

First-principles study on the electronic structure of Thiophenbithiol (TBT) on Au(100) surface

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Abstract

First principle calculations were performed using Density functional theory within the local spin density approximation (LSDA) to understand the electronic properties of Au(100)+TBT system and compare the results with Au(100) and bulk Au properties. Band structure, the total DOS and charge density for these materials are calculated. We found that the HOMO for Au(100)+TBT becomes broader than Au(100) and bulk Au and d orbitals have the most contribution in covalent band. The electron densities overlap between Au atoms implies a large covalent bonding. Our calculations indicate that conjugated systems such as (TBT) enhance electric conductance.

Keywords: *Electronic structure, Self assembled monolayers, Band structure, Density of states, Local density of states, Charge density*

1. Introduction

Organic “self assembled” molecular monolayers have been considered as useful electronic materials for several decades [1-3], while the idea of using organic materials as dielectric layers has undergone more than a century of demonstrated application and practice. The ability to utilize the unique structural and electronic properties of self-assembled monolayers (SAMs) in nano scale electronics is more recent and has rarely included consideration of spin. The electronic structure of noble metal surfaces has been studied in great detail by a variety of electron spectroscopy, deriving information about bulk and surface state [4]. Self assembly of organic molecules onto metal surfaces and nanoparticles via thiol groups in an area of importance to molecular electronics and for biotechnology applications [5]. Formation and electronic properties of self-assembled monolayers of oligomer on the Au(100) surface have been extensively studied [6]. Oligothiophen is an oligomer of TBT molecules (Figure 1).

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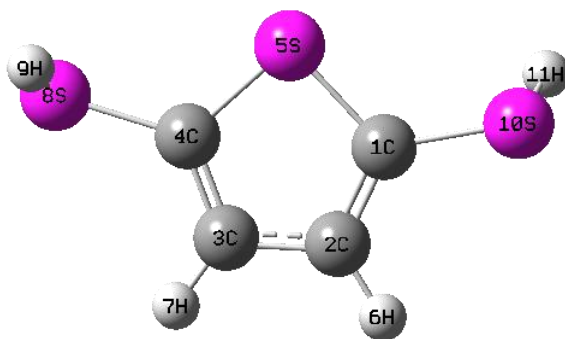


Fig.1. The structure picture of a Thiophenbithiol (TBT) molecule

TBT molecule in which a hydrogen atom in its end group has been replaced by an S atom, and attaching this to an Au electrode via sulfur-gold (S-Au) binding. Electrical, optical, and other properties, derived from their delocalized π frameworks, in conjunction with their synthetic and processing advantages as organic polymers, have led to real applications as a new generation of advanced materials. We have chosen oligothiophen due to their multiple potential technological applications. Many oligothiophens are used in novel electrical or optical devices. They are used in thiophen-based electronic components and devices, such as transistors [7], electroluminescent devices [8], photovoltaic cells [9], energy storage devices [10], electrochromic devices [11] and DNA sequencing as well as in microscopy markers [12]. Theoretical studies of thiolate bonding to gold surfaces [5,13,14] have focused upon the possible bonding configurations on the (100) surface. Conjugated gold nanoparticles are of fundamental interest because of their importance in the self-assembly process to develop potential miniature devices [15]. The gold nanoparticles, being nontoxic and highly biocompatible, are attractive candidates for therapeutic drug delivery vehicles [16]. In this work, we have used DFT to calculate, band structure, DOS and charge density of TBT adsorbed on Au(100) surface. A projected Density of States analysis allows us to understand the bonding characteristics.

