



# Structural, Electrostatic and Transport properties of tetracene under applied electric field using quantum chemical calculations

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## ABSTRACT

To understand the structural and electrical characteristics of Au and thiol substituted tetracene, a quantum chemical calculation has been carried out with Density Functional Theory (DFT) coupled with the Bader's AIM theory. The various levels of applied electric field (0 – 0.21  $\text{V}\text{\AA}^{-1}$ ) altered the geometrical conformation as well as the electronic energy levels of the molecule. Variations in MPA and NPA atomic charges of the molecule for the applied fields have been compared. The field polarizes the molecule and hence the dipole moment of the molecule increases from 0.0002 to 14.65 D. For the zero bias, the HOMO–LUMO gap is 1.752 eV, as the field increases this gap decreases to 1.03 eV, which reveals that it exhibits charge transfer ability for the applied field.

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## Introduction

Applied Chemistry concentrates on the uses of chemistry in modern society, in areas such as nanotechnology, computer designed molecules, new materials and drug delivery systems. Currently, Applied Chemistry aims to create a novel system of knowledge by investigating and understanding the fundamental nature of materials and to fabricate useful materials by designing new structures and controlling their properties [1]. Nowadays, numerous computational and theoretical studies on chemical properties of several organic molecules have been studied and reported by using quantum theory of atoms in molecules [2,3]. Quantum chemical calculations, primarily Density functional theory (DFT) and time-dependent DFT (TD-DFT) methods which includes optimization, are used to predict structural and electronic properties of molecules. Optimization is used to find minima on the potential energy surface of a molecule. Optimization to minima also known as energy minimization reduces the energy of a molecule by adjusting atomic coordinates [4]. Obtain a structure for a single-point quantum mechanical calculation provides a large set of structural and electronic properties [4,5]. The electronic structure of a molecule implies essentially its chemical properties. Tetracene is a molecular organic semiconductor, used in organic field-effect transistors (OFETs) and organic light-emitting diodes (OLEDs) [6]. The present study provides the Density functional analysis of structural, electrostatic and transport properties of Au and thiol substituted tetracene molecule (Fig.1) under various applied electric fields using quantum chemical calculations.

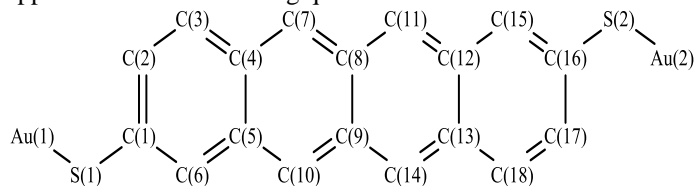


Fig.1 Au and Thiol substituted tetracene molecule

### Computational details

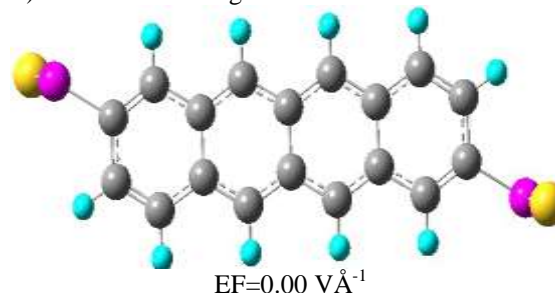
The effect of electric field on the structural and electronic properties of the Au and thiol substituted tetracene molecule has

