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Effect of Gate Electric Field on Single Organic Molecular Devices

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(Dated: Received on February 2, 2012; Accepted on March 7, 2013)

Based on the first-principles computational method and elastic scattering Green's function theory, we have investigated the effect of gate electric field on electronic transport properties of a series of single organic molecular junctions theoretically. The numerical results show that the molecular junctions that have redox centers and relatively large dipole moments parallel gate direction can respond to the gate electric field remarkably. The current-voltage properties of 2,5-dimethyl-thiophene-dithiol present N-channel-metal-oxide-semiconductor-like characteristics. Its distinct current-voltage properties can be understood from the evolution of eigenvalues, coupling energies, and atomic charges with gate electric field.

Key words: Gate electric field, Molecular junction, Electronic transport property

I. INTRODUCTION

In recent decades, with the improvement of the nanotechnology and the single-molecule-manipulation technology, rapid progress has been made for the molecular electronics both in experimental and theoretical research [1−5]. Due to the possession of plentiful and excellent non-linear electronic transport properties, single organic molecular junctions are considered as the most possible candidates of the new electronic devices to replace the conventional Si-based semi-conductor devices. Lots of investigations concentrate on molecular wires [2], molecular diodes [1, 6], molecular switches [7−12], and so forth, and most of them concern about the intrinsic properties of molecules [13, 14], length dependence of molecules [15−17], construction of electrodes [18, 19], and coupling interaction between molecules and metal electrodes [20, 21]. However, comprehensive understanding of external electric field effects is still need.

In recent years, the molecular field effect transistor as one of the most essential elements has been paid attention [4, 22−27]. Xu and his co-workers studied current-voltage properties under external gate voltage of single oligothiophene covalently linked to two Au electrodes [25]. Xu *et al.* also found a large gate modulation in the current of a room temperature single molecule transistor in experiment in another work, and they reported that the molecules with redox centers have more noticeable responses to external gate voltage [24]. Su *et al.* studied the electronic properties of the system theoretically and gave reasonable explanation [26]. However, all these studies didn't clarify why molecules containing redox centers have unusual response to external electric field.

In this work, the aromatic compounds and heterocyclic systems possessing rich delocalized π electrons are chosen to investigate their electronic transport with gate electric field. By comparison and deduction, we confirm that the structural characteristic of molecules respond to the external electric field intensely, and understand the internal mechanism of the strong response.

II. THEORETICAL MODEL AND COMPUTATIONAL DETAIL

The molecular junctions that we choose to investigate are single organic conjugated molecules with two thiol anchor groups as shown in Fig.1. The molecular junctions are formed by single molecules connected to two semi-infinite gold electrodes with the single terminal sulfur atoms at the hollow position of the Au(111) surface. Considering the influence of the electrodes on the molecules and the local interaction between them, we sandwich the single molecules between two gold atom equilateral triangles to form extended molecule systems in the calculations. The Au−Au bond lengths are fixed to be the lattice constant of Au (0.288 nm). The geometric optimizations and the electronic structure calculations are performed at the B3LYP level with LanL2DZ basis set implemented in Gaussian03 packages [28]. Based on the general Green's function formalism of Mujica *et al.* [29], the net current density of molecular junctions from source to drain for a three dimensional electrode can be written as

$$i_{\mathrm{SD}} = \frac{4em^*k_{\mathrm{B}}T}{\hbar^3}\int_{eV}^{\infty} \ln\frac{1+\exp[(E_{\mathrm{f}}+eV_{\mathrm{SD}}-E_z)/k_{\mathrm{B}}T]}{1+\exp[(E_{\mathrm{f}}-E_z)/k_{\mathrm{B}}T]} \cdot |\tau(E_z,V_{\mathrm{SD}})|^2\, n^{\mathrm{S}}(E_z)n^{\mathrm{D}}(E_z)\mathrm{d}E_z \quad (1)$$

