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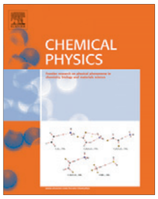

The conductance and stability of fused dithia-heterocyclic compounds contacted with gold and platinum electrodes

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ABSTRACT

The electronic transport properties of two kinds of fused dithia-heterocyclic compounds, 2,3,6,7-tetrahydrobenzo[1,2-*b*:4,5-*b*′]dithiophene (THBDT) and benzo[1,2-*b*:4,5-*b*]dithiophene (BDT), connected to gold and platinum electrodes are investigated using a self-consistent *ab initio* approach that combines the non-equilibrium Green's function formalism with density functional theory. Our calculations show that the transmission at the Fermi level of the Au–THBDT–Au junction, where the THBDT molecule is connected to two gold electrodes through a gold adatom on each side, is 3.1×10^{-2}, in good agreement with the experimentally measured value (1.2×10^{-2}). Replacement of the gold electrodes with platinum electrodes can improve the junction stability but cannot increase the zero-bias junction conductance. In contrast, due to the enhanced conjugation in BDT and the better molecule–electrode coupling, both the transmission and the stability of the Pt–BDT–Pt junction are improved significantly, demonstrating the close relation between the device performance and the device structure.

1. Introduction

In recent years tremendous efforts have been devoted to the fabrication and study of electronic devices with individual molecules as the active component, and understanding electron transport through a single molecule sandwiched between two metallic electrodes is crucial for the development of molecular devices [1,2]. It is well known that the current–voltage characteristics of a molecular device depend not only on the quantum nature of the central molecule but also on the band structure of the metal electrodes and the linking groups used to bind the molecule to the electrodes [3]. Due to their large conductivity and chemical inertness, gold and platinum are widely used as the electrode materials for the construction of molecular devices [4–14]. For gold electrodes, thiol, amine, methyl sulfide and dimethyl phosphine groups are often employed as the molecule–electrode linkers. In contrast to the thiol group where an Au–S covalent bond is formed, using amine, methyl sulfide or dimethyl phosphine groups the central molecule is bound to the electrodes through a donor–acceptor bond formed between an undercoordinated Au atom on the electrode surface and the lone pair of the corresponding N, S or P atom [8,15–19]. Therefore, it can be expected that the junction conductance of aromatic molecules will depend on the orientation of the π-type orbitals relative to the donor–acceptor bond formed at the molecule–electrode interface. This has been clearly demonstrated with the 2,3,6,7-tetrahydrobenzo[1,2-*b*:4,5-*b*′]dithiophene (THBDT) molecule connected to two gold electrodes [20], as the orientation of the lone pair of the two S atoms in the THBDT molecule is rigidly locked. However, detailed studies on the conducting mechanism for this specific molecular junction are still lacking. For example, which molecular orbital of the THBDT molecule dominates the low-bias junction conductance is unknown. A deep understanding of these details will guide the design of molecular electronic devices and improve their performance.

In this paper we focus on the atomic structure and the zero-bias conductance of the THBDT molecule connected to gold and platinum electrodes. This is investigated using a fully self-consistent *ab initio* method that combines the non-equilibrium Green's function formalism with density functional theory (that is, the NEGF + DFT approach) [21–31]. Our calculations demonstrate that the conductance of a symmetric Au–THBDT–Au junction, where the THBDT molecule is attached to two Au(111) electrodes through a gold adatom on each side, is $3.1 \times 10^{-2}\ G_0$, well consistent with the measured value $(1.20 \pm 0.05) \times 10^{-2}\ G_0$ [20]. Here, $G_0 = 2e^2/h$ is the conductance quantum. The transmission around the Fermi level (E_F) originates mainly from the highest occupied molecular orbital (HOMO) and the HOMO$-$1 of the THBDT molecule, which are both π-type orbitals delocalized over the benzene backbone and have a large density on the two S atoms. Furthermore, we study the transport properties of a single benzo[1,2-*b*:4,5-*b*]dithiophene (BDT) molecule sandwiched between gold and platinum electrodes. Compared with the Au–THBDT–Au junction, both the conductance and the stability of the Pt–BDT–Pt junction are much

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improved due to the enhanced conjugation of the central molecule and the strong molecule–electrode coupling.

2. Calculation method

In this work we use the SIESTA code [32] to study the atomic structure of the THBDT and BDT molecular junctions and the quantum transport code SMEAGOL [30] to study their electronic transport properties. SIESTA is an efficient DFT program, in which the wave functions of the valence electrons are expanded in terms of a finite range numerical basis and improved Troullier–Martins pseudopotentials are used for the atomic cores [33]. By means of extensive optimization, a user-defined double zeta plus polarization basis set is constructed for the carbon, sulfur and hydrogen atoms, and a single zeta plus polarization basis set is used for gold and platinum atoms. The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) for the exchange and correlation functional is used in all our calculations to account for the electron–electron interactions [34]. Geometry optimization is performed by conjugate gradient relaxation until the forces are smaller than 0.03 eV Å^{-1}. For comparison, all-electron DFT calculations for the isolated THBDT and BDT molecules are also carried out using both the PBE GGA functional and the Becke three-parameter Lee–Yang–Parr (B3LYP) semi-empirical hybrid functional with the Gaussian 03 code [35,36]. Here, the 6-311++G(d, p) basis sets are used for carbon, hydrogen and sulfur atoms [37].