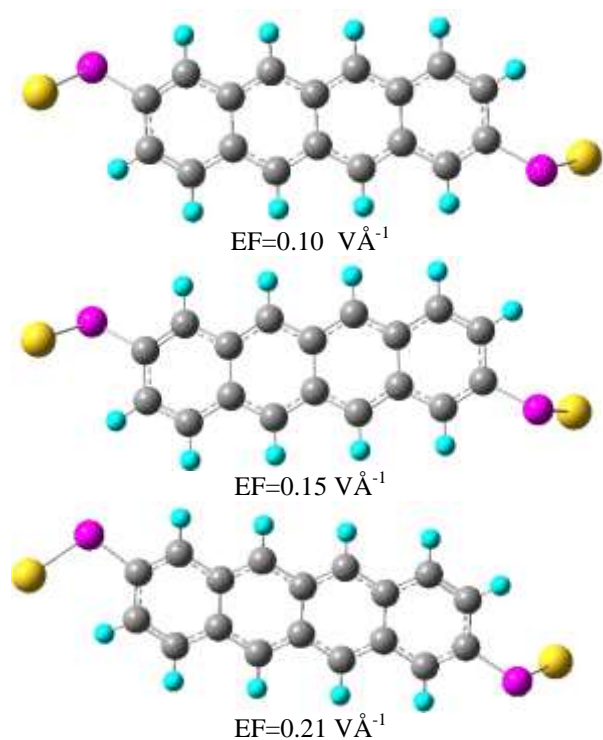
been analyzed by optimizing it for the zero and applied fields [four biasing steps 0.05, 0.10, 0.15, 0.21  $\text{V}\text{\AA}^{-1}$ ] for both direction. All calculations in this study have been carried out with Density Functional Theory (DFT) [7, 8] using Gaussian09 program [9]. Here, we used LANL2DZ basis set for whole DFT calculation with B3LYP hybrid function to obtain effective core potential and the detailed description of the effect of heavy metal atoms in the molecule [10]. All geometry optimizations were performed via Beryn algorithm in redundant internal coordinates. 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. The isosurface representation of molecular orbitals (HOMO and LUMO) has been plotted with Gview [9] to visualize the iso-surface. The GuassSum program [11] has been used to determine density of states (DOS) at various EFs.

## Results and discussion

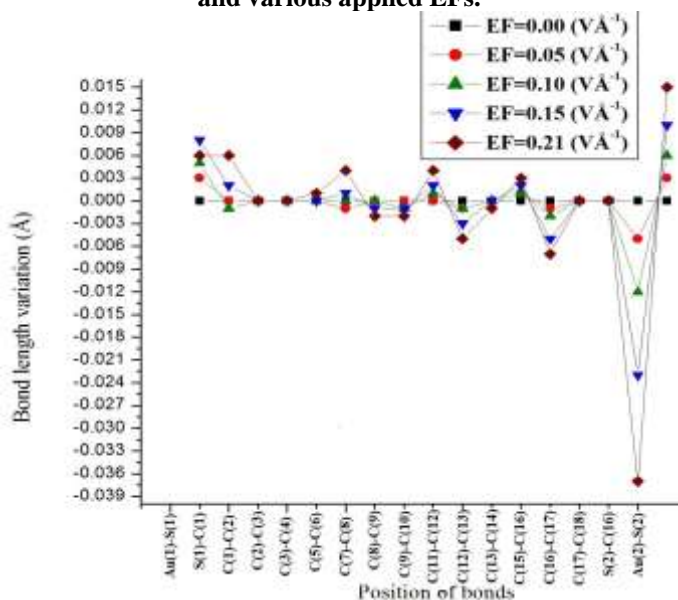
### Structural properties

The geometric parameters especially bond length is an important parameter for adjusting the electrical properties of a molecule. Therefore, a detailed study of bond length variation under the EF interaction is instructive for understanding the relationship between molecular structure and chemical properties. The optimized geometry of Au and S substituted tetracene molecule for the zero and the various applied EFs (0 - 0.21  $\text{V}\text{\AA}^{-1}$ ) is illustrated in Fig. 2.