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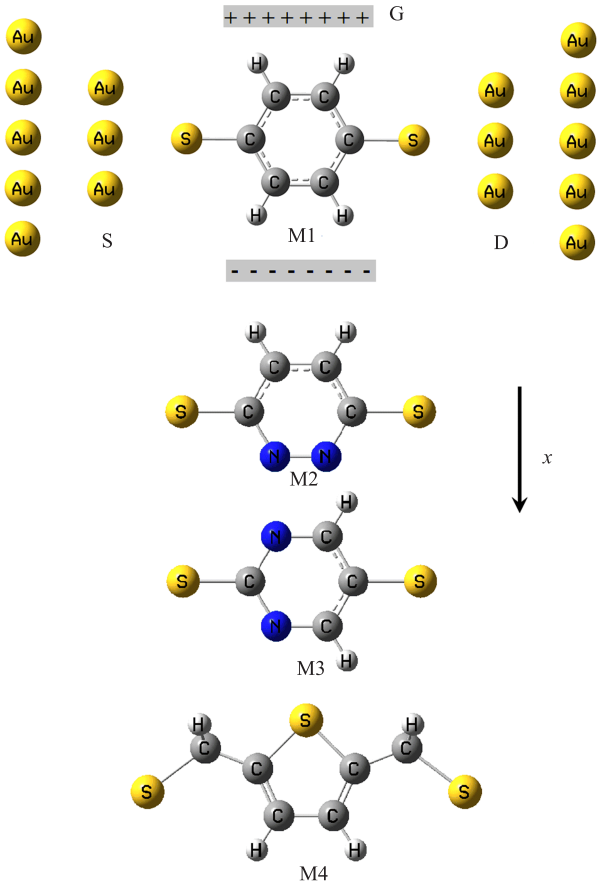

FIG. 1 Schematic structure of each molecular junction. M1: benzenedithiol, M2: pyridazinedithiol, M3: pyrimidinedithiol, M4: 2,5-dimethyl-thiophene-dithiol. S: source electronic reservoir, D: drain, and G: gate. The arrow indicates the direction of x axis.

where $V_{\rm SD}$ is the external bias, m^* is the effective mass of electron, e is the charge of electron, $E_{\rm f}$ is the Fermi level, $n^{\rm S}$ and $n^{\rm D}$ are the density of states of source and drain. $\tau(E_z, V_{\rm SD})$ is the transition matrix element, which can be written as

$$\tau(E_z, V_{\rm SD}) = \sum_J \sum_K U_{JS}(V_{\rm SD}) U_{KD}(V_{\rm SD}) \cdot \sum_n \frac{\langle J|n\rangle\langle n|K\rangle}{[E_z - E_n(V_{\rm SD})] + {\rm i}\Gamma_n} \qquad (2)$$

where $|n\rangle$ is an eigenstate of the Hamiltonian of a finite system that consists of molecular sandwiched between two clusters of metal atoms. The summation n runs over the eigenstates higher than the Fermi level. J and K run over all atomic sites from 1, 2, $\cdots$ to N, where sites 1 and N are the two end sites of the molecules connecting with two electron reservoirs S and D. U_{JS} (or U_{KD}) is the coupling energy between an atomic site J (or K) and a reservoir S (or D). Γ_n is the energy broadening. Then the total current from source to drain is $I_{\rm SD}$=$Ai_{\rm SD}$, where A is the effective injecting area.

TABLE I Current gain (CG), current ratio (CR) and inherent dipole moment (DM) of each molecular junction shown in Fig.1 ($E_{\rm G}$=3.0 V/nm).

	CG	CR	DM/Debye
M1	1.26	1.00	0.00
M2	1.40	1.15	3.90
M3	1.30	1.00	0.00
M4	3.17	4.88	3.17

The conductance is obtained by G=$\partial I_{\rm SD}/\partial V_{\rm SD}$. The details of our theoretical models are included in Ref.[19].

To investigate the gate electric field effect on the molecular junctions, we applied electric dipole field parallel the plane of the rings in gate direction, normal to the current direction. In our calculation, the positive direction of the gate electric field is chosen to be x axis, shown in Fig.1. The electronic transport properties were carried out using QCME codes [30, 31].

III. RESULTS AND DISCUSSION

The current-voltage curves of molecular junctions M1-M4 are calculated over low bias voltage range (0, 0.5) V, as shown in Fig.2. The current through the junctions rises with the bias voltage, nearly in linear variation relationship, indicating that nonresonant tunneling takes place. For each molecular junction, the current-voltage properties vary with different gate electric field. For M1 and M3, the current generally decreases with the gate electric field. That is to say, for these molecular junctions, the application of gate electric field has negative effect on their electronic transport. In addition, it can be detected and understood easily that the current-voltage curves of molecular junctions with symmetric configuration along the gate direction, such as M1 and M3, are also symmetric under the positive and negative gate electric field; while for M2 and M4, which have asymmetric configurations along the gate direction, the currents shows more interesting properties under electric field, no longer symmetric with the negative and positive gate electric field.

