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Citation: Applied Physics Letters **92**, 243303 (2008); doi: 10.1063/1.2924364
View online: http://dx.doi.org/10.1063/1.2924364
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APPLIED PHYSICS LETTERS **92**, 243303 (2008)

Negative differential resistance behaviors in porphyrin molecular junctions modulated with side groups

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(Received 20 March 2008; accepted 20 April 2008; published online 17 June 2008)

By applying nonequilibrium Green's functions in combination with the density-functional theory, we investigate the electronic transport properties of molecular junctions constructed by the porphyrin molecule with donor or acceptor side groups. The results show that the side groups play important role on the electron transport properties. Negative differential resistance (NDR) is observed in such devices. Especially for the molecule with electron-donating group ($-NH_2$), two NDR appear at different bias voltage regions, and the origins for both NDR behavior are different. A mechanism is proposed for the NDR behavior. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2924364]

Negative differential resistance (NDR) has been paid much attention because of their potential applications in electronic devices. NDR is a well-known concept in device physics, and it has been found in many physical systems such as double quantum wells,[1] superlattices,[2,3] and one-dimensional system.[4] The resonant[1] and off-resonant electronic tunnelling mechanism can give a satisfactory explanations for the NDR behavior.[2,4] NDR behavior has also been found in a variety of molecular devices. However, the origin for NDR in molecular devices is still under intense debate due to their structural complexity. Some groups experimentally[5,6] and theoretically[7–9] observed NDR in oligo(phenylene ethynylene) (OPE) molecular junctions with nitro and/or amine groups. Possible mechanism such as two-step reduction process,[5] intramolecular phenomenon,[6] the change in the molecular conformation due to the change in the electronic charge state of the molecule under increasing bias,[7] bias-induced alignment of molecular orbitals,[8] and side group effects[9] were proposed for the NDR behavior. However, Khondaker *et al.* observed NDR behavior in the OPE molecular junction irrespective of whether the system contains a nitro side group or not,[10] while Yin *et al.*[11] and Bauschilicher *et al.*[12] did not observed NDR in the same molecular junctions. More recently, authors observed NDR in a bilayer OPE molecular junction and attributed it to the combination of the splitting of the molecular orbitals due to the intermolecular interaction and the change in the coupling between the molecules and the electrodes at different bias.[13] NDR behavior has also been found in other molecular devices such as a self-assembled monolayer of 4-*p*-terphenylthiol molecules on the Au (111) surface measured using a platinum tip,[14] a single benzene ring with a nitro side group,[15,16] the mirror symmetrical straight carbon-nanotube heyerojunctions with different sizes and lengths,[17] organometallic molecular double-dot system,[18] tetrathiafulvalene-tetracyanoquinodimethane dimer,[19] and cobalt phthalocyanines molecule on a gold substrate.[20] The mechanism for the NDR such as resonance between the discrete electronic levels of the molecule and the very narrow density of states around the Fermi energy of the sharp metal tip,[14] the rotation of the ligand activated by temperature,[15] a one-electronic reduction,[16] the channel conduction being suppressed at a certain bias,[17] molecular-level crossing,[18] orbital match of molecule and electrodes, as well as intermolecular charge transfer,[19] local orbital symmetry matching between an electrode and a molecule[20] have been suggested in these systems, respectively.

In the present work, by applying a first-principles computational method based on the hybrid density-functional theory in combination with the nonequilibrium Green's functions theory, we investigate the transport properties of the molecular junction consisting of porphyrin molecules with donor/acceptor side groups sandwiched between two proximal gold electrodes, as shown in Fig. 1. The structures have been optimized and the quantum transport calculations have been carried out by an *ab initio* code package, TRANSIESTA-C.[21] The isolated porphyrin has been studied due to its interesting electrical properties.[22,23] Its long rigid π-bonded structures making them very suitable as molecular wires while their electronic properties can be modified through various mesosubstituted patterns and the use of porphyrin/metal complexation. Recently, a self-assembled structure of porphyrin was experimentally reported.[24] Theoretical study of the detailed *I-V* characteristics through such a molecular device is necessary.

