Electron Transport in Self-Assembled Polymer Molecular Junctions

Wenping Hu,[1,4,*] Jun Jiang,[2,3] Hiroshi Nakashima,[4] Yi Luo,[2,†] Yoshiaki Kashimura,[4] Ke-Qiu Chen,[5] Z. Shuai,[1,*] Kazuaki Furukawa,[4] Wei Lu,[3] Yunqi Liu,[1] Daoben Zhu,[1,*] and Keiichi Torimitsu[4]

[1]*Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China*
[2]*Theoretical Chemistry, Royal Institute of Technology, AlbaNova, S-106 91 Stockholm, Sweden*
[3]*National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai 200083, China*
[4]*NTT Basic Research Laboratories, 3-1 Morinosato Wakamiya, Atsugi, Kanagawa 243-0198, Japan*
[5]*Department of Physics, Hunan University, Changsha 410082, China*
(Received 20 April 2005; published 18 January 2006)

A molecular junction of a poly(*p*-phenyleneethynylene)s derivative with thioacetate end groups (TA-PPE) was fabricated by self-assembling. Nanogap electrodes made by electroplating technique was used to couple thiol end groups of TA-PPE molecules. Room temperature current-voltage characteristics of the molecular junction exhibited highly periodic, repeatable, and identical stepwise features. First-principles calculations suggest that one possibility for the equidistant step is due to the opening of different conducting channels that corresponds to the unoccupied molecular orbitals of the polymer in the junction. It is interesting to see that an 18 nm long polymer is of quantized electronic structures and behaves like a quantum transport device.

It has been a big challenge to measure the charge transport in organic molecules and to determine accurately their conductance because of the great difficulty of wiring one or several molecules into a circuit. Impressive progress has been made on low molecular weight materials (e.g., phenylene ethynylene oligomers) [1–3]. However, to the best of our knowledge very few reports have dealt with the wiring of conjugated polymer molecules into an electrical circuit, although the outstanding electronic-photonic properties of conjugated polymers have been well known since the 1990s [4]. One reason for this is due to the lack of rigidity for most polymers. It results in a failure to bridge them between electrodes or to stand on substrates; therefore, it fails to be characterized by scanning probe microscopy [5,6]. Another reason is that the nonfunctionalized end group of most polymers is impossible to graft on substrates through chemical bonds. Fortunately, these difficulties can be overcome by using the poly(*para*-phenylene ethynylene)s (PPEs), which have good conductivity [7,8] and rigidity [9]. Moreover, by modifying PPE with thiol/thioacetate-end-functionalized groups, there are good prospects for applying them in self-assembled nanoelectronic devices [10,11]. Recently, we have synthesized a derivative of PPEs with thioacetate end groups (TA-PPE) and demonstrated the connectivity of its double ends with gold nanoparticles [12,13]. As a natural continuation, we begin to control the length of TA-PPE to wire one or several TA-PPE molecules into electrical circuits and to investigate the electron transport in these self-assembled polymer molecular junctions.

The synthesis of TA-PPE [12] [Fig. 1(a)] and the fabrication of gold nanogap electrodes [14] [inset of 1(b), with gap width ≈ 18 nm] are described in previous studies. The wiring of TA-PPE molecules into nanogap electrodes was monitored *in situ* accurately with a current-time circuit. Several drops of NH_4OH were added into TA-PPE solution to promote the deprotection of acetyl-protected thiols before use [15,16]. We have observed that as soon as one polymer molecule or one polymer bundle (several molecules) was trapped between the nanogap electrodes, i.e., formed a successful connection between the nanogap electrodes, the nanojunction current jumped to a new value. We once observed ~19 jumps during ~130 h self-assembly process and got a connected nanowire with a diameter around 20 nm. It is very likely that each jump corresponded to one molecule connection. Therefore, the self-assembly process was stopped by gently removing out the polymer solution [Fig. 1(b)] as soon as the first current jump was observed. With that, we expect to obtain a single molecular junction. Furthermore, we used TA-PPE with 24 polymerization units (with molecular length around 18.3 nm) to match the electrode gap of 18 nm, which could enhance the probability of forming a single molecular junction. After wiring a PPE molecule or bundle into the nanogap electrodes, the Au/TA-PPE/Au molecular junction was formed as depicted in Fig. 1(c). It should be stressed that the lack of a proper experimental tool to visualize the molecular junction has made it difficult to identify the exact number of molecules in between electrodes.