From the above analyses, one can find that the responses of different molecular junctions to electric field are diverse. For clarification of the different responses to positive and negative gate electric field, current gain (denoted as CG) and current ratio (denoted as CR) are defined, as I_0/I_{-E} and I_E/I_{-E} respectively, where the gate electric field E is chosen to be a definite value, such as 3.0 V/nm. The calculated results are shown in Table I. Obviously, the current gains of M2-M4 are somewhat greater than that of M1. Comparing their geometric constructions, one can find that each of M2−M4 is heterocyclic molecular junction containing nitrogen atoms or sulfur atoms. As a factor in characterization of electric asymmetry of molecules, dipole moment plays

DOI:10.1063/1674-0068/26/02/185-190

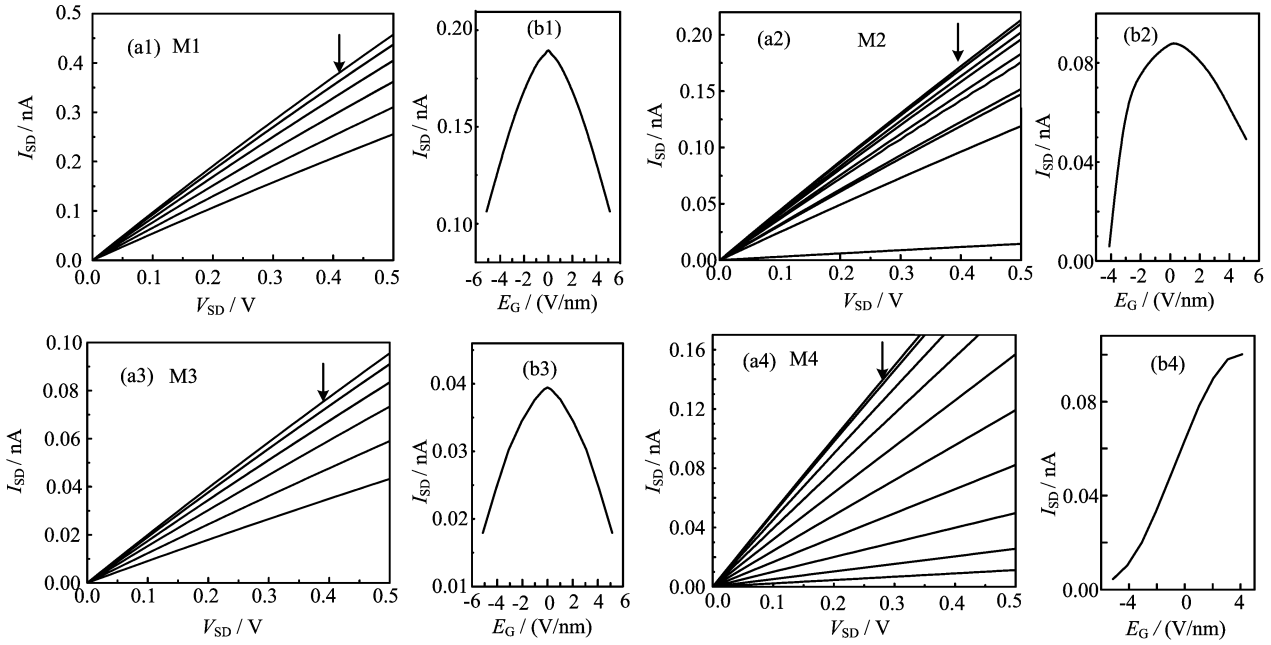

FIG. 2 (a) Current-voltage curves under different gate electric field for M1, M2, M3, and M4 molecular junctions shown in Fig.1. (b) The current under electric field with the bias voltage of 0.2 V. The arrows directions show different gate fields: (a1) 0, ±1, ±2, ±3, ±4 and ±5 V/nm respectively. (a2) 0, 1, −1, 2, −2, 3, −3, 4, 5, −4 V/nm, respectively. (a3) 0, ±1, ±2, ±3, ±4 and ±5 V/nm respectively. (a4) 4, 3, 2, 1, 0, −1, −2, −3, −4, and −5 V/nm, respectively.