In Figs. 2(a1)–2(a3), we show the transmission coefficient $T(E,V_b)$ and the corresponding projection of the density of states (PDOS) at zero bias ($V_b=0$) for M1, M2, and M3 given in Fig. 1. It is clearly seen from the figures that both the transmission and PDOS spectra are strongly correlated, especially in the location of their peaks. For all system, there exists a highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO-LUMO) gap (HLG). The gap in the transmission spectra can be attributed to the intrinsic semiconducting nature of porphyrin molecule. From the figure, we can find that the HLG of M2 is smaller than

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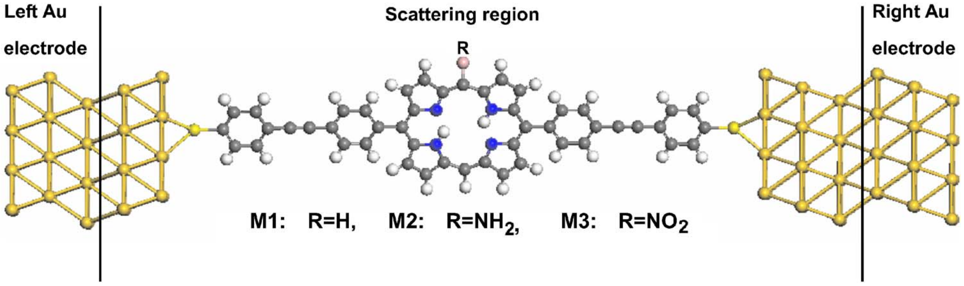

FIG. 1. (Color online) Structures of the molecular junctions in our simulation: porphyrin is sandwiched between two gold electrodes through the thiol end group. The sulfur atom is chosen to be located at the hollow site of the gold triangle. M1, M2, and M3 correspond to three porphyrin junctions without side group, with NH_2 side group, and NO_2 side group, respectively.

that of M1, while the HLG of M3 is bigger than that of M1. This indicates that the donor group can decreases the HLG but the acceptor group increases the HLG. It is known that the larger the HLG, the more stable the molecule, and therefore the harder it is to rearrange its electron density under the presence of an external electron. Thus, the easier it is to transport electron across the molecular junction in M2 and the harder it is in M3.

Figure 3(a) describes the currents as a function of the applied bias voltage for all three systems. The threshold bias voltage is different for the molecular junctions with different side groups. The molecular junction M2 is of the smallest threshold bias voltage, while M3 is of the biggest one, which indicates that the threshold bias voltage can be modulated by the substituted groups. When the applied bias voltage is larger than the threshold bias voltage the current rapidly increases with bias voltage, which means that the corresponding transmission channels are opened and make contributions to the electronic transport. When the applied bias voltage is smaller than 1.3 V, we can find the currents are $M2 > M1 > M3$ for the same bias voltage, which is consistent with their HLG. This means that at low bias voltage the NH_2 side group can strength the electron transport, and the NO_2 side group weaken the electron transport. This is similar to the case of the work of Xiao *et al.*[25] From the figure, we can find that the current obviously decreases with the increase in the bias voltage when the bias voltage being larger than certain value (about 2.0 V for M1 and M2, and 1.8 V for M3). This shows that NDR appears in such bias voltage ranges for these systems. However, for M2, another NDR behavior appears at lower bias (about between 1.2 and 1.6 V). Note that NDR especially multiple NDR behavior is of important application in molecular electronics circuits.