2. Materials and methods

2.1. Computational methods

All calculations were performed by the Quantum-ESPRESSO suite of codes, in which the density functional theory (DFT) [17] methodology is implemented using plane waves expansions and pseudopotentials[18]. All the core-valence interactions were described by Vanderbilt ultrasoft pseudopotentials (USPP) [19] with a kinetic energy cutoff of 50 Ry for the plane wave basis set and a cutoff of 500 Ry for the charge density. The local spin density approximation (LSDA) was selected for the exchange-correlation part of the energy functional. Bulk and surface was simulated using the supercell techniques. The (100) surface was simulated with the periodic slab method with (1×1) surface unit cell and 4 layers of gold (total of 12 atoms). Brillouin zone integrations were approximated by discrete sums over k-point grids built according to the scheme of Monkhorst and Pack [20]. A 9×9×1 grid was selected after SCF convergence tests, resulting in

41 k-points. An empty inter-slab separation of 10 Å along the surface normal was found adequate to avoid spurious interactions between facing surfaces of successive slabs.

3. Results and discussion

Thiophenbithiol contains two S-H terminal groups which covalently bond to the Au electrodes by removing hydrogen atom. These types of molecules have been widely studied experimentally due to their use in molecular junctions. In the TBT ring, the π electrons are delocalized, and this is the main reason for the electronic conductance [21]. The S atom contains free electrons which participate in the ring resonance although the sulfur atoms, however, partially insulate the π electron states of the molecules, leading to a decrease in their conductivity. Similar results have been obtained for phenyl dithiol [22]. Recent studies have suggested that the binding to a hollow site is energetically more favorable [23], while others suggest this to be true for a single-atom connection [24]. Consequently, the geometry of a molecule-metal contact is, as yet, not well understood. The optimized S-C and S-Au bond lengths in Au(100)+TBT system (Figure 2) are 1.787 Å and 2.21 Å, respectively. For the surface calculations, the slab unit cells possess different symmetry than the bulk fcc primitive cell. For the (100) surfaces, the unit cells have tetragonal symmetry. The tetragonal supercell lattice parameter was 10.7147 Bohr, determined by SCF calculations.

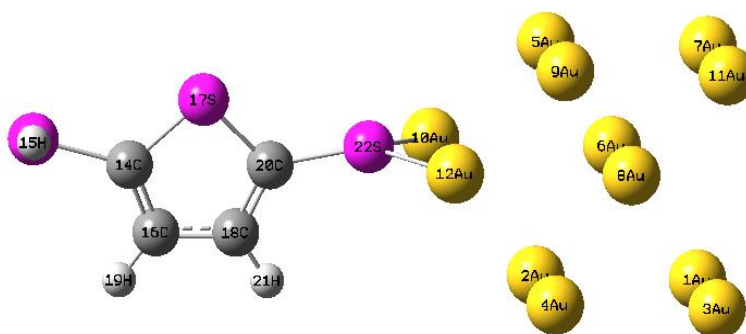


Fig.2. The structure picture of a Au(100) + TBT

3.1. Band structure calculation

Based on optimized geometries, we calculated the electronic band structure of the relaxed bulk Au, Au(100) and Au(100)+TBT (Figure 3). (Au: [Xe+4f] 5d¹⁰6s¹, H: 1S¹, C: [He] 2s²2p², S: [Ne] 3s²3p⁴) is studied at its equilibrium lattice, along high symmetry points in the Brillouin zone. For convenience, the Fermi level is taken at $E_F = 0$. Metallic crystals are characterized by the Fermi level lying within a band or bands of delocalized states. It can be seen from Figure 3a that the Fermi level for Au (5d¹⁰6s¹) intersects several bands. There are 11 valence electrons and 5.5 bands are expected to be filled on average in the BZ. Indeed 5 bands with little dispersion near the bottom of the energy range are observed. Among mentioned bands there is also one band with large dispersion, which intersects the Fermi level at several points.