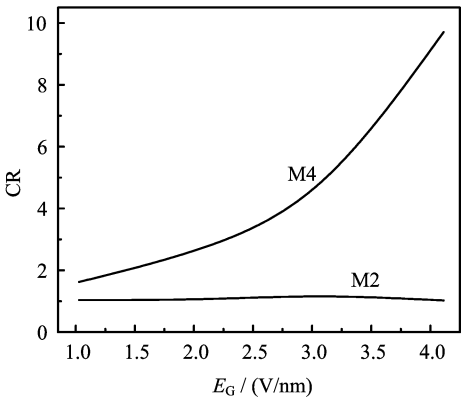

FIG. 3 Current ratio with gate electric field for M2 and M4.

a vital role in current-voltage properties with gate electric field, especially that parallels the gate direction. M2 and M4, of which the current-voltage properties have different responses to positive and negative gate field, have relatively great inherent dipole moment parallel gate direction, as large as 3.9 and 3.17 Debye respectively (see Table I). Based those analyses, one can deduce that the molecular junctions that contain redox centers and remarkable inherent dipole moment parallel gate direction have more desirable responses to gate electric field.

Figure 3 shows the current ratio under gate electric field in certain range for M2 and M4. The current ratio of both molecular junctions is above 1.0, meaning that the current under positive gate electric field is higher than that under negative one. Although the current-voltage properties of both M2 and M4 show asymmetric responses to gate electric field, the efficiencies are different. As shown in Fig.3, the current ratio of M2 under each gate electric field is near 1.0, while that of M4 is generally larger than 2.0, showing more intense response to gate electric field than M2.

See the current-voltage properties of M4 shown in Fig.2, within the bias range (0, 0.5) V. From the figure one can find that the current-voltage curves under different gate electric field show regular variation. That is to say, the current rises with positive gate electric field and descends with negative one. When the applied electric field is 3.0 V/nm, the current gain is 3.17, about twice as large as those of the others. Also, the current ratio at 3.0 V/nm is up to 4.88, obviously larger than others. Moreover, the inherent dipole moment of M4 is 3.17, which plays an essential role in its distinctive current-voltage properties. Such a visible response to gate electric field provides a potential application of M4 in field effect transistor. It can be concluded that the current-voltage properties of the molecular junction containing redox centers such as thiophene have obvious monotonous response to gate electric field. That is to say, the gate electric field has more noticeable effect on the current-voltage properties of those molecular junctions containing thiophene-like redox centers, which is consistent with the conclusion reported by Xu *et al.* [24].

To further investigate the different response of dif-

DOI:10.1063/1674-0068/26/02/185-190

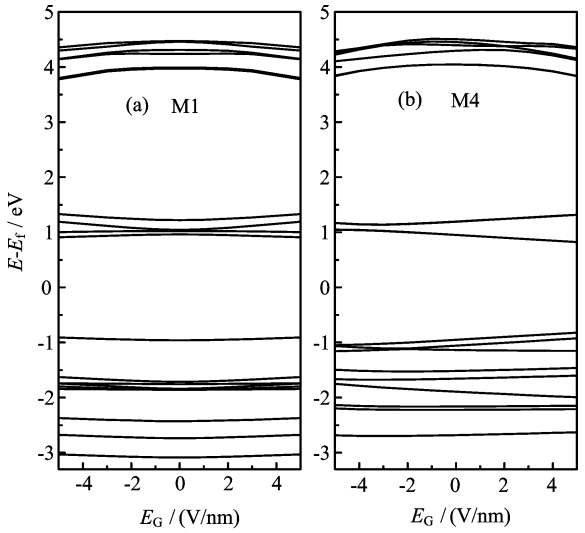

FIG. 4 Evolution of eigenvalues under gate electric field for the molecular junctions M1 and M4 respectively.

