Commun. Comput. Chem.
doi: 10.4208/cicc.2013.v1.n2.5

Vol.**1**, No.**2**, pp. 145-151
April 2013

REGULAR ARTICLE

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

Jing-Fen Zhao[1], Chuan-Lu Yang[1,*], Jie-Ma[1] and Mei-Shan Wang[1]

[1]*School of Physics and Optoelectronic Engineering, Ludong University, Yantai 264025, China P. R.*

Received 3 December 2012; Accepted (in revised version) 5 February 2013

Special Issue: Guo-Zhong He Festschrift

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.

AMS subject classifications: 81V55

Key words: current switching, contact sites, nonequilibrium Green's function, density functional theory, electronic transport

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

---

*Corresponding author. Tel: +86 535 6672870 fax: +86 535 6672870. *E-mail address:* scuycl@gmail.com (C.L. Yang).

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 Dmol^3 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 in the case of our three dimensional two-probe system. Electrostatic potentials were determined on a real-space grid with a mesh cutoff energy of 150 Ry to achieve balance between calculation efficiency and accuracy.

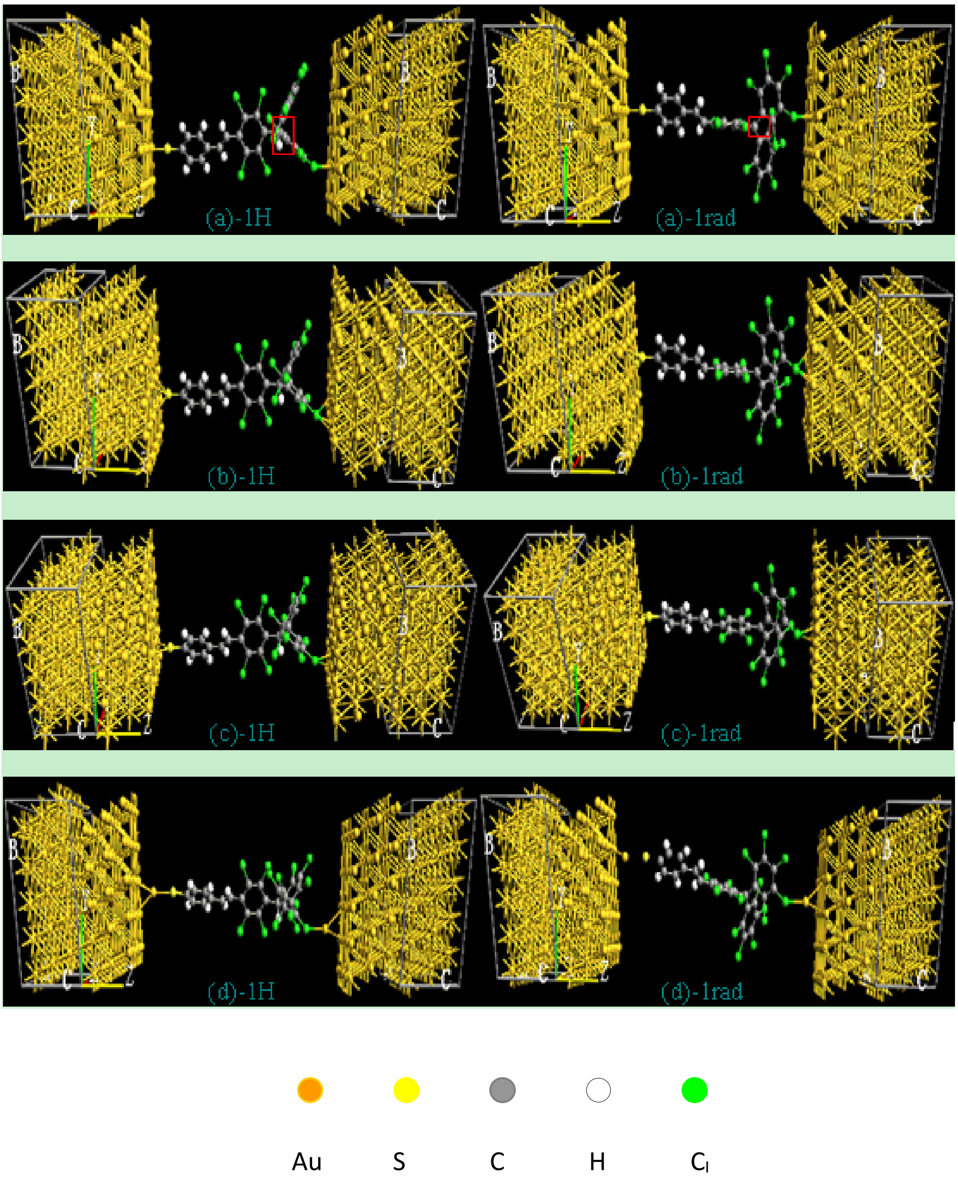

Figure 1: Geometry of two-probe system: (**a**) atop (**b**) hollow (**c**) bridge and (**d**) adatom. Closed and open-forms transform to each other via redox reaction.

Conductance value can be obtained from the transmission coefficients T by $G= T(E_F)^*G_0$, where $T(E,V_b)=\mathrm{Tr}[\Gamma_L(E)G^R(E)\Gamma_R(E)G^A(E)]$ is the transmission spectrum, in which $G^R(E)$ and $G^A(E)$ are the retarded and advanced Green's function of the central scattering region and Γ_L and Γ_R are the contact broadening functions associated with the left and right electrodes, respectively. E_F is the Fermi energy, and $G_0=2e^2/h$ is the quantum of conductance. *I-V* curves are obtained by integrated self-consistent transmission spectra at different bias voltages in the energy window from $-V/2$ to $+V/2$.

3 Results and discussion

3.1 The effect of contact sites on electronic transport properties