In order to understand the NDR behavior, in Fig. 3(b), we give the transferred charge of molecules at different bias voltages. It is clearly seen that at low bias voltage the transferred charges are very small. This is because the electron hardly enter into the molecules from electrodes due to the HLG at low bias voltage. With the increase in bias voltage, the transferred charge rapidly increases and the current also rapidly rises. With further increase in the bias, the transferred charge reaches a maximum, then decreases. Note that the bias voltage corresponding to the maximum of the transferred charge is different for molecular junctions with different side groups. This indicates that the side groups can affect the transferred charge. Interestingly, the current-voltage characteristics display a NDR behavior when the transferred charge decreases, which means the NDR behavior is very related to the change of the transferred charge. However, when the bias voltage is taken the value between 1.2 and 1.6 V, we can also observe another NDR behavior for M2. This NDR seems not to be related to the transferred charge because the transferred charge does not change near the 1.2 V and monotonically increases with the bias voltage, different from the case of the NDR at higher bias voltage. This indicates that both NDR at different bias for M2 may originate from different mechanism.

To further understand this interesting phenomena, in Fig. 3(c1)–3(c3), we plot the change of HOMO and LUMO orbitals with the bias voltages for all molecular junctions. Compare Figs. 3(b) with 3(c1)–3(c3), we can see that with the increase in bias voltage, the changes in HOMO and LUMO orbitals are similar to that the transferred charge, which shows that the charge transferred can lead to the shift of the frontier molecular orbitals, as pointed by Xue *et al.* and Taylor *et al.*. Thus, we can infer that the NDR behavior at higher bias voltage originates from the change in the coupling between the molecular orbitals and the electrodes due to the shift of the molecular orbitals. Compare Figs. 3(c2) with 3(c1) and 3(c3), when the bias voltage is about 1.0 V, LUMO orbital of M2 enters into the bias window, but when the bias is further increased to be between 1.2 and 1.6 V, LUMO orbital of M2 lies outside of the bias window. However, similar phenomena do not occur for M1 or M3. Thus, the NDR behavior appearing in M2 at low bias (between 1.2 and 1.6 V) may be caused by the shift out the bias window of the LUMO orbital. In order to give further analysis for this phenomenon, we calculate the transmission coefficient

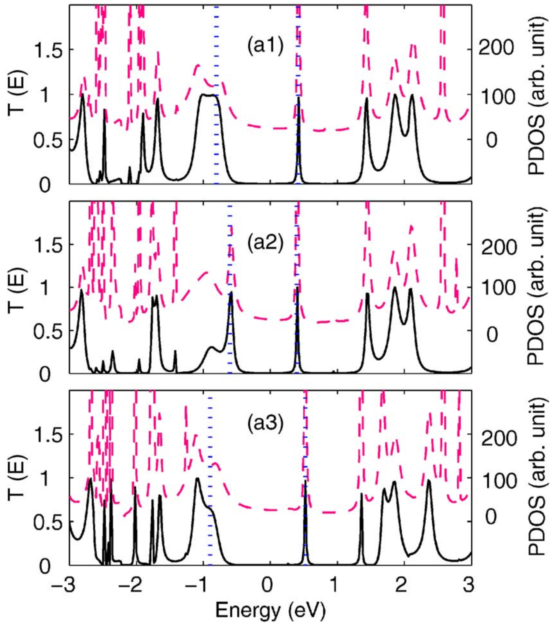

FIG. 2. (Color online) Dependence of the transmission coefficient (solid curve) and the corresponding PDOS (dashed curve) on the electron energy at zero bias: (a1)–(a3) correspond to M1, M2, and M3, respectively. The Fermi level is set to be the origin of energy.

