

REGULAR ARTICLE

Electronic Transport Behavior of the Closed and Open-Shell Forms of Polychlorotrimethylphenyl

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Abstract: The current switching behavior of closed and open-shell forms of Polychlorotrimethylphenyl between gold electrodes are studied by using nonequilibrium Green's functions in combination with density functional theory. The present computational results show that the two forms of polychlorotrimethylphenyl molecule really demonstrate switching behavior, which confirms the experimental observation. It is also found that the switching behavior depends on the electronic properties of the two forms of polychlorotrimethylphenyl but not on the contact modes. The transmission coefficients and current-voltage curves under low-bias voltage are also reported.

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1 Introduction

The investigations of electronic transport through single molecule have attracted much attention in nanoscale science and technology because of their novel physical properties and

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potential for device applications. Many interesting physical properties such as negative difference resistance [1], molecular rectification [2], and current switching [3], have been reported. Recently, two discrete conductance states were discovered experimentally based on the closed and open-shell forms of a fully conjugated polychlorotrimethylphenyl (PTM) derivative (1H and 1rad, respectively) on gold [4]. This kind of system controlled by redox reaction shows distinct conductance behavior making it attractive to be constructed into molecular sensors or switches with large on/off ratios.

Zero-bias conductances of 1H and 1rad molecules have been measured experimentally but the contact sites between the molecule and electrodes are not clear. To understand the experimental results and to see if the contact sites influence the property, we performed computational studies on electronic transport properties of 1H and 1rad coupling to Au electrodes with different contact sites including the atop, bridge, hollow and adatom positions. The adatom position describes an under-coordinated Au surface. We focus on the effects of contact sites on the characteristics of *I-V* curves to understand their switching behavior in detail.

2 Computational methods

The stable geometry structures of 1H and 1rad were determined by using first-principles density functional theory (DFT) method as implemented in the Dmol³ software package [5]. Exchange–correlation energy was calculated by using generalized gradient approximation (GGA) via Perdew–Burke–Ernzerhof (PBE) parametrization [6]. Then the electronic transport properties of 1H and 1rad were carried out using the Atomistix ToolKit (ATK) software based on the combination of DFT with non-equilibrium Green’s functions (NEGF) [7-9]. The method has been used by many studies and was well documented. Our calculations used the two-probe models shown in **Figure 1**. The two-probe system is divided into three parts: the left electrode, right electrode, and central scattering region. The scattering region includes a portion of the semi-infinite electrodes. To equilibrate the computational efforts and the precision and reliability of the results, we expanded the valence electrons in single-zeta plus polarization basis sets for metal electrodes (Au atoms) and double-zeta plus polarization basis sets for other atoms. The improved Troullier–Martins pseudopotentials were used to describe the core electrons of all atoms [10]. The GGA–PBE for the exchange and correlation functional was used in all our calculations of electron–electron interactions. Periodical boundary conditions are applied in the transverse directions. The Au surface consists of a (5×5) supercell three monolayers thick and oriented along the Au (111) direction. The Brillouin zone was sampled with 3×3×100 points