It is well known that the molecule-electrode distance is an important factor but it is difficult to precisely measure and control in the available experiment related to the molecular conductance [4]. So we first optimized the contact distances in Dmol^3 software package to determine a favorable contact distance to investigate the electronic transport properties. The optimized distances of Au-S and Au-Cl are both 2.5 Å. Then we use this contact distance to the ATK software in calculations. The most important physical quantity in NEGF-DFT calculations for electronic transport through single molecular junctions is the transmission function $T(E)$. Its value at the Fermi energy defines the zero-bias conductance and its integral over the bias-dependent energy window gives the current. Thus we calculate the transmission function $T(E)$ under zero bias with different contact sites and show them in **Figure 2**. The Fermi level has been shifted to $E_F = 0$. The switching behavior of the PTM can be clearly seen from **Figure 2** that the conductance of 1rad is always greater than that of 1H at Fermi level regardless of the contact sites. It is shown that the switching behavior is from the molecule itself but not the junction between the molecule and electrodes.

The properties of HOMO and LUMO are important because electron transition typically occurs between these two orbitals. So we calculated the molecular projected self-consistent Hamiltonian (MPSH) for the two-probe systems to analyze the contribution of the frontier molecular orbitals in **Figure 3**. Examining the positions of HOMOs in the figure carefully, we can find the HOMO orbitals of 1rad is closer to the E_F which correspond to a large transmission peak near the E_F. The HOMO orbital should play the main role during transmission because the value of LUMO is much higher than E_F. In **Figure 4**, we present the HOMO orbitals for the different adsorption sites of the two-probe systems. It shows that the HOMOs of 1rad for all adsorption sites are similarly delocalized, which implies higher conductance values of the molecule. For each contact site, the coupling interactions between molecule and electrodes affect both the widths and positions of the transmission peak, thus resulting in different transmission effects at E_F.