**Fig. 2** Optimized geometry of tetracene molecule for the zero and various applied EFs.



**Fig. 3.** Variation of bond lengths for various applied EFs with reference to zero EF.

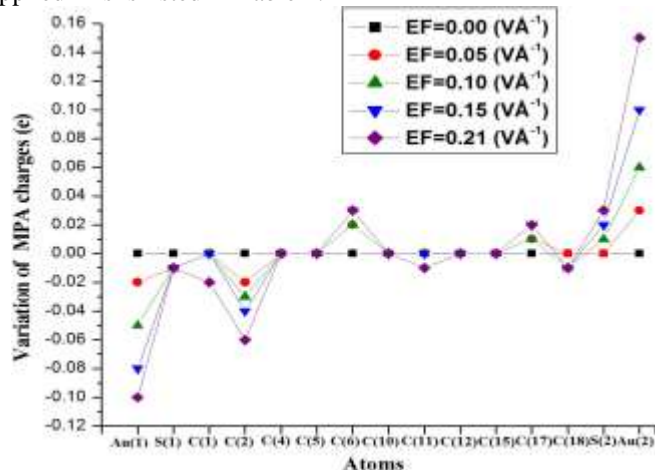
For the zero field, the single and double C–C bond distances of the molecule are  $\sim 1.377$  and  $\sim 1.459$  Å respectively. When the field applied, these distances are slightly modified; however, the EF dependence of bond length evolution is not identical for all the bonds; the minimum and maximum observed variation in C–C bonds are 0.001 and 0.007 Å respectively. The zero field distance of C–H bonds are  $\sim 1.088$  Å, which remains almost the same value for the increase of field. The zero field distance of S–C bonds in the tetracene is  $\sim 1.835$  Å; as the field increases, the maximum variation observed is 0.015 Å. Notably, the variation in the R-end is slightly greater than the L-end. As the field increases, the distance of Au–S bonds in the L-end decreases from 2.402 to 2.394 Å, while in the R-end, the distance increases from 2.402 to 2.439 Å; however, the variations in both ends are unequal. And, for the maximum applied field ( $0.21 \text{ VÅ}^{-1}$ ) the variations at L- and R-ends are

0.008 and 0.037 Å respectively. These bond distances [C–C, S–C and Au–S bonds] are very close to the previously reported experimental as well as theoretical values [12–14]. Even though almost all the bond distances have been varied by the application of external field, specifically, the S–C and Au–S bonds have uniform and systematic variation (Fig. 3). The bond lengths of Au and S substituted tetracene for various applied EFs are presented in Table 1.

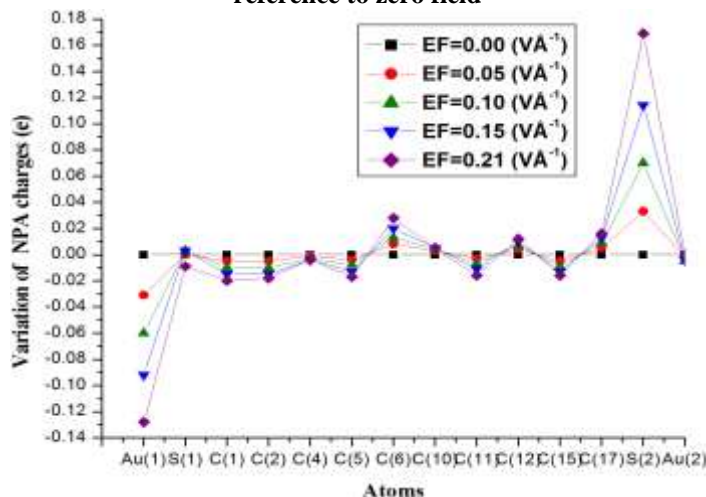
#### Atomic charges

To determine the atomic charges, various methods are available, the most frequently used are Natural population analysis, Mulliken population analysis and Chelpg scheme. In the present study the charges have been calculated by MPA and NPA methods and compared [15,16]. The MPA charges of all C-atoms atoms vary with the increase of field; however, the charge of H atoms (0.25e) remains the same for the increase of field.