The recorded *I-V* curve of the polymer molecular junction at room temperature in a 1 Pa vacuum chamber is shown in Fig. 2. It is noticed that the current of the pure nanogap electrodes (18 nm gap) has a noise level of several fA in the same conditions. Several features have been clearly demonstrated in the current-voltage characteristics: (i) highly periodic, identical, and repeatable stepwise behavior appears, which is more profound under the positive bias; (ii) the separation between the
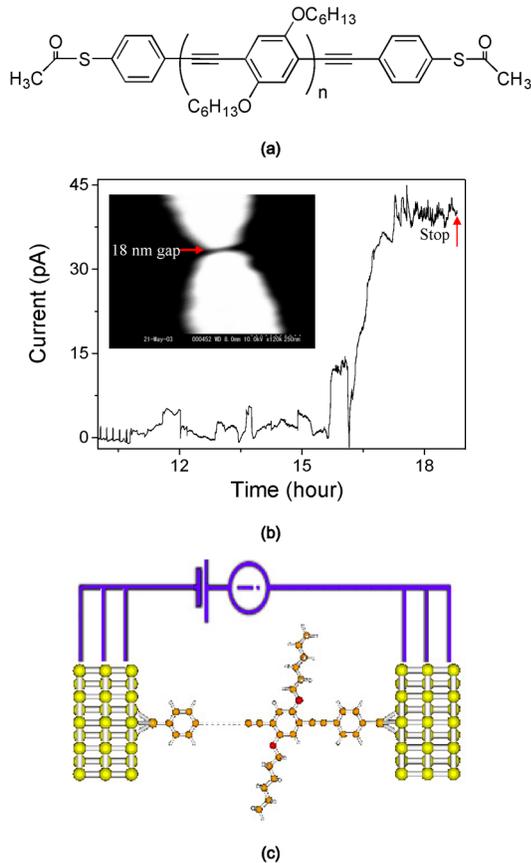
(a)

(b)

(c)

FIG. 1 (color online). (a) Molecular structure of TA-PPE, $n \approx$ 24. (b) *In situ* monitoring the wiring of TA-PPE between the Au nanogap electrodes in polymer solution ($\sim 10^{-8}$ M); the wiring process was stopped as soon as the first current jump appeared. Inset: 18 nm nanogap electrodes. (c) Connection model of a TA-PPE between Au nanogap electrodes.

neighboring steps (or peaks) is always around 0.23–0.26 V; (iii) the *I-V*s are not symmetric with respect to the voltage inversion.

The nice steps in the *I-V* curve are not due to conductance quantization [17] because the step height is 6 orders of magnitude smaller than the conductance quantum, $2e^2/h$. It cannot be caused by the molecular deformation and defect that often tend to smear out the structures. Although the polymer molecule is chemically bonded to the gold electrodes through the end sulfur atoms, the conjugated π orbitals of the polymer molecule might not be able to extend over to the electrodes. The self-assembled molecular junction could be similar to a quantum dot junction, with the conjugated polymer molecules as a quantum dot and the terminal sulfur atoms acting as two tunnel barriers. One possible explanation could be related to the Coulomb charging effect [18–20], each step (or peak) corresponds to the injection of one electron into the polymer molecule. Another possible mechanism for the stepwise behavior could be related to the resonant electron tunneling: each step is a sign of an opening of
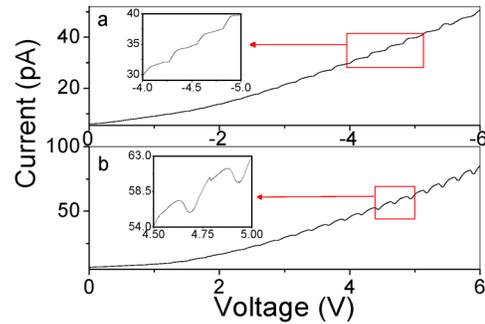

FIG. 2 (color online).   *I-V* characteristics of a TA-PPE molecular junction. (a) Negative scan direction; inset, enlarged steps from −4.0 to −5.0 V. (b) Positive scan direction; inset, enlarged steps from 4.5 to 5.0 V.

each conducting channel that corresponds to the molecular orbitals of the polymer molecule [21–26].

