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RESEARCH ARTICLE

First-principles calculation on the conductance of ruthenium-quasi cumulene-ruthenium molecular junctions

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The conductance of a family of ruthenium-quasi cumulene-ruthenium molecular junctions including different numbers of carbon atoms, both in even numbers and odd numbers, are investigated using a fully self-consistent ab initio approach which combines the non-equilibrium Green's function formalism with density functional theory. Our calculations demonstrate that although the overall transport properties of the Ru-quasi cumulene-Ru junctions with an even number of carbon atoms are different from those of the junctions with an odd number of carbon atoms, the difference between the corresponding current-voltage (I–V) characteristics of these molecular junctions declines to lesser than 16% when the voltage goes up. In each group, the molecular junctions give a large transmission around the Fermi level since the Ru–C π bonds can extend the π conjugation of the carbon chains into the Ru electrodes, and their I–V characteristics are almost linear and independent of the chain length, illustrating potential applications as conducting molecular wires in future molecular electronic devices and circuits.

Keywords molecular electronic devices, density functional theory, non-equilibrium Green's function, carbon monatomic chains

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1 Introduction

Electron transport properties of single molecules have been attracting incremental attention due to their promising applications in future electronic devices and circuits [1−3]. In order to build molecular electronic devices and circuits with ultrahigh density, one basic step is to find an ideal conducting molecular wire with high and stable conductance over a wide bias region and for various lengths. Recently, the electronic structure and transport properties of a series of polyynes connected to gold electrodes via thiol caps have been reported [4], showing an almost constant conductance in a wide range of bias voltages that weakly depend on molecular length. However, it has been shown that the Au–S contact is not good enough for the construction of molecular electronic devices due to its uncontrollable interface structures [5]. Thus, other more suitable contacts are highly desired.

In our previous work we have demonstrated the advantage of using the ruthenium–carbon (Ru–C) multiple bonds as the linkage of conjugated organic molecules [6, 7], because the Ru–C π bond can create an efficient channel for charge carriers. Since π conjugation is the main characteristic of the electronic structure of carbon chains including both polyynes and cumulenes, placing carbon chains in contact with Ru electrodes might extend the π conjugation continuity and improve their transmission properties. Therefore, in this paper, we investigate the low-bias conductance of a family of carbon–chain molecular junctions in contact with Ru electrodes, especially in terms of length dependence. This is realized using a fully self-consistent ab initio approach that combines the non-equilibrium Green's function (NEGF) formalism with density functional theory (DFT) [8−11], that is, the NEGF+DFT method [12−16]. Our calculations show that the carbon–carbon bond lengths along the molecular chains vary slightly from each other, all much like the C=C double bond. Thus, we name these carbon chains "quasi cumulene". Although the Ru–quasi cumulene–Ru junctions with an even number of carbon atoms give a slightly better transmission property around the Fermi level than the junctions with an odd number of carbon atoms, the current–voltage (I–V) characteristics of both kinds are linear and almost independent of the chain length. Molecular orbital analysis confirms that the transmission around the Fermi level of both kinds of Ru–quasi cumulene–Ru junctions is contributed to equally by two perpendicular degenerate π-type orbitals.

2 Methodology

The Ru–quasi cumulene–Ru molecular junctions are constructed by sandwiching a series of carbon chains ranging from 6 to 13 carbon atoms between two Ru(0001) electrode surfaces, as shown in Fig. 1. To avoid prolixity, these molecular junctions are denoted by the number of carbon atoms within the molecular chain, namely, "RuC6", "RuC7", "RuC8", "RuC9", "RuC10", "RuC11", "RuC12" and "RuC13".