The linker S(1)-atom possess positive MPA charge for zero field (0.08e), which slightly increases with increase of field (0.09e). The charge of S(2)-atom decreases from 0.08 to 0.05e. As the field increases, the charges of Au atom at L-end slightly increase from -0.06 to 0.04e, but the same at the R-end varies from -0.06 to -0.21e. As the field increases, the maximum variation observed in the C, S and Au atoms are 0.06, 0.03 and 0.15e respectively. Fig. 4 shows the variation of MPA charges of the molecule for various applied EFs with reference to zero field. The variation of MPA charges of the molecule for various applied EFs is listed in Table 2.



**Fig. 4** Variation of MPA charges of the molecule with reference to zero field



**Fig. 5** Variation of NPA charges of the molecule for various applied EFs with reference to zero field

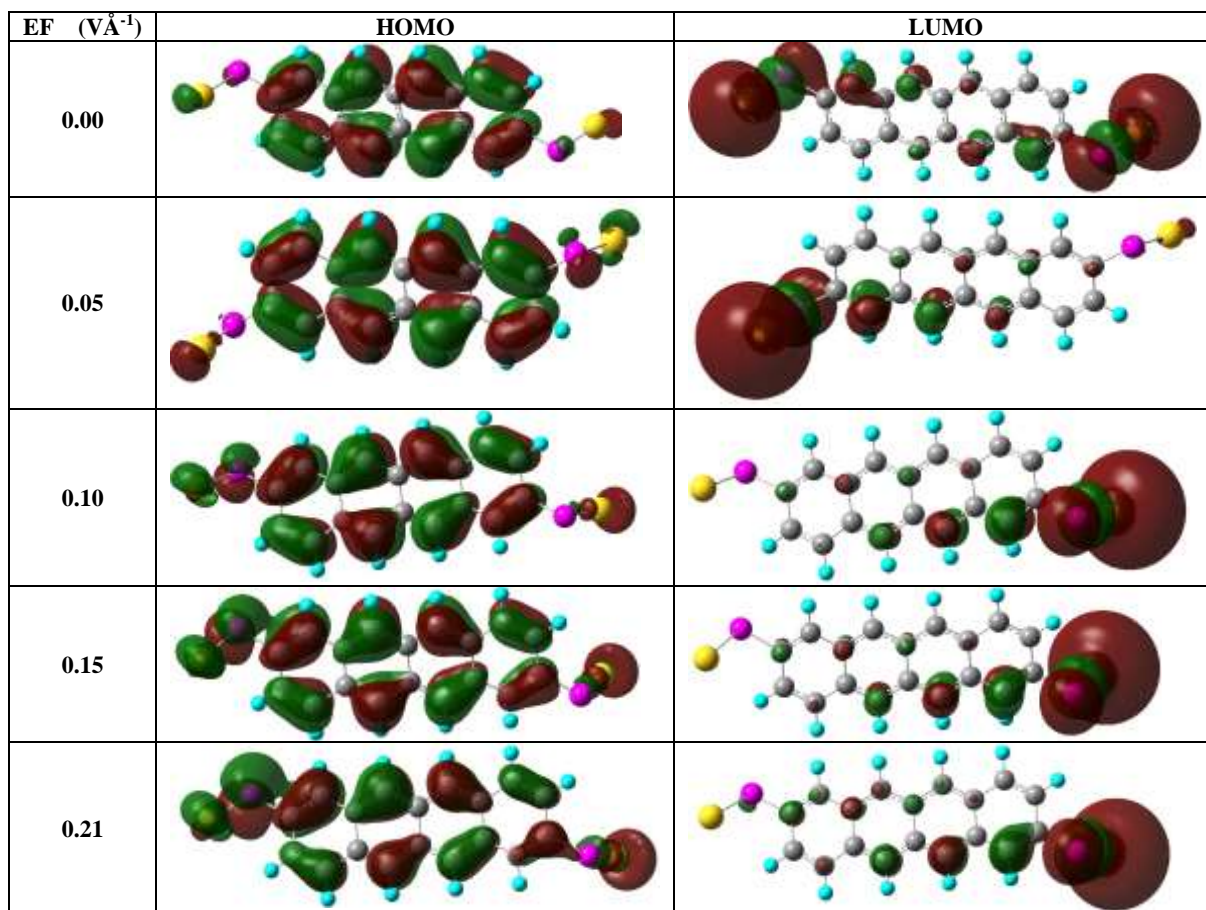


Fig. 6 Isosurface representation of molecular orbitals of Au and S substituted tetracene molecule for the zero and maximum applied electric field ( $0.21 \text{ V}\text{\AA}^{-1}$ ), which are drawn at  $0.02 \text{ au}$  surface values.