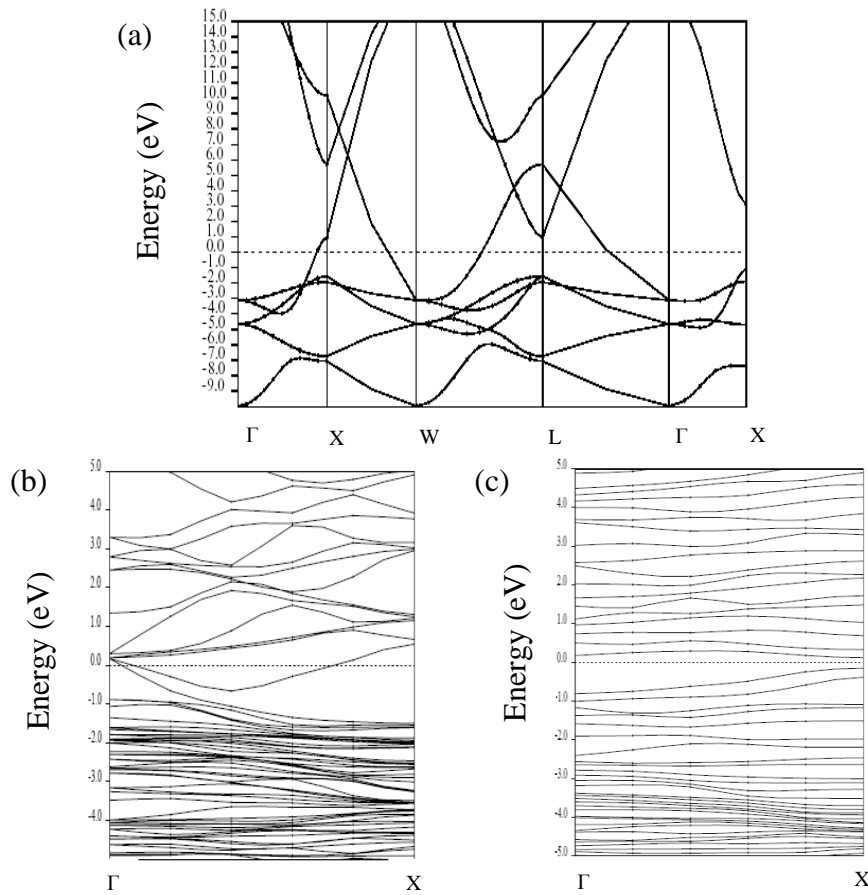


Fig.3. Calculated band structure of **a.** bulk Au, **b.** Au(100) and **c.** Au(100)+TBT. The Fermi level (E_f) is indicated by a horizontal dotted line

The 5 low energy occupied bands are essentially arising from the 5d states. Their low dispersions indicate weak interactions among these orbitals. The next band can be identified by the s-like bonding band. This band interacts and hybridized with the d bands. The Fermi level intersects bands with high dispersion, and thus there are plenty of states immediately below and above the Fermi level for thermal and electrical excitation of electrons. This indicates that Au solid will act as a good metal, which be able to carry current when placed in external electric field. The important point as presented in Figure 3 is that the plenty of bands below and above the Fermi level in Au(100)+TBT are more than Au(100), because TBT increase the carry current ability, by increasing the orbitals coupling.

3.2. Density of states

The electronic properties of Au alloys have been analyzed in terms of the electronic DOS and its angular decomposition in s and d components. The calculated total DOS for (a) bulk Au, (b) Au(100) and (c) Au(100)+TBT for both spin up and down polarizations are shown in Figure 4. The energy levels below the zero of energy are all occupied levels correspond to valence band, whereas those above the zero of energy represent virtual levels correspond to conduction band.