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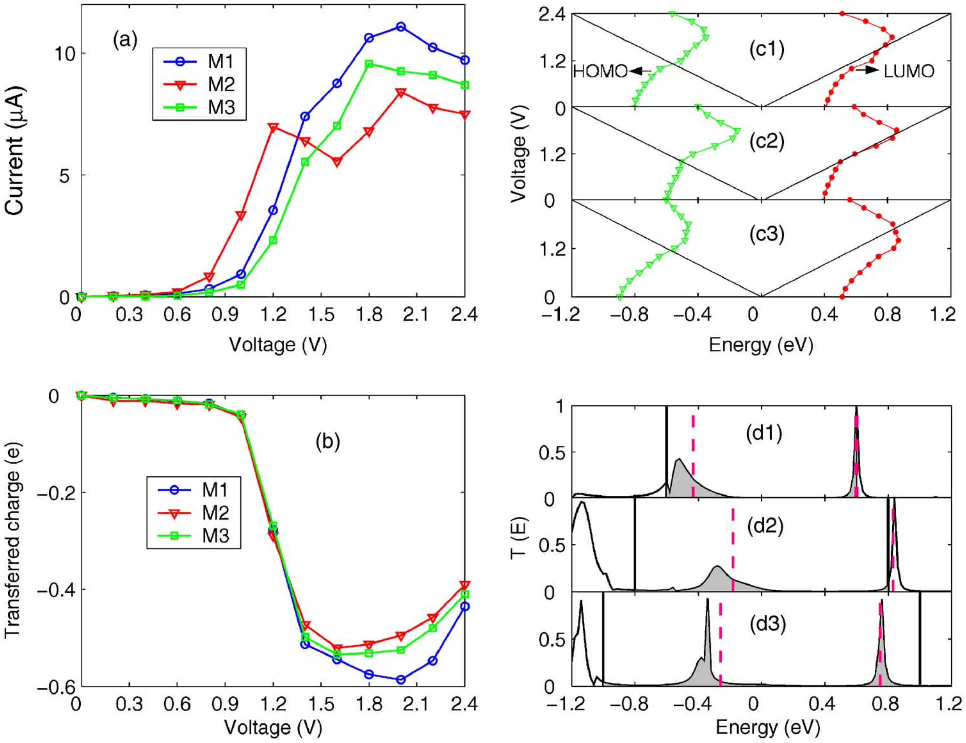

FIG. 3. (Color online) (a) *I*-*V* curves of the molecular junctions M1–M3. (b) shows the transferred charge at different bias voltages. The negative value represents that electrons are transferred from the electrode to the molecules. (c1)–(c3) describe the shift of the HOMO and LUMO orbitals with the increase of bias voltage for M1–M3, respectively. The region between the solid curves is the bias window. (d1)–(d3) describe the transmission coefficient of M2 at bias voltages V_b=1.2, 1.6, and 2.0 V, respectively. The region between the solid lines is the bias window, and the shaded area denotes the integral area inside the bias window.

of M2 for bias voltage V_b=1.2, 1.6, and 2.0 V, as shown in Figs. 3(d1)–(d3). Comparing (d1) with (d2), we find that when the external bias voltage is V=1.6 V the LUMO shift out of the bias window and the integral area inside the bias window gets smaller. As a result, the current is decreased and NDR appears. From Fig. 3(d3), we find that when the bias is further increased, the transmission peak contributed by LUMO enters into the bias window and the current increases again. The above results indicate that the NDR behavior appearing at higher bias for all three systems M1, M2, and M3 results from the change in the coupling between the molecular orbitals and the electrodes due to the shift of the molecular orbitals caused by the change in the transferred charge of the molecule under the increasing bias voltage, while shift out of the bias window of LUMO orbital under certain bias voltage range may be responsible for the NDR appearing at the lower bias voltage of M2.

In summary, the calculated results show that the side group plays an important role on the electronic transport properties. NDR behaviors can be observed in such devices, especially for the molecule with electron-donating group ($-NH_2$), two NDR appear at different bias voltage regions. We suggest that the change in the coupling between the molecular orbitals and the electrodes due to the shift of the molecular orbitals caused by the change in the transferred charge of the molecule is the origin of the NDR appearing at higher bias for all three systems M1, M2, and M3, and shift out of the bias window of LUMO orbital under certain bias voltage range can explain the NDR appearing at the lower bias voltage of M2.

This work was supported by the National Natural Science Foundation of China (Nos. 90403026 and 10674044), by the Ministry of Science and Technology of China (No. 2006CB605105), by Hunan Provincial Natural Science Foundation of China (Nos. 06JJ20004 and 07JJ107), and by the Program for New Century Excellent Talents in University.

