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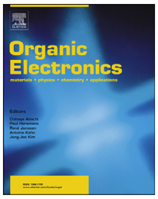

Tuning the conductance of benzene-based single-molecule junctions

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ABSTRACT

Single-molecule junctions are elementary building blocks in novel electronics devices, and therefore, it is essential to understand the charge transport mechanisms at the single-molecular level. According to recent studies, the linker atoms connecting the organic molecule with the electrodes play a crucial role in optimizing the transport properties as well as thermodynamical stability of a molecular junction. We address this issue by considering N, O, S, and Se atoms as prospective linkers anchoring the benzene molecule to the Au(1 0 0) electrodes. Calculations based on non-equilibrium Green's function approach are performed within the framework of the density functional theory. Electron transport is studied in detail by analyzing the transmission spectra, density-of-states distributions, and current–voltage characteristics. Results show that the choice of linkers strongly affects the conductance of the junctions under study: at low bias regime, the current through N-linked molecules is remarkably higher as compared to the case of S and Se linkers, whereas the thermodynamical stability is similar. This offers an additional means of modifying the current–voltage characteristics of benzene-based molecular junctions by an appropriate selection of linkers.

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1. Introduction

Understanding the charge transport mechanisms in organic molecular junctions is essential for the development of molecular electronic devices. Transport characteristics of a metal–molecule–metal junction are affected by several parameters, such as the structural and electronic properties of both the molecule and the electrodes, their mutual interactions, and the molecular conformation. It has already been demonstrated that the conductance of a molecular junction can be tuned by using chemical substituents, i.e. functional groups [1,2], or by varying the chemical linker and its anchoring position [3].

A key factor influencing the transport properties of molecular junctions, other than the intrinsic properties of the molecule, is the linker atoms connecting the molecule with the electrodes. Indeed, by modifying the strength of the metal–molecule coupling, the anchoring atoms determine the thermodynamical stability of a junction on the one hand, and affect the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) on the other. Moreover, they also have a considerable impact on the alignment of the molecular energy gap with respect to the metal Fermi level, and thus, influence the conductance of a junction. Consequently, it is a challenge to achieve highly conductive contacts between metal electrodes and organic molecules by an appropriate choice of linkers that would result in electronically transparent and thermodynamically stable molecular junctions.

Highly conductive single-molecule junctions have already been obtained with the conductance close to one quantum unit G_0 ($G_0 = 2e^2/h$) employing benzene [4] and hydrogen molecule [5] bridging platinum electrodes. Also the direct covalent σ-type Au–C bond between the C backbone of alkane molecules and the Au electrodes has been demonstrated to exhibit conductance of 0.1 G_0 [6], an order of magnitude higher than obtained with conventional linkers such as thiols and amines. According to recent studies [7–10], the linker atoms or anchoring groups play a crucial role in optimizing the transport properties as well as thermodynamical stability of a single-molecule junction. Typically, a thiol group (–SH) or amine linker (–NH_2) are used to electronically couple organic backbones to metal electrodes, but both the measured and theoretically predicted conductances are of the order of 10^{-2} G_0 [1–3,11–14], significantly smaller than the ideal limit of 1 G_0 for a

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single conducting channel. However, several other anchoring groups were also studied, including Se [12,15], Te [12], and I [11] atoms or −NC [16,17], −CN [9], and −COOH groups [7].

To shed more light on how the conductance of a molecular junction can be tuned by an appropriate choice of anchoring atoms, we followed the strategy of a systematic variation of only one element of the junction structure, namely, the linker atom. To this end, we theoretically studied the model system consisting of a single benzene ring connected to gold electrodes via different atoms, all in the same *para*-configuration. More specifically, we examined the transport properties of benzene-based single-molecule junctions in the *para*-X−(C_6H_4)−X conformation, where X = S, Se, N, and O stands for the linker atom forming the BDT, BDSe, BDA, and BDO molecule, respectively.

2. Computational methodology

2.1. First-principles simulations

All calculations presented in this paper were based on the density functional theory (DFT) with a local-orbital basis, as implemented in the Fireball package [18–21]. The Fireball code was designed to deal with large-scale first-principles simulations, offering a very favorable accuracy-to-efficiency balance, provided that the basis set is carefully chosen [22]. DFT computations were carried out within the local-density approximation (LDA) for the exchange-correlation functional [23]. A set of 25 irreducible special *k*-points sampling the transverse Brillouin zone was used. Electronic and structural optimizations were performed until the convergence criteria of 10^{-4} eV for the total energy and 0.05 eV/Å for the forces acting on unconstrained atoms were satisfied, respectively.