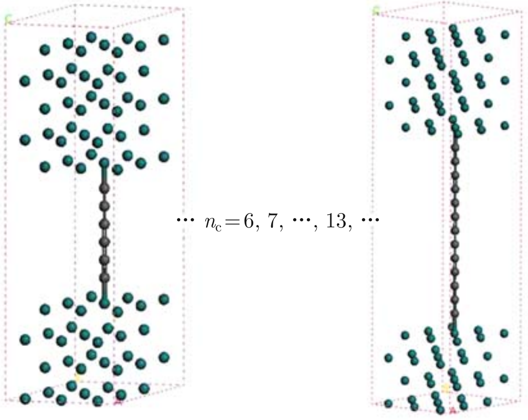


Fig. 1 Geometric structure of the Ru–quasi cumulene–Ru molecular junctions, where n_c is the number of carbon atoms included in the junction.

The geometric structure of these molecular junctions are optimized using the efficient DFT package SIESTA [17], which adopts a finite-range numerical basis set for the valence electrons and makes use of pseudopotentials for the atomic cores. The electron transport properties of these model devices are calculated using the quantum transport code SMEAGOL [16], which is a practical implementation of the NEGF+DFT approach based on SIESTA. The pseudopotentials of the ruthenium and carbon atoms are generated with the atomic valence electron configurations d^7s^1 and s^2p^2, respectively. By means of much testing work, a user-defined double ζ plus polarization (DZP) basis set has been constructed for the carbon atoms, and a single ζ plus polarization (SZP) basis set has been used for Ru atoms. The Perdew-Burke–Ernzerhof (PBE) generalized-gradient approximation (GGA) for the exchange and correlation energy is used in all of our calculations [18]. Periodic boundary conditions are considered in the transverse directions. The unit cell of the extended molecule comprises a quasi cumulene chain and four Ru atomic layers with a (3×3) supercell on each side (as shown in Fig. 1). For the transport calculations we use an equivalent cutoff of 120.0 Ry for the real space grid, and the charge density is integrated over 60 energy points along the semi-circle, 20 energy points along the line in the complex plane and 5 poles in the Fermi distribution (the electronic temperature is 25 meV). The transmission coefficient as a function of energy, $T(E)$, is evaluated as

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

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

$$T(\boldsymbol{k}; E) = \mathrm{Tr}[\Gamma_L G_M^R \Gamma_R G_M^{R+}] \tag{2}$$

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 calculation details of the transmission coefficient can be found in Ref. [16]. Here, we calculate the transmission coefficient by sampling 100 k-points in the 2DBZ perpendicular to the transport direction.

The orbital isosurfaces of these carbon chains are investigated using the Cambridge serial total energy package (CASTEP) included in the Material Studio package, which employs the DFT plane-wave method [19]. Here, the orbital is the square of the absolute value of the wave function for a given electronic band summed over all k-points, and a band is defined by the position of its eigenvalue in the ordered list of electronic energies at each k-point. The PBE functional is also employed in these simulations, and the cutoff energy, which determines the number of plane-wave basis functions, is chosen to be 240.0 eV.

3 Results and discussion

3.1 Geometry and molecular orbital analysis

The geometry of the Ru–quasi cumulene–Ru junctions are optimized using SIESTA until the forces are smaller than 0.03 eV·Å^{-1}. The optimized Ru–C and C–C bond lengths are listed in Table 1. The C–C bond lengths of polyynes with the thiol cap reported in reference 4 are also given for comparison. The Ru–C bond is relaxed to be in the range from 1.852 Å to 1.868 Å, which can be still regarded as the Ru=C double bond known from our previous calculations [6, 7]. Compared with the C–C bond lengths in the reported polyynes [4], the C–C bonds along