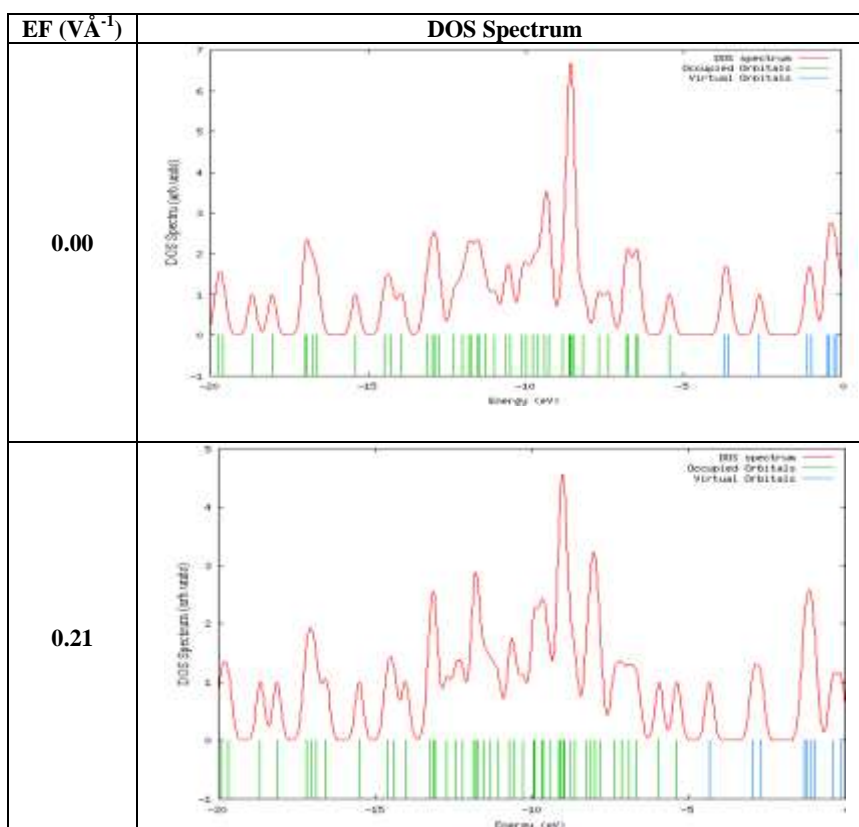


Fig. 7 DOS of Au and S substituted tetracene for various applied EFs.

**Table 1. Bond lengths (Å) of the Au and S substituted Tetracene molecule for the zero and various applied EFs (V Å<sup>-1</sup>).**