[1] L. L. Chang, L. Esaki, and R. Tsu, Appl. Phys. Lett. **24**, 593 (1974).
[2] Z. K. Tang and X. R. Wang, Appl. Phys. Lett. **68**, 3449 (1996).
[3] X. R. Wang and Q. Niu, Phys. Rev. B **59**, R12755 (1999).
[4] X. R. Wang, Y. Wang, and Z. Z. Sun, Phys. Rev. B **65**, 193402 (2002).
[5] J. Chen, M. A. Reed, A. M. Rawlett, and J. M. Tour, Science **286**, 1550 (1999); J. Chen, W. Wang, M. A. Reed, A. M. Rawlett, D. W. Orice, and J. M. Tour, Appl. Phys. Lett. **77**, 1224 (2000).
[6] A. M. Rawlett, T. J. Hopson, L. A. Nagahara, R. K. Tsui, G. K. Ramachandran, and S. M. Lindsay, Appl. Phys. Lett. **81**, 3043 (2002).
[7] J. M. Seminario, A. G. Zacarias, and J. M. Tour, J. Am. Chem. Soc. **122**, 3015 (2000).
[8] J. Cornil, Y. Karzazi, and J. L. Bredas, J. Am. Chem. Soc. **124**, 3516 (2002).
[9] J. Taylor, M. Brandbyge, and K. Stokbro, Phys. Rev. B **68**, 121101 (2003).
[10] S. I. Khondaker, Z. Yao, L. Cheng, J. C. Henderson, Y. Yao, and J. M. Tour, Appl. Phys. Lett. **85**, 645 (2004).
[11] X. Yin, H. Liu, and J. Zhao, J. Chem. Phys. **125**, 094711 (2006).
[12] C. W. Bauschlicher and J. W. Lawson, Phys. Rev. B **75**, 115406 (2007).
[13] M.-Q. Long, K.-Q. Chen, L. Wang, B. S. Zou, and Z. Shuai, Appl. Phys. Lett. **91**, 233512 (2007).
[14] Y. Xue, S. Datta, S. H. Hong, R. Reifenberger, J. I. Henderson, and C. P. Kubiak, Phys. Rev. B **59**, R7852 (1999).
[15] M. Di Ventra, S.-G. Kim, S. T. Pantelides, and N. D. Lang, Phys. Rev. Lett. **86**, 288 (2001).
[16] Y. Luo and Y. Fu, J. Chem. Phys. **117**, 10283 (2002).
[17] X.-F. Li, K.-Q. Chen, L. Wang, M.-Q. Long, B. S. Zou, Z. Shuai, Appl. Phys. Lett. **91**, 133511 (2007).
[18] R. Liu, S.-H. Ke, H. U. Baranger, and W. Yang, J. Am. Chem. Soc. **128**, 6274 (2006).
[19] H. Geng, Y. Hu, Z. Shuai, K. Xia, H. Gao, and K.-Q. Chen, J. Phys. Chem. C **111**, 19098 (2007).
[20] L. Chen, Z. Hu, A. Zhao, B. Wang, Y. Luo, J. Yang, and J. G. Hou, Phys. Rev. Lett. **99**, 146803 (2007).
[21] M. Brandbyge, J. L. Mozos, P. Ordejon, J. Taylor, and K. Stokbro, Phys. Rev. B **65**, 165401 (2002).
[22] B. J. Littler, Y. Ciringh, and J. S. Lindsay, J. Org. Chem. **64**, 2864 (1999).
[23] R. C. Jagessar and J. M. Tour, Org. Lett. **2**, 111 (2000).
[24] X. Lu, M. Li, C. Yang, L. Zhang, Y. Li, L. Jiang, H. Li, L. Jiang, C. Liu, and W. Hu, Langmuir **22**, 3035 (2006).
[25] X. Xiao, L. A. Nagahara, A. M. Rawlett, and N. Tao, J. Am. Chem. Soc. **127**, 9235 (2005).

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