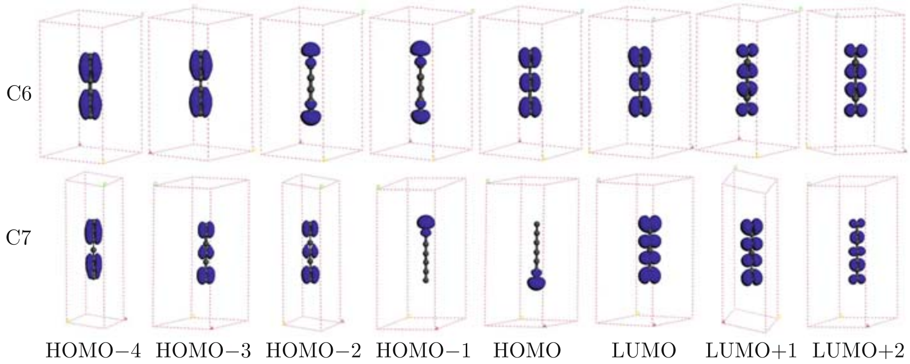


Fig. 2 Frontier molecular orbitals of the quasi cumulenes C6 and C7.

Table 1 Calculated bond lengths for the Ru–quasi cumulene–Ru molecular junctions (in Angstroms).

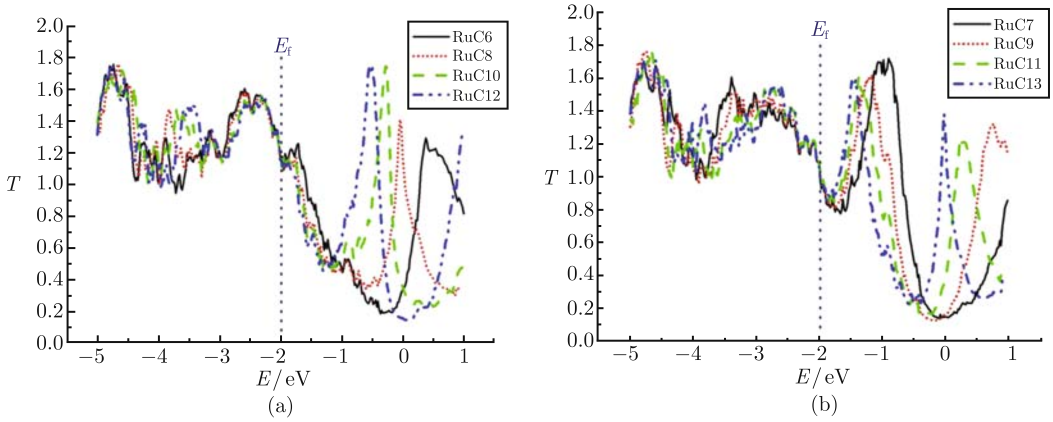
	Ru–C1	C1–C2	C2–C3	C3–C4	C4–C5	C5–C6	C6–C7
$HS(CC)_6SH$		1.253	1.332				
$AuS(CC)_6SAu$		1.286	1.316				
RuC6	1.859	1.292	1.305	1.284			
RuC7	1.852	1.299	1.298	1.293			
RuC8	1.868	1.289	1.304	1.283	1.302		
RuC9	1.861	1.298	1.299	1.292	1.294		
RuC10	1.858	1.291	1.302	1.283	1.298	1.284	
RuC11	1.857	1.300	1.300	1.293	1.295	1.294	
RuC12	1.862	1.290	1.303	1.282	1.298	1.283	1.298
RuC13	1.864	1.299	1.302	1.292	1.297	1.293	1.294

the molecular backbone in the Ru–quasi cumulene–Ru junctions are more uniform. In the Ru–quasi cumulene–Ru junctions with an odd number of carbon atoms, the C–C bond lengths are almost the same, with the difference less than 0.01 Å. In the even number cases, the C–C bond length becomes stable when adding more carbon atoms into the molecular chain and varies very little along the molecular backbone within the range of 1.305 Å and 1.282 Å.