First-principles calculation has been well applied for transport properties of molecular devices (small molecules, e.g., benzene-1,4-dithiolate [27]) as well as alkanethiols [28]. Here, we carried out density functional theory calculations for polymer molecules of different lengths to understand both Coulomb charging and resonant tunneling mechanisms. Geometry optimizations for the polymer molecules were done with the PM3 method. The sulfur atom is assumed to bond to the center of a triangle gold plan and Au-S bond length is set to be 2.93 Å for systems under investigation. Electronic structures and ionization potentials of polymer molecules are calculated using the GAUSSIAN03 [29] program at hybrid density functional theory B3LYP level with Lanl2dz (for Au) and 6-31G (for the rest) basis sets. A generalized quantum chemical Green function approach [30] implemented in the QCME program [31] has been used to simulate the current-voltage characteristics of polymer molecular devices.

The calculated molecular orbitals of polymers with different units are shown in Fig. 3(a). The energy gap of the polymer is already converged at 10 units, whereas the bandlike density of state forms only after 40 units. We use a TA-PPE oligomer of 10 units (poly10) as model system to examine two different mechanisms. The equidistant distribution of conductance peaks in the experiment (Fig. 4) indicates that the addition energies of redox states, $I(n \rightarrow n + 1)$ [18], should be constant with respect to the number of the electrons (n) injected if the Coulomb charging effect should be dominated. The calculated addition energies of redox states do not show a constant dependence, but an oscillating behavior. One might attribute such a difference to the uncertainty of the computational method used [18]. However, a very recent first-principle calculation shows that for a molecular junction like ours charging is not sustainable unless a contactless gate is added on [32].

Based on the elastic scattering Green function approach, we have calculated current and conductance curves for the neutral poly10 which show clearly repeatable stepwise
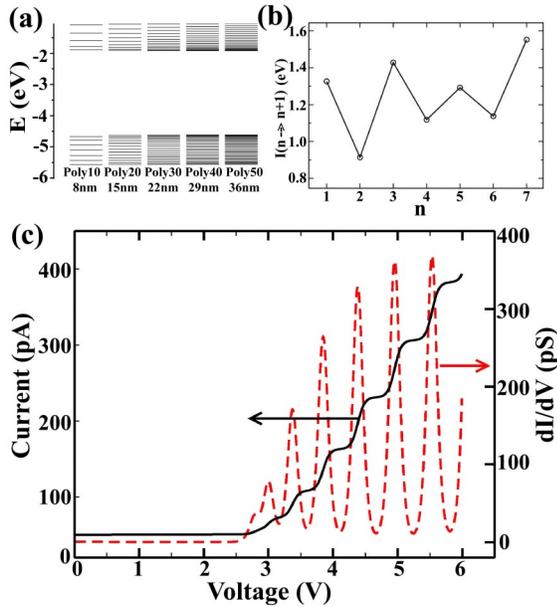
FIG. 3 (color online). (a) The evolution of molecular orbitals with respect to the length of the polymer (8 to 36 nm), (b) the calculated addition energies of redox states with respect to the number of extra electron (n) injected, (c) and the current/conductance-voltage characteristics of the neutral poly10.

FIG. 4 (color online). Comparison between the experimental (I, solid line) and the theoretical (II, dashed lines) I-V characteristics. The dephasing factor is assumed to be 3 under the negative bias (a) and 10 under the positive bias (b).

behavior. In the simulations, we have assumed that the potential drops mostly at the interfaces, which is a reasonable approximation for a weakly bonded long chain system [32–35]. The energy separation between different peaks is found to be 0.5 eV, which is exactly twice the orbital energy difference between different conducting channels of the poly10 molecule. The resonant electron tunneling mechanism seems to provide straightforward explanation for the experimental results.