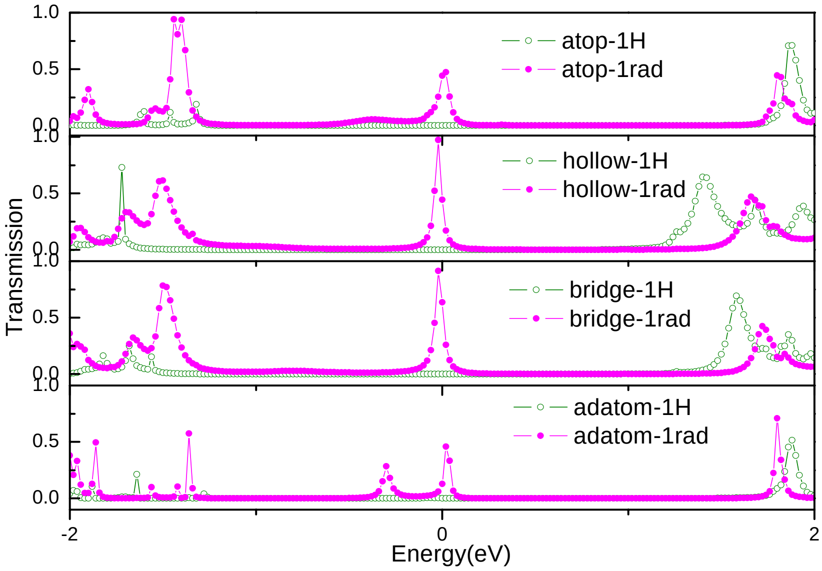

Figure 2: The transmission spectrums of SAMs at zero-bias with different contact sites. The Fermi energy is set to zero.

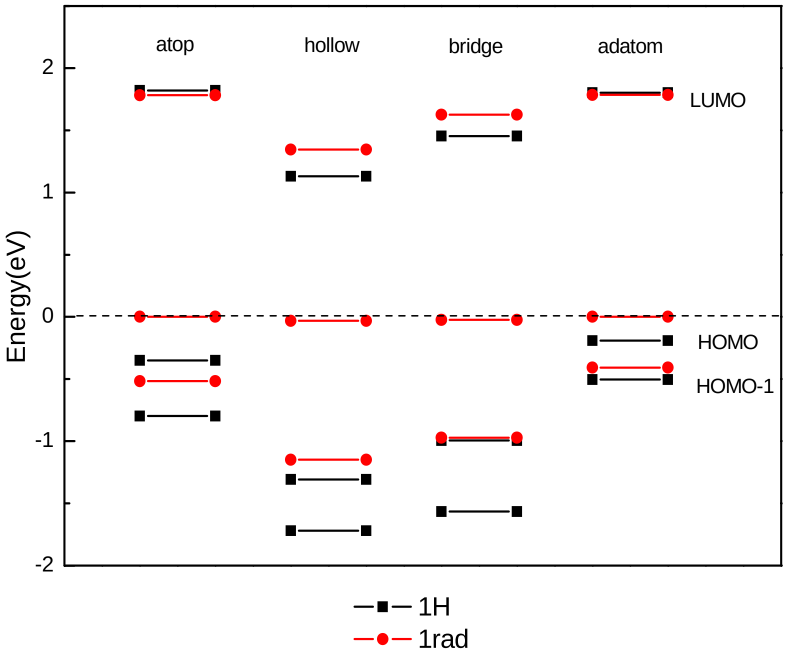

Figure 3: The frontier molecular orbitals of the two-probe devices with different adsorption

sites of the closed and open forms.

3.2 Electron transport properties under finite bias voltage

The zero-bias transmission spectra are not sufficient to completely describe the electronic transport properties of PTM. It is necessary to investigate the change of electronic transport under the applied bias voltages. **Figure 5** shows the calculated *I-V* curves of the molecule with different contact sites at a bias up to 1.6V. It is quite clear from **Figure 5** that the 1rad conformations of PTM display current larger than that of the 1H systems and 1H conformations show an almost complete suppression of current no matter which contact sites is.