Figure 2 gives the frontier molecular orbitals of the quasi cumulenes C6 and C7, with the C–C bond lengths listed in Table 1, which are typical examples of these quasi cumulenes with an even or odd number of carbon atoms. As we can see, the frontier molecular orbitals of the quasi cumulene C6 are mostly π-type orbitals, except for the HOMO–1 and HOMO–2 states which are two σ-type orbitals. The HOMO and LUMO states of C6 are two degenerate π-type orbitals perpendicular to each other. The same situation occurs for the LUMO+1 and LUMO+2 states, and the HOMO–3 and HOMO–4 states. In contrast, the frontier molecular orbitals of the quasi cumulene C7 are different; the HOMO and HOMO–1 states are two σ-type orbitals, while the HOMO–2 and HOMO–3 states, and the LUMO and LUMO+1 states are two pairs of degenerate π-type orbitals perpendicular to each other. The electronic structures of C8, C10 and C12 are the same in nature as C6, whereas the electronic structures of C9, C11 and C13 are the same in nature as C7. Therefore, the Ru–quasi cumulene–Ru junctions can be expected to show good conducting performance [6, 7].

3.2 Transmission properties of the Ru–quasi cumulene–Ru molecular junctions

The calculated transmission coefficients of these Ru–quasi cumulene–Ru molecular junctions can be divided into two groups, one with the even number of carbon atoms and the other with the odd number of carbon atoms, which are shown in Fig. 3. Obviously, in each group the transmission properties around and below the Fermi level of these junctions are almost the same. Above the Fermi level, in both groups the first transmission peak goes towards the Fermi level following the increase in the number of carbon atoms included in the molecular chain, though the peaks of the junctions with an odd number of C atoms are much closer to the Fermi level than those of the junctions with an even number of C atoms. At the Fermi level (-1.99 eV), for both groups of Ru–quasi cumulene–Ru junctions the transmission coefficients are calculated to be about 1.2, though the transmission properties around the Fermi level of the junctions with an even number of C atoms is a bit more superior to those with an odd number of C atoms. The corresponding I–V characteristics of these molecular junctions are calculated using the Landauer–Büttiker



(a) (b)

Fig. 3 Equilibrium transmission coefficients of energy for the Ru–quasi cumulene–Ru molecular junctions. **(a)** Junctions with an even number of carbon atoms and **(b)** Junctions with an odd number of carbon atoms.

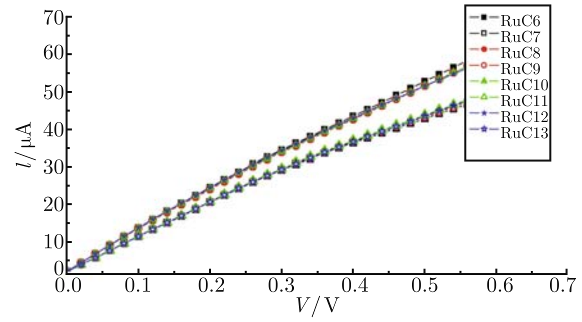


Fig. 4 Current–voltage characteristics of the Ru–quasi cumulene–Ru molecular junctions.

formula with the above equilibrium transmission coefficients [20], which are given in Fig. 4. As can be seen, at the same voltage the Ru–quasi cumulene–Ru junctions with the even number of carbon atoms carry a larger current than those with the odd number of carbon atoms. If we set the I–V curves of the junctions with the even number of carbon atoms as a datum line, the difference margin between the two groups declines to less than 16% when the voltage goes up. However, in the same group the difference is negligibly small. For example, if we set the I–V curve of the junction RuC6 as a datum line for the junctions with an even number of carbon atoms, the difference margin is less than 3%. In other words, the I–V characteristics of these molecular junctions are almost independent of the molecular length.

