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Different influence of pyrimidine and benzene rings on current-voltage characteristics of molecular devices

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Abstract. By using *ab initio* method and elastic scattering Green's function theory, the electronic transport properties of symmetric tetraphenyl and non-symmetric diblock dipyrimidinyldiphenyl molecules covalently bonded to two electrodes are investigated. The numerical results show that, the tetraphenyl molecule has better electronic conductivity than the diblock molecule. The latter exhibits pronounced rectification behavior. Those molecular orbitals of the tetraphenyl molecule delocalized into two gold electrodes simultaneously result in better electronic conductivity. However, the non-symmetric structure of the diblock molecule leads to the localization of molecular orbitals, which is a disadvantage to electronic transport.

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Key words: tetraphenyl molecule, dipyrimidinyldiphenyl molecule, elastic scattering Green's function, current-voltage characteristic

1 Introduction

In recent years, due to the continuous improvement and widespread application of single-molecule technology, molecular electronics has developed rapidly and achieved encouraging results both in experiment and theory [1–13]. In the 1980s, the scanning tunneling microscope (STM), fluorescence probe method and optical tweezers appeared, subsequently the atomic force microscope (AFM), electrostatic force microscope, scanning particle conductance microscope, and scanning tunneling spectroscope (STS) emerged, form a rich scanning probe system. The emergence of these single molecule manipulation techniques makes the single-molecule studies no longer on paper. In experiment, people applied these techniques to create a series of molecular devices with special features successfully, such as molecular wires, molecular rectifiers [2], molecular switches [3], molecular memories and molecular

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motors [5]. With the progress of experimental work, theoretical staffs developed a variety of methods to simulate the working mechanism of molecular devices and research the relationship between molecular structure and electronic transport properties of them. It was discovered that the electronic transport properties of molecules are related to not only the molecular electronic structure but also the interaction between the molecule and metal electrodes, such as the mode of the molecule coupled to the electrodes, the molecular orientation on the metal surface [14], the type of electrodes, the distance of two electrodes [15–17], electrode force, electrode dimensions [18]. In addition, temperature and solvent effect [19], etc. also have some effect on the molecular electronic transport properties.

The functional molecules including the conjugated molecule composed of π bond, the saturated alkyl thiol chain formed by σ bond, single or multi-layer carbon nanotubes, Fullerenes, and bio-organic molecules (e.g. DNA molecules) have been paid much attention to in research. Since the molecules containing benzene ring possess rich π electrons which are beneficial to electronic transport, the aromatic compounds in which the benzene ring exists as a basic structural unit, are of great concern in the study. Containing nitrogen atoms or sulfur atoms, the heterocyclic system similar to the benzene ring is also rich in π-electrons, and therefore a good choice for molecular devices. However, in previous studies, people paid more attention to molecules with symmetrical geometry. In fact, asymmetric molecules formed by π-electron systems of different structures, have more abundant non-linear electronic transport properties than symmetrical ones [20–22]. Recently, Yu synthesized dipyrimidinyldiphenyl molecules with benzene and heterocyclic pyrimidine as the basic unit in experiment, finding that the asymmetry of the molecular geometric structure results in obvious rectification property [23]. In order to understand the transport properties of two different molecules better, we use density functional theory based on elastic scattering Green function approach to investigate the two kinds of molecules theoretically. The different effects of pyrimidine and benzene rings on the optimized molecular structure, current-voltage characteristic, molecular orbital and coupling coefficient, are discussed.

1.1 Theoretical model and numerical method

The organic molecule is sandwiched between two electron reservoirs (the source and the drain, abbreviated as S and D). For a three-dimensional electrode, when an external bias is applied, the net current of the device from the source to the drain can be written as

$$I_{SD}=\left(\frac{9\pi}{4}\right)^{\frac{1}{3}}\frac{9ek_BT}{2\hbar E_f^2}\int\left\{\ln\left[1+\exp\left(\frac{E_f+eV_{SD}-E_z}{k_BT}\right)\right]-\ln\left[1+\exp\left(\frac{E_f-E_z}{k_BT}\right)\right]\right\}\left|T(E_z,V_{SD})\right|^2\frac{dE_z}{E_z}, \tag{1}$$