In Fireball, the wave functions of valence electrons are expanded in terms of the so-called *fireball* orbitals [19,24], i.e. a set of strictly localized pseudoatomic orbitals, which are exactly zero for distances larger than the cutoff radius R_C. An important point of this approach is the proper choice of the local-orbital basis and the R_C values that give consistent results for both the electronic and atomic structure of the junction constituents. Thus, several tests were performed to optimize the basis set that yields a good description of the structural and electronic properties of the considered molecules as well as the Au electrodes. In particular, the work function of 5.04 eV computed for the Au(1 0 0) surface well reproduces the experimental value of 5.22 eV [25]. The following optimized basis sets of pseudoatomic orbitals were used to describe valence electrons of distinct elements [22,24]: ss^* for H, spd^* for C, N, S, and Se, sps^*p^* for O, and spd for Au. The corresponding cutoff radii R_C (all given in a.u.) of (3.8, 3.8) for H, (4.0, 4.5, 5.4) for C, (3.6, 4.1, 5.2) for N, (3.4, 3.8, 3.4, 3.8) for O, (4.3, 4.7, 5.5) for S, (4.3, 4.7, 5.7) for Se, and (5.0, 5.6, 4.7) for Au orbitals were accepted.

2.2. Transmission spectra

All transport calculations were performed by employing the non-equilibrium Green's function technique (the quantum transport code Smeagol [26,27]), coupled to the Fireball DFT package. This method allows the simulation of the electronic transmission in a class of systems comprising a molecule, an atomic contact, or an arbitrary potential barrier in-between conducting electrodes. An eigenchannel analysis [28] was used, enabling an eigenchannel decomposition of the transmission spectra. The eigenchannels are special scattering states with a well-defined transmission probability, indicating which molecular orbitals are mainly responsible for the transmission.

It should be noted here that—although the DFT simulations became a method of choice for investigating the correlation between the atomic configuration, electronic structure and transport characteristics of molecular systems—the predicted energies of molecular orbitals quite often deviate from the experimental data. Typically, the HOMO−LUMO gap is underestimated within DFT [2,3,9,29,30], which can lead to significantly higher conductance values with respect to experiment. In spite of that, DFT framework is widely used in theoretical studies of the charge transport mechanisms in organic molecular junctions.

3. Results and discussion

3.1. Gas-phase molecules

To obtain a detailed picture of single-molecule junctions, first the structural and electronic properties of all considered molecules in their gas-phase configuration were determined. The schematics of BDT and BDA molecules, along with their frontier molecular orbitals (HOMO and LUMO) as well as HOMO−1 and LUMO+1 are displayed in left- and right-hand-side panels of Fig. 1, respectively. In addition to the occupied (HOMO−1 and HOMO) and unoccupied (LUMO and LUMO+1) orbitals, the sum of the latter, i.e. LUMO and LUMO+1, is also presented (see second panel in Fig. 1). We find them useful in explaining some features of the transmission

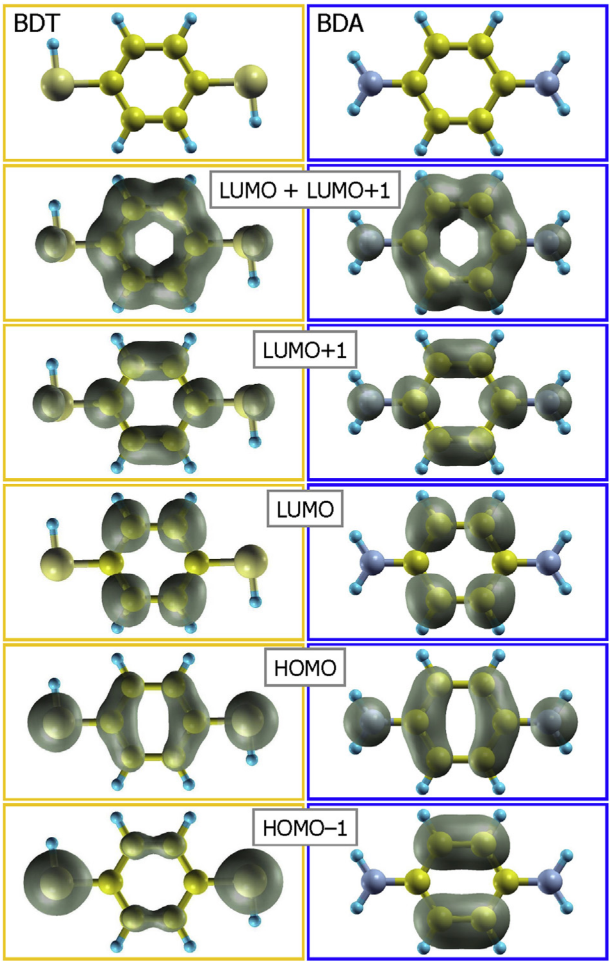

Fig. 1. The schematics (top panel), the sum of LUMO and LUMO+1 orbitals (second panel) and the occupied (HOMO−1 and HOMO) as well as unoccupied (LUMO and LUMO+1) molecular orbitals of the gas-phase BDT and BDA molecules (remaining panels). All isosurfaces correspond to the electron density value of 0.01 $e/\text{Å}^3$.

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