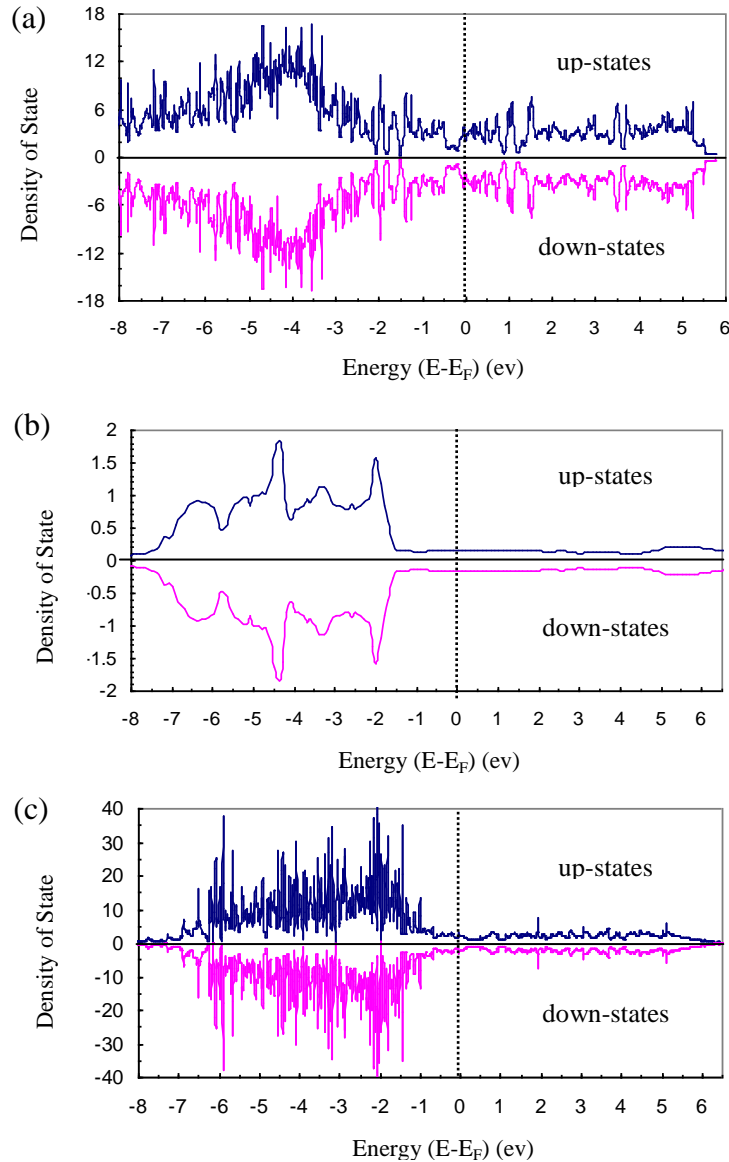


Fig.4. Calculated spin-polarized total densities of states for , a. bulk Au, b. Au(100) and c

We observed that the DOS for spin up and down orientation are completely equal. The HOMO for Au(100)+TBT becomes broader than Au(100) and bulk Au, due to their orbitals coupling of Au contacts (atoms : Au (10) and Au (12) with s atom (Figure 2). This broadening enhances the electronic transmission. In Au(100)+TBT the valence band are broaden while the

values of the total density of states at the Fermi Level for both of them are similar, nearly (2 states/eV). The number of valence electrons are constant although the Au(100)+TBT band is broader than Au(100). Au(100)+TBT bands width is implemented the extent of electrons delocalization, thus the interaction between atoms is strength. The peaks appear in the DOS graph in Au(100)+TBT represent the resonance Au HOMOs. The LUMO is also coupled with the Au states, but the contribution of this transmission is smaller than the HOMOs contribution. In bulk Au, Au(100) and Au(100)+TBT, we can observe that The contribution of d orbital in HOMO region are important but in the lower part of the valence band, contribution of s orbital is partially high. On the other hand the d orbital plays a very large role in covalent band. In all of compounds the contribution of d orbital near the Fermi level is important.

3.3. Charge density

In the first principle calculations, the valence charge density is always used to discuss interatomic interactions and prove the nature of the bond character among the Au atoms. In the interatomic region, the electrons distribution is evenly explained by the nearly free electron model. Charge densities are basic physical quantities in the local density functional theory [25]. A contour plot of the total charge density in the same layer of bulk Au, Au(100) and Au(100)+TBT are theoretically calculated is plotted in (Figure 5).