Bonds	Applied electric field				
	0.00	0.05	0.10	0.15	0.21
C(1)–C(2)	1.445	1.445	1.445	1.445	1.445
C(1)–C(6)	1.385	1.384	1.384	1.386	1.388
C(2)–C(3)	1.377	1.377	1.377	1.377	1.377
C(3)–C(4)	1.444	1.444	1.444	1.444	1.443
C(4)–C(5)	1.459	1.459	1.459	1.459	1.459
C(4)–C(7)	1.401	1.401	1.401	1.401	1.401
C(5)–C(6)	1.439	1.44	1.439	1.438	1.435
C(5)–C(10)	1.405	1.405	1.406	1.407	1.409
C(7)–C(8)	1.421	1.421	1.421	1.422	1.423
C(8)–C(9)	1.461	1.461	1.462	1.462	1.463
C(8)–C(11)	1.418	1.418	1.418	1.417	1.416
C(9)–C(10)	1.418	1.418	1.417	1.416	1.414
C(9)–C(14)	1.421	1.422	1.422	1.423	1.424
C(11)–C(12)	1.405	1.406	1.406	1.408	1.410
C(12)–C(13)	1.459	1.459	1.459	1.459	1.46
C(12)–C(15)	1.439	1.438	1.437	1.435	1.433
C(13)–C(14)	1.401	1.400	1.400	1.399	1.398
C(13)–C(18)	1.444	1.444	1.444	1.444	1.445
C(15)–C(16)	1.385	1.386	1.387	1.390	1.392
C(16)–C(17)	1.445	1.445	1.445	1.445	1.445
C(17)–C(18)	1.377	1.377	1.377	1.377	1.377
C(3)–H(3)	1.088	1.088	1.088	1.088	1.088
C(18)–H(18)	1.088	1.088	1.088	1.088	1.088
S(1)–C(1)	1.835	1.835	1.836	1.833	1.829
S(2)–C(16)	1.835	1.832	1.829	1.825	1.820
Au(1)–S(1)	2.402	2.399	2.397	2.394	2.394
Au(2)–S(2)	2.402	2.407	2.414	2.425	2.439

**Table 2. MPA atomic charges (e) of the molecule for various applied EFs (V Å<sup>-1</sup>).**

Atom	Applied electric field				
	0.00	0.05	0.10	0.15	0.21
C(1)	-0.23	-0.23	-0.23	-0.23	-0.21
C(2)	-0.18	-0.16	-0.15	-0.14	-0.12
C(3)	-0.41	-0.41	-0.41	-0.41	-0.41
C(4)	0.43	0.43	0.43	0.43	0.43
C(5)	0.39	0.39	0.39	0.39	0.39
C(6)	-0.37	-0.39	-0.39	-0.40	-0.40
C(7)	-0.66	-0.66	-0.66	-0.66	-0.66
C(8)	0.43	0.43	0.43	0.43	0.43
C(9)	0.43	0.43	0.43	0.43	0.43
C(10)	-0.66	-0.66	-0.66	-0.66	-0.66
C(11)	-0.66	-0.66	-0.66	-0.66	-0.65
C(12)	0.39	0.39	0.39	0.39	0.39

C(13)	0.43	0.43	0.43	0.43	0.43
C(14)	-0.66	-0.66	-0.66	-0.66	-0.66
C(15)	-0.37	-0.37	-0.37	-0.37	-0.37
C(16)	-0.23	-0.23	-0.23	-0.23	-0.23
C(17)	-0.18	-0.19	-0.19	-0.20	-0.20
C(18)	-0.41	-0.41	-0.40	-0.40	-0.40
H(2)	0.25	0.25	0.25	0.25	0.25
S(1)	0.08	0.09	0.09	0.09	0.09
S(2)	0.08	0.08	0.07	0.06	0.05
Au(1)	-0.06	-0.04	-0.01	0.02	0.04
Au(2)	-0.06	-0.09	-0.12	-0.16	-0.21