ferent molecular junctions to gate electric field, we take M1 and M4 for example to study the evolution of eigenvalues under gate electric field. Commonly recognized, the external gate electric field can couple with the inherent dipole moment of molecular junctions, generating additional potential energy described as $V=-\vec{p}\cdot\vec{E}=-pE\cos\alpha$, where α is the angle between $\vec{p}$ and $\vec{E}$ (herein, α=0). That additional energy can lead to energy shift of molecular orbitals, including the frontier molecular orbitals, which will have a certain effect on current-voltage properties of molecular junctions. From Fig.4(a), one can see that, for M1, whose dipole moment parallel gate direction is zero, the gate electric field has slight effect on its orbitals especially the frontier molecular orbitals, of which the eigenvalues are nearly invariable with electric field. That's one reason why the response of the current of M1 to gate electric field is so weak. For M4 (shown in Fig.4(b)) , with the electric field varying from negative to positive, both HOMO (the highest occupied molecular orbital) and LUMO (the lowest unoccupied molecular orbital) get nearer to E_f, leading to the narrower gap between LUMO and HOMO, and then the current rises. That is to say, eigenvalues of M4 have more obvious response to the gate electric field, resulting in more intense response of current-voltage properties to the gate field.

From Eq.(1) and Eq.(2), we know that the coupling energy plays an important role in electronic transport of the molecular junctions. Figure 5 shows the source-drain currents and coupling energies between the molecules and electrodes of M2 and M4 with the gate electric field. Obviously, for both molecular junctions, the evolution of the coupling energies with gate electric field shows similar trend to that of the currents with the field. Also, the coupling energy of M4 is influenced by gate electric field more clearly compared with that of

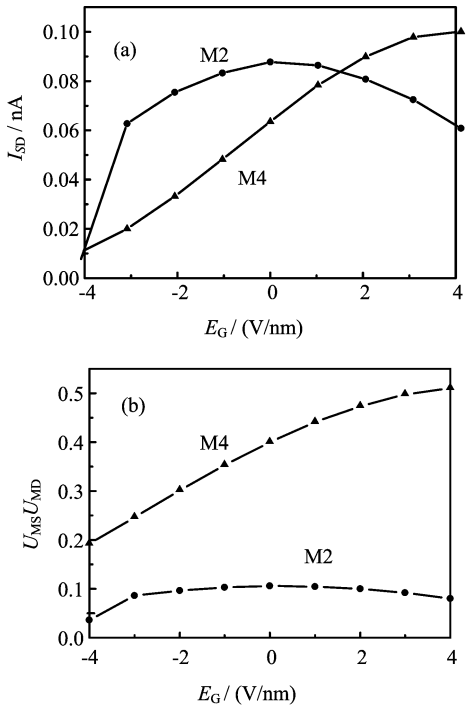

FIG. 5 (a) Source-drain currents of M2 and M4 molecular junctions under different gate electric field with the bias voltage of 0.2 V. (b) The coupling energy between the molecules and the electrodes.

M2. Thus, one can conclude that the gate electric field can influence the current-voltage properties through imposing on the coupling energy between the molecules and electrodes to certain extent.

To further understand the mechanism of distinctive current-voltage properties of M4, with the atomic label and symbol of the molecule shown in Fig.6(a), we study the influence of gate electric field on its atomic charge. The evolution of atomic charge of M4 with gate electric field is shown in Fig.6(b). Since the molecular junction is axisymmetric, only charges on representative atoms are present. From the figure, one can see that, charges condensed on different atoms have different responses to the variation of gate electric field. For 2S, and 7C, the atomic charges decrease with gate electric field, while those of 1C, 5C and 15S increase with electric field. From Fig.3 we have known that the current of M4 rises with positive gate electric field and drops with negative one. That is to say, positive gate electric field is beneficial to electronic transport, while negative one is adverse to it. When positive gate electric field is applied, the atomic charges on 2S and 7C decrease, meaning that the electrons move to the top of the M4 and a dipole moment of opposite direction to the inherent one emerges, which is favorable to electronic transport. On the contrary, when negative gate electric field is applied, the atomic charges on 2S and 7C increase, indicating that the electrons accumulate in the bottom of the M4 and the dipole moment become larger