In order to gain a deeper insight into the conducting mechanism of these two groups of Ru–quasi cumulene–Ru junctions, we project the transmission onto frontier molecular orbitals of the central quasi cumulene chains [21]. Figure 5 shows the projected transmission coefficients for the junctions RuC6 and RuC7, which are chosen as the representatives of the Ru–quasi cumulene–Ru junctions with an even number of carbon atoms and those with an odd number of carbon atoms, respectively. For the RuC6 junction, the HOMO and LUMO states equally make the main contribution to the transmission around the Fermi level; the LUMO+1 and LUMO+2 states dominate the first transmission peak above the Fermi level, and they also contribute to the transmission around the Fermi level but much less than the HOMO and LUMO states. However, the HOMO–1 and HOMO–2 states, as well as other molecular orbitals have almost nothing to do with the transmission around the Fermi level. For the RuC7 junction, the LUMO and LUMO+1 states play the central role in the transmission around the Fermi level and the first transmission peak above the Fermi level. Although the HOMO–2 and HOMO–3 states also contribute to the transmission around the Fermi level, the contribution of the HOMO, HOMO–1 and other frontier orbitals can be ignored.

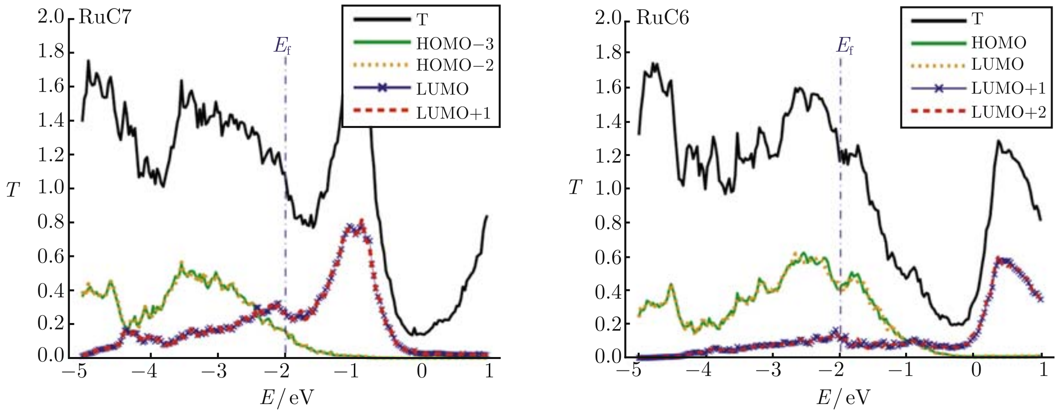


Fig. 5 The transmission coefficients as a function of energy for the RuC6 junction **(a)** and the RuC7 junction **(b)** projected onto frontier molecular orbitals of the central carbon chain.

Comparing the projected transmission with the bonding nature of these frontier molecular orbitals (Fig. 2), we can conclude that the transmi ssion of all of these Ru–quasi cumulene–Ru molecular junctions are dominated by π-type orbitals, that is, the HOMO and LUMO states for the junctions with an even number of carbon atoms and the LUMO and LUMO+1 states for the junctions with an odd number of carbon atoms. Since these molecular orbitals are pairs of perpendicular degenerate states, they make an equal contribution to the transmission. In our previous work [6], the Ru–octene–Ru molecular junction based on the Ru=C double bonds gives a transmission at the Fermi level of 0.67, in which only one π-type orbital contributes to the transmission. The transmission coefficients at the Fermi level of these Ru–quasi Cumulene–Ru junctions are just about two times that of the Ru–octene–Ru junction, because two perpendicular degenerate π-type molecule orbitals are available in each junction.

4 Conclusion

A self-consistent NEGF+DFT method is employed to investigate the low-bias conductance of Ru–quasi cumulene–Ru molecular junctions. Our calculation results show that the C–C bond length becomes stable when adding more C atoms into the molecular backbone in each group, and the symmetry of the frontier molecular orbitals will not change as the molecular length is extended. As a result, around the Fermi level the transmission properties of these Ru–quasi cumulene–Ru junctions are not affected by the length of the molecular chain. Though the junctions with the even number of carbon atoms and those with the odd number of carbon atoms behave a little differently due to their different bonding natures, they both give good transmission around the Fermi level and their *I*–*V* curves are almost independent of the molecular length. Thus, the Ru–quasi cumulene–Ru junctions have potential applications as molecular conducting wires in future molecular devices and circuits.

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