SMEAGOL is a practical implementation of the NEGF + DFT approach, which uses SIESTA as the DFT platform [30]. We use an equivalent cutoff of 120.0 Ry for the real space grid, while the charge density is integrated over 60 energy points along the semi-circle, 20 energy points along the line in the complex plane and five poles are used for the Fermi distribution (the electronic temperature is 25 meV). We always consider periodic boundary conditions in the plane transverse to the transport. The unit cell of the extended molecule, for which the self-consistent calculation is performed, comprises one THBDT or BDT molecule and eight Au/Pt(1 1 1) atomic layers with a (3×3) supercell. The transmission coefficient $T(E)$ of the molecular junctions is evaluated as

$$T(E) = \frac{1}{\Omega_{2DBZ}} \int_{2DBZ} T(\vec{k}; E) d\vec{k}, \tag{1}$$

where Ω_{2DBZ} is the area of the two-dimensional Brillouin zone (2DBZ) in the transverse directions. The k-dependent transmission coefficient $T(\vec{k}; E)$ is obtained as

$$T(\vec{k}; E) = Tr\left[\Gamma_L G_M^R \Gamma_R G_M^{R+}\right], \tag{2}$$

where G_M^R is the retarded Green's function matrix of the extended molecule and $\Gamma_{L(R)}$ is the broadening function matrix describing the interaction of the extended molecule with the left (right) electrode. More details on the method can be found in Ref. [30].

3. Results and discussion

3.1. Transport properties of the THBDT molecule connected to Au and Pt electrodes

First we investigate the atomic and electronic structure of the THBDT molecule in the gas phase. As shown in Fig. 1a, THBDT is a non-planar molecule with the C_i symmetry. Though the two carbon atoms at position 2 and position 6 are out of the benzene plane, the two S atoms are almost in the benzene plane since the torsion angle S1–C9–C10–C4 is calculated to be 179.14°. The optimized geometrical parameters of the THBDT molecule are listed in Table 1. As we can see, the two S–C bond lengths are, respectively, calculated to be 1.773 Å and 1.842 Å, which are much larger than the S–C bond length (1.712 Å) of the gas-phase thiophene [38]. The differences between the bond lengths calculated using SIESTA and those obtained from all-electron DFT calculation with the same PBE functional but a much larger basis set (Gaussian 03) are less than 0.01 Å, confirming the appropriateness of the pseudopotentials and basis functions for the C, S and H atoms built for this work. Furthermore, similar results are also obtained with the more computationally expensive and more accurate B3LYP hybrid functional.

Since the electronic transport properties of molecular junctions are strongly affected by the electronic interaction, the charge transfer and the energy level alignment at the molecule/electrode interfaces, it is interesting to take a look at frontier molecular orbitals of THBDT (see Fig. 1b). As we can see, all of the frontier molecular orbitals going from HOMO−3 to LUMO + 1 are basically π-type orbitals, which are mainly composed of the π-type orbitals of the

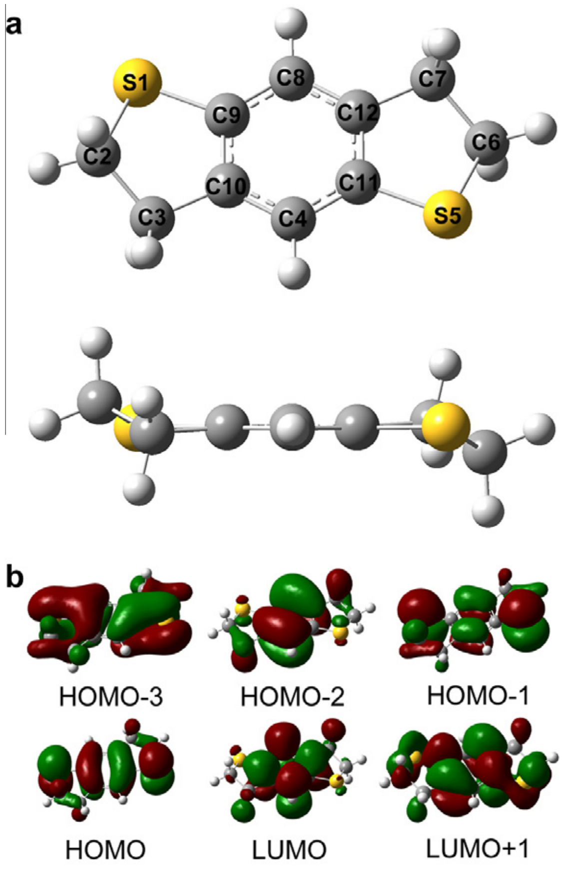

Fig. 1. (a) Optimized molecular structure (up panel: top view, down panel: side view) of the gas-phase THBDT molecule, (b) frontier molecular orbitals of THBDT.

Table 1
Optimized bond lengths (in Å) of the THBDT molecule in the gas phase. The 6-311++G(d, p) basis sets are used for hydrogen, carbon and sulfur atoms in the all-electron DFT calculations with the Gaussian 03 code.

Bond	SIESTA PBE	Gaussian 03	
		PBE	B3LYP
S1–C2	1.842	1.851	1.851
S1–C9	1.773	1.781	1.783
C2–C3	1.531	1.535	1.536
C3–C10	1.511	1.512	1.512
C4–C10	1.400	1.398	1.392
C4–C11	1.404	1.402	1.395
C9–C10	1.409	1.410	1.402