DOI:10.1063/1674-0068/26/02/185-190

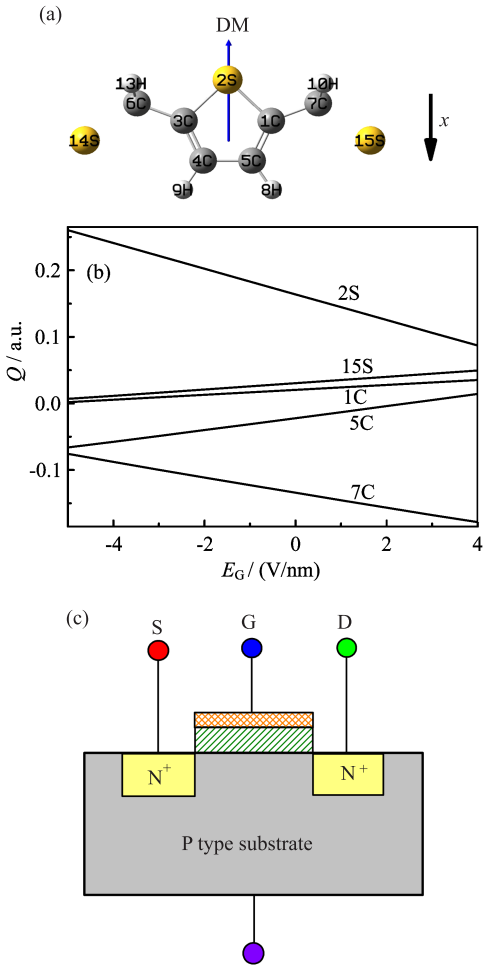

FIG. 6 (a) The atomic label and symbol of molecular junction M4. The long arrow indicates the direction of the inherent dipole moment, and the short one indicates the direction of x axis. (b) Evolution of atomic charge Q (1 a.u.=1 electron) with gate electric field for the molecular junction M4, where the atomic charge of hydrogen is summed into heavy atoms. (c) Schematic structure of N-channel MOS.

based on the inherent one, which is unfavorable to electronic transport. From the constituents of frontier orbitals, we found that the current is mainly contributed by non-resonant tunneling electrons, so it can be concluded that the top part of M4 plays a primary role in its conductance. This mechanism is similar to that of N-channel metal-oxide-semiconductor system (abbreviated as N-channel MOS) shown in Fig.6(c). As for N-channel MOS, when a certain positive bias is added to the gate electrode, an opposite type layer will appear on the surface of the P-type substrate, connecting the source and drain, then the conductance increases. For M4, the conductance can be controlled to be high or low state by adjusting the polarity and magnitude of gate electric field. So, it may be a good candidate for molecular devices, such as field-effect transistors.

IV. CONCLUSION

In this work, we have investigated the gate electric field effect on electronic transport properties of a series of single organic molecular junctions theoretically, including the aromatic compounds and heterocyclic systems. The numerical results show that 2,5-dimethyl-thiophene-dithiol junctions have redox centers and relatively large dipole moment parallel gate direction, and can respond to the gate electric field remarkably as well, which consists with experimental conclusion. Also, its current-voltage properties have intense monotonous response to gate external electric field, distinct from those of others. The evolution of eigenvalues can reveal its different current-voltage properties with gate electric field to some extent. In addition, the coupling energy between the molecules and electrodes can also explain the response of current to gate electric field to a certain extent. By analyzing the evolution of atomic charges with gate electric field, we find that the top part of 2,5-dimethyl-thiophene-dithiol containing S atom makes the main contribution to its electronic transport, showing an N-channel-metal-oxide-semiconductor-like character.

V. ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (No.10804064 and No.10974121).

[1] A. Aviram and M. A. Ratner, Chem. Phys. Lett. **29**, 277 (1974).
[2] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, and J. M. Tour, Science **278**, 252 (1997).
[3] Z. Pan, Q. X. Li, Q. W. Shi, and X. P. Wang, Chin. J. Chem. Phys. **22**, 7 (2009).
[4] R. Pfattner, M. Mas-Torrent, I. Bilotti, A. Brillante, S. Milita, F. Liscio, F. Biscarini, T. Marszalek, J. Ulanski, A. Nosal, M. Gazicki-Lipman, M. Leufgen, G. Schmidt, L. W. Molenkamp, V. Laukhin, J. Veciana, and C. Rovira, Adv. Mater. **22**, 4198 (2010).
[5] X. X. Fu, L. X. Zhang, Z. L. Li, and C. K. Wang, Chin. Phys. B **22**, 028504 (2013).
[6] I. Díez-Pérez, J. Hihath, Y. Lee, L. Yu, L. Adamska, M. A. Kozhushner, I. I. Oleynik, and N. Tao, Nature Chem. **1**, 635 (2009).
[7] S. J. van der Molen and P. Liljeroth, J. Phys.: Condens. Matter **22**, 133001 (2010).
[8] M. Alemani, M. V. Peters, S. Hecht, K. H. Rieder, F. Moresco, and L. Grill, J. Am. Chem. Soc. **128**, 14446 (2006).
[9] V. Ferri, M. Elbing, G. Pace, M. D. Dickey, M. Zharnikov, P. Samor, M. Mayor, and M. A. Rampi, Angew. Chem. **120**, 3455 (2008).