The electrode gap in the experiment is around 18 nm, which corresponds to the length of TA-PPE polymer with 24 units (poly24). The calculated I-V characteristics of the poly24 are shown in Fig. 4 together with the corresponding experimental results. The theoretical and experimental results agreed with each other very well. It is clear that the well-spaced molecular orbital in the poly24 is responsible for the stepwise feature in the I-V curve. Different step corresponds to the opening of different conducting channels. The calculated voltage spacing between different steps of poly24 is around 0.26 V, in perfect agreement with the experimental value of 0.23–0.26 V. It is interesting to see that the electronic structure of an 18 nm long TA-PPE polymer is still largely quantized. It should be mentioned that in the calculations the Fermi energy level is determined in such a way that the best agreement between theory and experiment is achieved. It is found that in this case the Fermi energy is much closer to the unoccupied molecular orbitals of the polymer than to its occupied molecular orbitals. Furthermore, the occupied molecular orbitals are not equally spaced with energy separation less
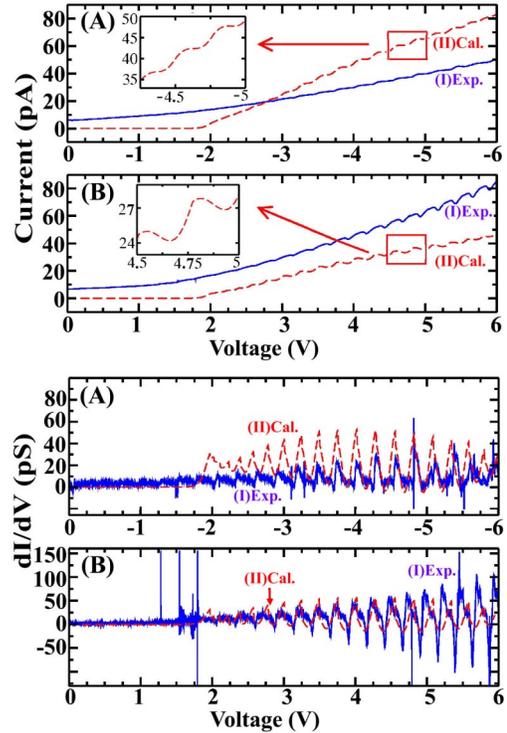
than 0.13 eV. Calculations thus favor the electron transport for the current device.

The unsymmetrical behavior of the experimental I-V characteristics is more difficult to model, especially when the structure information at the interfaces is unknown. However, one might anticipate that such a behavior could be associated with the nonperfect polymer-metal bonding. Because of this unbalanced coupling between polymer and electrodes, the chemical and electronic structures of polymer could respond to the positive and negative external biases differently. As the first order approximation, the external field effect can be modeled by introducing a quantum dephasing factor, ρ, which describes the changes of scattering time with respect to the external bias, i.e., $\Gamma_i(E_i) = \Gamma_i(0)(1 + \rho E_i)$, where Γ_i is the escape rate and E_i is the injecting energy [30]. The calculated results, as shown in Fig. 4, are in quite good agreement with the experiments. The dephasing factor is found to be 3 under the negative bias, and 10 under the positive bias, which implies that the negative external bias has smaller effect on the electronic structures of polymer than that of the positive bias. The presence of the external bias dephases the electron transport processes, resulting in destructive interferences between different tunneling channels, hence the negative differential resistance effects. The dephasing of the electronic states is associated with the incoherent contribution of the tunneling. It describes the energy exchange

between the molecule and the surroundings and the change of electron lifetime on different molecular orbitals. In other words, the single electron transfer in this device is not a coherent one-step process.

We have examined two possible mechanisms for the electron transport in the polymer molecular junction. The calculated current-voltage characteristics based on the resonant electron tunneling mechanism reproduce the experimental results with very high accuracy. Although it is difficult to completely rule out the possible Coulomb charging effects, we are inclined to believe that such an 18 nm long polymer junction is mainly a ballistic transport device. Based on the calculation, it can be concluded that the observed highly periodic and identical stepwise features in the room temperature I-Vs of the self-assembled TA-PPE molecular junction correspond to the opening of different conducting channels that are associated with the unoccupied molecular orbitals of the polymer molecule.

---

*To whom correspondence should be addressed.
Electronic address: huwp@iccas.ac.cn
†To whom correspondence should be addressed.
Electronic address: luo@theochem.kth.se

[1] M. A. Reed, C. Zhou, C. J. Muller, and J. M. Tour, Science **278**, 252 (1997).

[2] J. M. Tour, Chem. Rev. **96**, 537 (1996).

[3] D. Dulić, S. J. van der Molen, T. Kudernac, H. T. Jonkman, J. J. D. de Jong, T. N. Bowden, J. van Esch, B. L. Feringa, and B. J. van Wees, Phys. Rev. Lett. **91**, 207402 (2003).

[4] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, Nature (London) **347**, 539 (1990).

[5] D. J. Wold and C. D. Frisbie, J. Am. Chem. Soc. **123**, 5549 (2001).

[6] Z. J. Donhauser, B. A. Mantooth, K. F. Kelly, L. A. Bumm, J. D. Monnell, J. J. Stapleton, D. W. Price, Jr., A. M. Rawlett, D. L. Allara, J. M. Tour, and P. S. Weiss, Science **292**, 2303 (2001).

[7] U. H. F. Bunz, Chem. Rev. **100**, 1605 (2000).

[8] A. Kokil, I. Shiyanovskaya, K. D. Singer, and C. Weder, J. Am. Chem. Soc. **124**, 9978 (2002).

