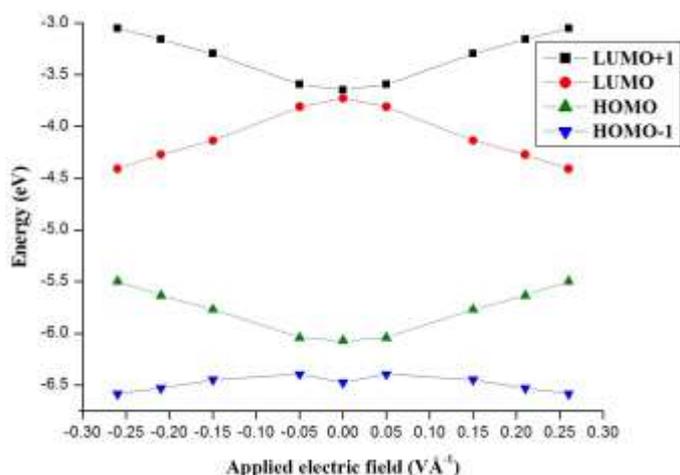


**Fig. 5 Energy level diagram of Au and S substituted DVT based molecule for the zero and various applied EFs**

**Molecular dipole moment**

A bond connecting two atoms differing in electro negativity is associated with an electrical moment called bond moment. The dipole moment of a molecule is the vectorial sum of the individual bond moments present in it. The dipole moments of polyatomic molecules depend on the nature of the atoms and on their arrangement. The dipole moment of a molecule can be calculated based on the molecular structure. By using the total dipole moment of the molecules one can compute the dielectric constant which is more related with the concept of conductivity [27,28].

**EF=0.00 VÅ$^{-1}$**



**EF=0.26 VÅ$^{-1}$**
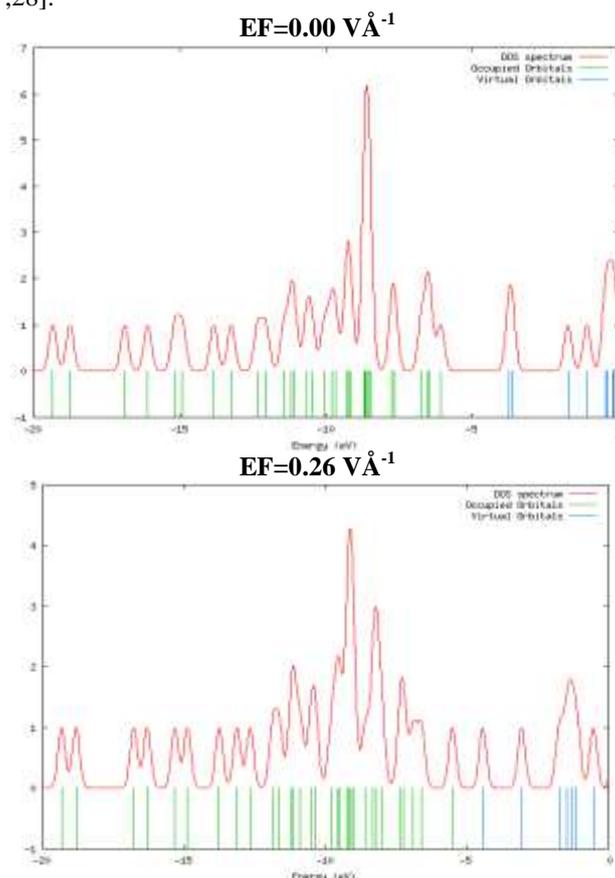


**Fig. 6 shows the density of states (DOS) for the zero and maximum applied EF.**

Dipole moments in molecules are responsible for the behavior of a substance in the presence of external EFs. The application of external EF polarizes the molecule, in consequence of that the value of the dipole moment of the molecule changes. Hence, it is necessary to calculate the dipole moment of the molecule for various levels of applied EFs. Recently, researchers reported the variations of molecular dipole moment for the various applied EFs and found a linear character [29,30]. Here, the dipole moment of the molecule has been determined for zero as well as various applied EFs. Fig. 7 shows the variation of molecular dipole moment for various applied EFs. The molecular dipole moment for zero bias is 0.98 debye, which increases almost linearly with the increase of field. The molecule becomes highly polarized to have high molecular dipole moment value 13.21 debye for the higher field (0.26 VÅ$^{-1}$).
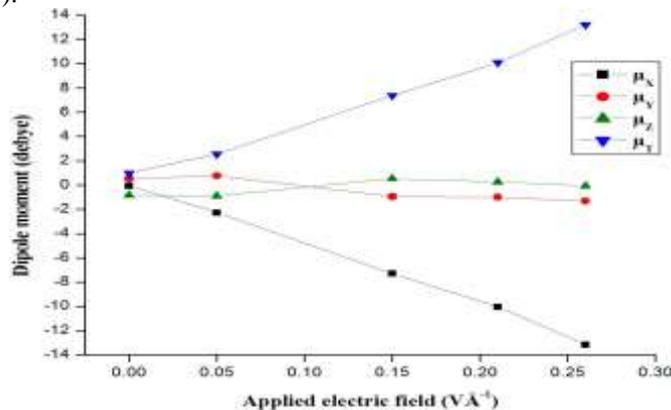