DOI:10.1063/1674-0068/26/02/185-190

[10] J. Liao, J. S. Agustsson, S. Wu, C. Schönenberger, M. Calame, Y. Leroux, M. Mayor, O. Jeannin, Y. F. Ran, S. X. Liu, and S. Decurtins, Nano Lett. **10**, 759 (2010).
[11] Y. D. Li, Z. L. Li, J. C. Leng, W. Li, and C. K. Wang, Acta Phys. Sin. **60**, 073101 (2011).
[12] K. Smaali, S. Lenfant, S. Karpe, M. Ocafrain, P. Blanchard, D. Deresmes, S. Godey, A. Rochefort, J. Roncali, and D. Vuillaume, ACS Nano **4**, 2411 (2010).
[13] Y. Lee, B. Carsten, and L. Yu, Langmuir **25**, 1495 (2009).
[14] S. Yuan, C. Dai, J. Weng, Q. Mei, Q. Ling, L. Wang, and W. Huang, J. Phys. Chem. A **115**, 4535 (2011).
[15] A. Saraiva-Souza, B. G. Sumpter, V. Meunier, A. G. S. Filho, and J. D. Nero, J. Phys. Chem. C **112**, 12008 (2008).
[16] G. C. Hu, G. P. Zhang, J. F. Ren, C. K. Wang, and S. J. Xie, Appl. Phys. Lett. **99**, 082105 (2011).
[17] A. Tan, J. Balachandran, S. Sadat, V. Gavini, B. D. Dunietz, S. Y. Jang, and P. Reddy, J. Am. Chem. Soc. **133**, 8838 (2011).
[18] Z. L. Li, Chin. J. Chem. Phys. **24**, 194 (2011).
[19] Z. L. Li, B. Zou, and C. K. Wang, Phys. Rev. B **73**, 075326 (2006).
[20] G. P. Zhang, G. C. Hu, Z. L. Li, and C. K. Wang, Chin. Phys. B **20**, 127304 (2011).
[21] X. Chen, S. Yeganeh, L. Qin, S. Li, C. Xue, A. B. Braunschweig, G. C. Schatz, M. A. Ratner, and C. A. Mirkin, Nano Lett. **9**, 3974 (2009).
[22] H. Song, Y. Kim, Y. H. Jang, H. Jeong, M. A. Reed, and T. Lee, Nature **462**, 1039 (2009).
[23] Z. L. Li, G. P. Zhang, and C. K. Wang, J. Phys. Chem. C **115**, 15586 (2011).
[24] B. Xu, X. Xiao, X. Yang, L. Zang, and N. Tao, J. Am. Chem. Soc. **127**, 2386 (2005).
[25] B. Q. Xu, X. L. Li, X. Y. Xiao, H. Sakaguchi, and N. J. Tao, Nano Lett. **5**, 1491 (2005).
[26] W. Su, J. Jiang, W. Lu, and Y. Luo, Nano Lett. **6**, 2091 (2006).
[27] Y. Y. Liang, H. Chen, H. Mizuseki, and Y. Kawazoe, J. Chem. Phys. **134**, 144113 (2011).
[28] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Jr. Montgomery, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03*, Revision D.01, Wallingford CT: Caussian Inc., (2005).
[29] V. Mujica, M. Kemp, and M. A. Ratner, J. Chem. Phys. **101**, 6849 (1994).
[30] J. Jiang, M. Kula, and Y. Luo, J. Chem. Phys. **124**, 034708 (2006).
[31] J. Jiang, C. K. Wang, and Y. Luo, *QCME-V1.1, Quantum Chemistry for Molecular Electronics*, Stockholm, Sweden: Royal Institute of Technology, (2006).

DOI:10.1063/1674-0068/26/02/185-190