**Table 3.** NPA atomic charges (e) of the molecule for various applied EFs ( $\text{V\AA}^{-1}$ ).

Atom	Applied electric field				
	0.00	0.05	0.10	0.15	0.21
C(1)	-0.156	-0.151	-0.146	-0.141	-0.136
C(2)	-0.213	-0.208	-0.203	-0.198	-0.195
C(3)	-0.180	-0.181	-0.182	-0.181	-0.179
C(4)	-0.050	-0.049	-0.047	-0.046	-0.046
C(5)	-0.047	-0.043	-0.039	-0.034	-0.030
C(6)	-0.174	-0.182	-0.187	-0.194	-0.202
C(7)	-0.162	-0.162	-0.160	-0.158	-0.153
C(8)	-0.046	-0.047	-0.048	-0.050	-0.051
C(9)	-0.046	-0.045	-0.044	-0.044	-0.044
C(10)	-0.156	-0.159	-0.160	-0.161	-0.161
C(11)	-0.156	-0.153	-0.149	-0.145	-0.140
C(12)	-0.047	-0.051	-0.054	-0.057	-0.059
C(13)	-0.050	-0.053	-0.055	-0.057	-0.060
C(14)	-0.162	-0.162	-0.161	-0.159	-0.158
C(15)	-0.174	-0.169	-0.165	-0.161	-0.158
C(16)	-0.156	-0.160	-0.163	-0.166	-0.168
C(17)	-0.213	-0.218	-0.222	-0.226	-0.229
C(18)	-0.180	-0.178	-0.176	-0.174	-0.174
H(18)	0.222	0.222	0.221	0.221	0.220
S(1)	-0.131	-0.131	-0.134	-0.134	-0.134
S(2)	-0.131	-0.129	-0.126	-0.127	-0.127
Au(1)	0.190	0.221	0.250	0.282	0.318
Au(2)	0.190	0.157	0.120	0.076	0.021

For the zero field, the NPA charge for all C-atoms are found almost negative, and the H-atoms are positive; when the field increases, the charges of the atoms are found almost increases. For the zero field, the NPA charges of all H-atoms are  $\sim 0.220e$  and almost remains same for the increase of field. As the field increases, the NPA charge of S-atom at the L-end increases gradually from  $-0.131$  to  $-0.134e$ , while at the R-end the zero field charge ( $-0.131e$ ) decreases to  $-0.127e$ . As the field increases, the charges of Au(1) atom increases from  $0.190$  to  $0.318e$ , but the same for Au(2), the effect is opposite ie the value decreases from  $0.190$  to  $0.021e$ . The complete values of NPA charge distribution for zero and various applied EFs are presented in Tables 3. The variations of NPA charges of the molecule for various applied EFs with reference to zero field are shown in Fig.5. On the whole, it is found that the linker thiol atoms and the metal Au atoms at both ends of the molecule exhibit systematic variation for the increase of field.

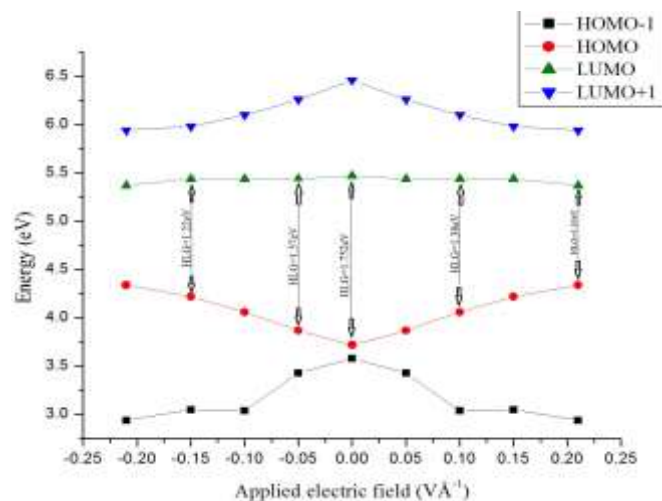
#### Molecular orbital analysis

Generally, for any molecular level device, the charge transport characteristics are mainly controlled by the nature of the molecular orbitals. The spatial distribution and the energy level of a molecular orbital (MO) determine its contribution to the conductivity [12,17]. The charge transfer through a particular MO gradually decreases as we go away from the Fermi level of the electrode. Further, the MOs, which are fully delocalized, contribute more to conduction channel [17,18]. The frontier molecular orbitals are the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the difference between them is known as HOMO-LUMO gap (HLG). The charge transport properties of the molecule [13,17] are determined by the difference of energy between HOMO and LUMO. Hence, it is essential to examine the variations of HLG and molecular orbital energy levels for the various applied EFs. Fig. 6 shows the spatial redistribution of molecular orbital of Au and S substituted tetracene for various applied EFs. The applied EF partially localizes the frontier orbitals (HOMO and LUMO) of the molecules, which are opposite to each other, this can be well understood from the Fig. 6.