**Fig. 7 Molecular dipole moment of Au and S substituted DVT molecule for the zero and various applied EFs**

**Table 1. Bond lengths (Å) of the Au and S substituted DVT molecule for the zero and various applied EFs (VÅ⁻¹).**

| Bonds | Applied electric field | | | | |
|---|---|---|---|---|---|
| | 0.00 | 0.05 | 0.15 | 0.21 | 0.26 |
| C(1)−C(2) | 1.365 | 1.364 | 1.363 | 1.364 | 1.365 |
| C(2)−C(3) | 1.447 | 1.449 | 1.451 | 1.451 | 1.449 |
| C(3)−C(4) | 1.387 | 1.386 | 1.385 | 1.385 | 1.386 |
| C(4)−C(5) | 1.443 | 1.444 | 1.446 | 1.447 | 1.446 |
| C(5)−C(6) | 1.390 | 1.390 | 1.392 | 1.393 | 1.396 |
| C(5)−C(7) | 1.464 | 1.462 | 1.458 | 1.455 | 1.453 |
| C(7)−C(8) | 1.36 | 1.362 | 1.365 | 1.367 | 1.370 |
| C(1)−H(1) | 1.086 | 1.086 | 1.086 | 1.085 | 1.085 |
| C(8)−H(8) | 1.086 | 1.086 | 1.086 | 1.086 | 1.086 |
| S(3)−C(3) | 1.826 | 1.826 | 1.829 | 1.832 | 1.835 |
| S(3)−C(6) | 1.784 | 1.784 | 1.780 | 1.778 | 1.774 |
| S(1)−C(1) | 1.816 | 1.818 | 1.818 | 1.816 | 1.814 |
| S(2)−C(8) | 1.816 | 1.815 | 1.809 | 1.806 | 1.802 |
| Au(1)−S(1) | 2.411 | 2.407 | 2.398 | 2.397 | 2.393 |
| Au(2)−S(2) | 2.407 | 2.409 | 2.422 | 2.427 | 2.437 |

**Table 2. MPA and NPA atomic charges(e) of the molecule for various applied EFs(VÅ⁻¹).**

| Atoms | Applied electric field | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 0.00 | 0.05 | 0.15 | 0.21 | 0.26 | 0.00 | 0.05 | 0.15 | 0.21 | 0.26 |
| | MPA | | | | | NPA | | | | |
| C(1) | -0.473 | -0.453 | -0.408 | -0.383 | -0.350 | -0.336 | -0.329 | -0.314 | -0.306 | -0.297 |
| C(2) | -0.049 | -0.062 | -0.095 | -0.115 | -0.139 | -0.212 | -0.223 | -0.253 | -0.270 | -0.292 |
| C(3) | -0.076 | -0.077 | -0.071 | -0.065 | -0.055 | -0.191 | -0.187 | -0.173 | -0.164 | -0.153 |
| C(4) | -0.386 | -0.388 | -0.394 | -0.398 | -0.404 | -0.210 | -0.216 | -0.232 | -0.242 | -0.254 |
| C(5) | -0.589 | -0.588 | -0.586 | -0.586 | -0.585 | -0.101 | -0.104 | -0.107 | -0.108 | -0.106 |
| C(6) | -0.724 | -0.725 | -0.725 | -0.725 | -0.724 | -0.336 | -0.336 | -0.337 | -0.337 | -0.338 |
| C(7) | -0.146 | -0.141 | -0.130 | -0.122 | -0.119 | -0.192 | -0.184 | -0.168 | -0.160 | -0.156 |
| C(8) | -0.503 | -0.508 | -0.519 | -0.528 | -0.530 | -0.329 | -0.335 | -0.344 | -0.348 | -0.350 |
| H(1) | 0.237 | 0.240 | 0.244 | 0.246 | 0.246 | 0.234 | 0.235 | 0.238 | 0.240 | 0.243 |
| H(8) | 0.238 | 0.239 | 0.242 | 0.244 | 0.246 | 0.217 | 0.218 | 0.220 | 0.221 | 0.222 |
| S(1) | 0.055 | 0.051 | 0.034 | 0.021 | 0.001 | -0.165 | -0.168 | -0.177 | -0.180 | -0.181 |
| S(2) | 0.062 | 0.061 | 0.056 | 0.052 | 0.045 | -0.152 | -0.147 | -0.141 | -0.142 | -0.142 |
| S(3) | 0.294 | 0.296 | 0.304 | 0.309 | 0.313 | 0.400 | 0.407 | 0.418 | 0.422 | 0.425 |
| Au(1) | -0.041 | -0.014 | 0.046 | 0.082 | 0.126 | 0.227 | 0.255 | 0.324 | 0.362 | 0.406 |
| Au(2) | -0.040 | -0.047 | -0.143 | -0.174 | -0.208 | 0.206 | 0.177 | 0.113 | 0.079 | 0.040 |

**Conclusion**

The present theoretical study on Au and S substituted 2,5-divinylthiophene describes the bond structural parameters and the electrical characteristics for zero and various external applied field. As the field increases, the structural variations are found to be systematic and almost uniform. When the field increases from 0.00 to 0.26 VÅ⁻¹, the hybridization of molecular levels broadens the DOS and decreases the HLG from 2.34 to 1.08 eV; the decrease of band gap at the high field implies that this molecule exhibit significant electrical conductivity. The applied EF polarizes the molecule and hence the dipole moment of the molecule increases from 0.98 to 13.21 D. The structural confirmation, analysis of MPA and NPA atomic charges and molecular orbital analysis of the molecule allow for understanding the molecule at electronic level for zero and various applied EFs. Further, this study may be useful to design several new molecular nanowires with number of thiophene rings.

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