[9] M. Moroni and J. Le Moigne, Macromolecules **27**, 562 (1994).

[10] V. Francke, T. Mangel, and K. Muellen, Macromolecules **31**, 2447 (1998).

[11] P. Samorí, N. Severin, K. Muellen, and J. P. Rabe, Adv. Mater. **12**, 579 (2000).

[12] H. Nakashima, K. Furukawa, Y. Kashimura, and K. Torimitsu, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) **44**, 482 (2003).

[13] H. Nakashima, K. Furukawa, K. Ajito, Y. Kashimura, and K. Torimitsu, Langmuir **21**, 511 (2005).

[14] Y. Kashimura, H. Nakashima, K. Furukawa, and K. Torimitsu, Thin Solid Films **438–439**, 317 (2003).

[15] J. M. Tour, L. Jones II, D. L. Pearson, J. J. S. Lamba, T. P. Burgin, G. M. Whitesides, D. L. Allara, A. N. Parikh, and S. V. Atre, J. Am. Chem. Soc. **117**, 9529 (1995).

[16] A. Aviram, in *Molecular Electronics: Science and Technology*, AIP Conf. Proc. No. 262 (AIP, New York, 1992).

[17] B. J. van Wees, H. van Houten, C. W. J. Beenakker, J. G. Williamson, L. P. Kouwenhoven, D. van der Marel, and C. T. Foxon, Phys. Rev. Lett. **60**, 848 (1988).

[18] S. Kubatkin, A. Danilov, M. Hjort, J. Cornil, J. L. Bredas, N. Stuhr-Hansen, P. Hedegard, and T. Bjornholm, Nature (London) **425**, 698 (2003).

[19] H. Park, J. Park, A. K. L. Lim, E. H. Anderson, A. P. Alivisatos, and P. L. McEuen, Nature (London) **407**, 57 (2000).

[20] J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abruna, P. L. McEuen, and D. C. Ralph, Nature (London) **417**, 722 (2002).

[21] V. Mujica, M. Kemp, A. Roitberg, and M. Ratner, J. Chem. Phys. **104**, 7296 (1996).

[22] W. Liang, M. Bockrath, D. Bozovic, J. H. Hafner, M. Tinkham, and H. Park, Nature (London) **411**, 665 (2001).

[23] J. Kong, E. Yenilmez, T. W. Tombler, W. Kim, H. Dai, R. B. Laughlin, L. Liu, C. S. Jayanthi, and S. Y. Wu, Phys. Rev. Lett. **87**, 106801 (2001).

[24] A. Javey, P. Qi, Q. Wang, and H. Dai, Proc. Natl. Acad. Sci. U.S.A. **101**, 13 408 (2004).

[25] A. Javey, J. Guo, M. Paulsson, Q. Wang, D. Mann, M. Lundstrom, and H. Dai, Phys. Rev. Lett. **92**, 106804 (2004).

[26] A. Javey, J. Guo, Q. Wang, M. Lundstrom, and H. Dai, Nature (London) **424**, 654 (2003).

[27] M. Di Ventra, S. T. Pantelides, and N. D. Lang, Phys. Rev. Lett. **84**, 979 (2000).

[28] Y. C. Chen, M. Zwolak, and M. Di Ventra, Nano Lett. **5**, 621 (2005).

[29] M. J. Frisch *et al.*, computer code GAUSSIAN03, Revision A.1, Gaussian, Inc., Pittsburgh, PA, 2003.

[30] C. K. Wang, Y. Fu, and Y. Luo, Phys. Chem. Chem. Phys. **3**, 5017 (2001); C. K. Wang and Y. Luo, J. Chem. Phys. **119**, 4923 (2003); J. Jiang, W. Lu, and Y. Luo, Chem. Phys. Lett. **400**, 336 (2004).

[31] Jun Jiang and Yi Luo, QCME-V1.0 (Quantum Chemistry for Molecular Electronics), 2004.

[32] Y. Gohda and S. T. Pantelides, Nano Lett. **5**, 1217 (2005).

[33] S. N. Yaliraki, M. Kemp, and M. A. Ratner, J. Am. Chem. Soc. **121**, 3428 (1999).

[34] B. Q. Xu and N. J. Tao, Science **301**, 1221 (2003).

[35] X. D. Cui, A. Primak, X. Zarate, J. Tomfohr, O. F. Sankey, A. L. Moore, T. A. Moore, D. Gust, G. Harris, and S. M. Lindsay, Science **294**, 571 (2001).