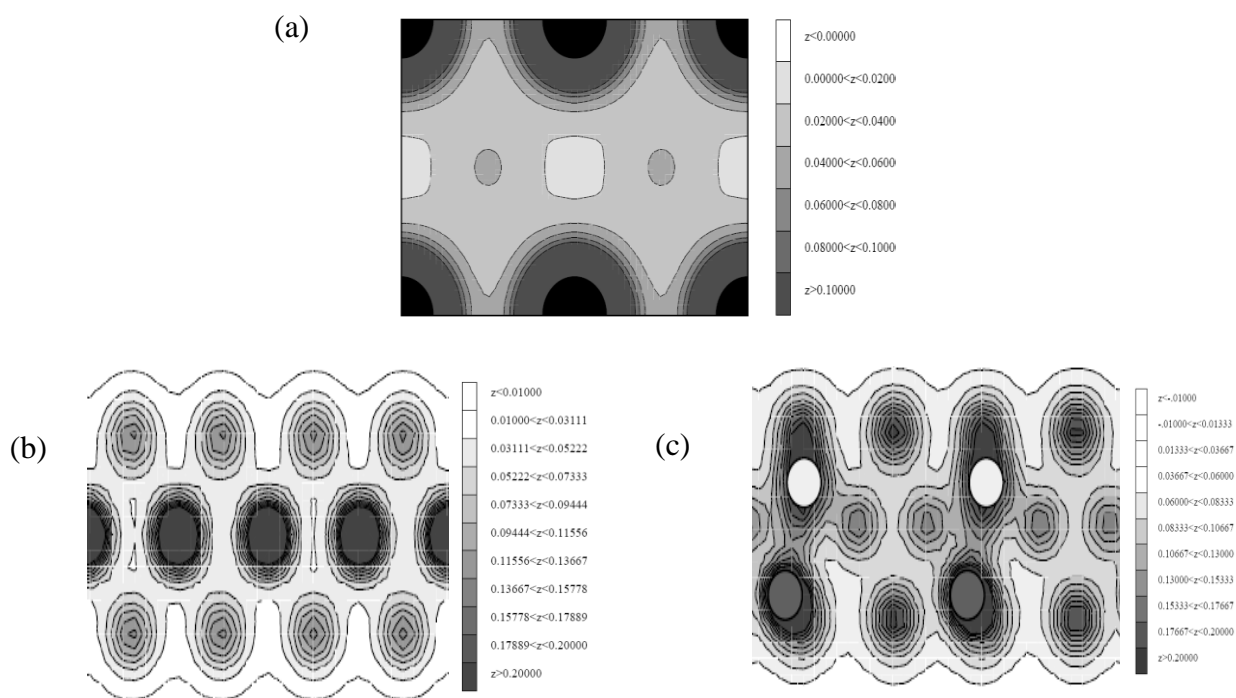


Fig.5. Contour plot of charge density for , a. bulk Au, b. Au(100) and c. Au(100)+TBT

4. Conclusion

In summary, by performing First principles plane wave pseudopotential the electronic properties of bulk Au, Au(100) and Au(100)+TBT was investigated. We have used DFT to calculate band structure, DOS and charge density of all compounds. All calculations were carried out using spin polarization. The important point as presented in band structure calculation is that the plenty of bands immediately below and above the Fermi level in Au(100)+TBT, increase the carry current ability and orbital coupling in this compound. The DOS revealed that The HOMO for Au(100)+TBT becomes broader than Au(100) and bulk Au, due to their orbitals coupling of Au contacts. This broadening enhances the electronic transmission. The results show that The contribution of d orbital near the Fermi level is important and The relative intensities of d LDOS for Au(100)+TBT is wider than Au(100) and bulk Au Therefore in Au(100)+TBT the overlap in orbitals are the strongest. A contour plot of the total charge density in the same layer of these compound shows that in Au(100)+TBT, electron densities overlap between Au atoms implies a large covalent bonding where wise in Au(100) charge density is mostly concentrated around the atoms, and there are small interactions across neighboring sites.

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