For the applied field ( $0 - 0.21 \text{ V\AA}^{-1}$ ), the HLG decreases from  $1.752$  to  $1.03 \text{ eV}$ . This variation is also confirmed from the spectrum of density of states (DOS). Fig. 7 shows the DOS of Au substituted molecule for the zero and maximum applied fields, in which, the HOMO (green lines) and the LUMO (blue lines) and the HLG are shown. Notably, the presence of gold atoms in the molecule broadens the DOS peaks. Seemingly, the significant decrease of HLG may facilitate for large electron conduction through the molecule. Fig. 8 represents the energy levels of the molecule for various applied EFs.

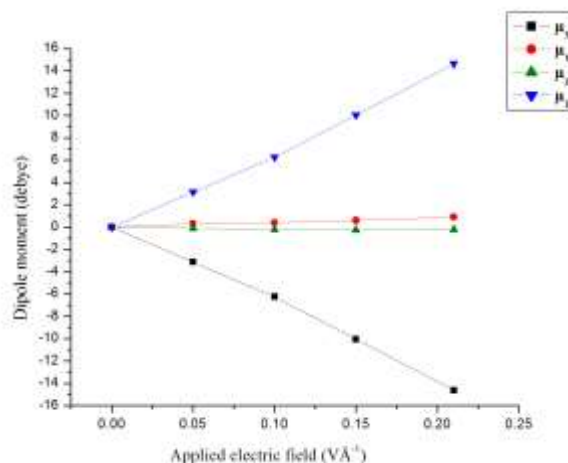
#### Molecular dipole moment

When the molecule is subjected to an external EF, the delocalization of  $\pi$ - electron of the conjugated organic molecules leads to redistribution of charges of the molecular chain, consequently, the dipole moment of the molecule changes [13,19]. Hence, we can roughly estimate the ability of electron transport by simply comparing the dipole moments of the molecule for various applied EFs. The variations of molecular dipole moment for the various applied EF were analyzed by several researchers [20] and found a linear character. Here, we have calculated the dipole moment of the molecule for zero as well as various applied EFs.



**Fig. 8** Energy level diagram of Au and S substituted Tetracene molecule for the zero and various applied EFs.

The resultant molecular dipole moment ( $\mu_T$ ) for zero bias is  $0.0002 \text{ D}$ , which increases almost linearly with the increase of field. The molecule becomes highly polarized for the higher field ( $0.21 \text{ V\AA}^{-1}$ ) and the dipole moment becomes  $14.65 \text{ D}$ . Fig. 9 shows the variation of x, y and z components of dipole moment ( $\mu_x$ ,  $\mu_y$ , and  $\mu_z$ ) and the resultant molecular dipole moment ( $\mu_T$ ) for various applied EFs, the large variation of x-component may be due to the application of field along x-direction.



**Fig. 9** Molecular dipole moment of Au and S substituted Tetracene molecule for the zero and various applied EFs.

#### Conclusions

The present theoretical study on Au and S substituted Tetracene molecule describes the structural parameters and the electrical characteristics for zero and various external applied fields. Systematic and almost uniform variation has been observed for the terminal bonds of the molecule for various applied EFs. When the field increases, the hybridization of molecular levels broaden the DOS and decreases the HLG. The large decrease of band gap from  $1.752 \text{ eV}$  to  $1.03 \text{ eV}$ , at the high field, facilitates to have high electrical conductivity. The EF polarizes the molecule, in consequence of that the dipole moment of the molecule increases from  $0.0002$  to  $14.65 \text{ D}$ . The study of structural properties of the molecule gives an idea to tune the molecule for appropriate biasing voltages for the operation of molecular devices. Over all, the terminal groups of the molecule are found to be very sensitive to applied EF on compared with the molecular region. The structural confirmation, distribution of atomic charges, and electrostatic

properties of the molecule in the study may support to design several kinds of new charge transfer molecules.

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