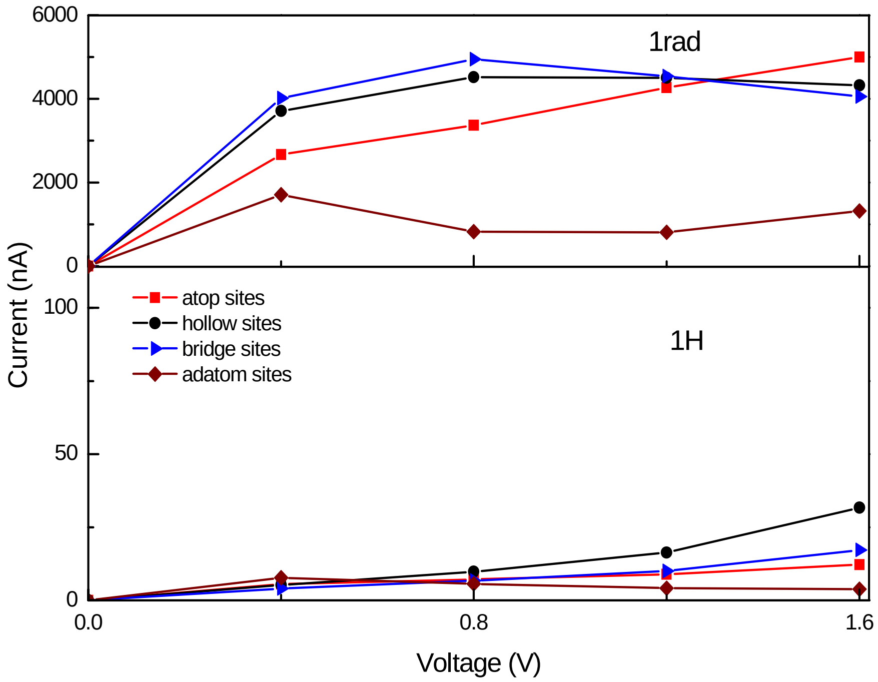

Figure 5: *I-V* characteristics for the molecular switch with closed and open forms.

4 Conclusion

The electronic transport of 1H and 1rad with four different contact sites on gold electrodes were investigated by using first-principles calculations. Transmission coefficients and *I-V* curves are calculated and analyzed. The calculated results show that the current switching behavior really exists in the two-probe system. It can be enhanced by the 1rad forms while the 1H forms can suppress it and the molecule itself plays an important role in determining the switching performance of the molecular devices. The results will be helpful to understand the possible situation in experiments and design functional molecular devices.

Acknowledgments

The present work was supported by the National Science Foundation of China under Grant No. NSFC-11174117 and NSFC-10974078.

References

[1] J. R. Heath and M. A. Ratner, Molecular electronics, Phys. Today, 56 (2003), 43-49.

[2] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin and J. M. Tour, Conductance of a molecular junction, Science, 278 (1997), 252-254.

[3] R. H. M. Smit, Y. Noat, C. Untiedt, N. D. Lang, M. C. Van Hemert and J. M. Van Ruitenbeek, Measurement of the conductance of a hydrogen molecule, Nature, 419 (2002), 906-909.

[4] C. Nu'ria, P. Markos, M. T. Marta and T. B. Stefan, Negative differential resistance in similar molecules with distinct redox behaviour, chem.commun., 47 (2011), 4664–4666.

[5] B. Delley, An all-electron numerical method for solving the local density functional for polyatomic molecules, J. Chem. Phys., 92 (1990), 508-517.

[6] J. P. Perdew, K. Burke and M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett., 77(1996), 3865.

[7] J. M. Soler, E. Artacho, J. D. Gale, A. García and J. Junquera, The SIESTA method for ab initio order-N materials simulation, J. Phys., 14 (2002), 2745–2779.

[8] J. Taylor, H. Guo and J. Wang, Ab initio modeling of quantum transport properties of molecular electronic devices, Phys. Rev. B., 63 (2001), 245407–245419.

[9] J. Taylor, H. Guo and J. Wang, Ab initio modeling of open systems: charge transfer, electron conduction, and molecular switching of a C_{60} device, Phys. Rev. B., 63 (2001), 121104–121107.

[10] N. Troullier and J. L. Martins, Efficient pseudopotentials for plane-wave calculations, Phys. Rev. B., 43 (1991), 1993–2006.