

Electromechanical and Conductance Switching Properties of Single Oligothiophene Molecules

Bingqian Q. Xu,[†] Xiulan L. Li,[†] Xiaoyin Y. Xiao,[†] Hiroshi Sakaguchi,[‡] and Nongjian J. Tao^{*,†}

Department of Electrical Engineering & The Center for Solid State Electronics Research, Arizona State University, Tempe, Arizona 85287, and Research Institute of Electronics, Shizuoka University, Hamamatsu 432-8011, Japan

Received May 9, 2005; Revised Manuscript Received May 29, 2005

ABSTRACT

We have studied the electron transport and electromechanical properties of single oligothiophenes with three and four thiophene repeating units covalently linked to two Au electrodes. The four-repeating unit molecule is found to be more conductive than the three-repeating unit molecule. This unusual length dependence is due to the different electronic states of the molecules. Both molecules can be switched reversibly between a high and low conducting state by oxidizing and reducing the molecules using an electrochemical gate. The conductance of the molecules decreases upon stretching, which is attributed to a force-induced increase in the HOMO–LUMO gap.

The ability to control current through a single molecule is an important goal in molecular electronics.^{1–3} One way to reach this goal is to switch the conductance of a redox molecule by electrochemically oxidizing or reducing it.^{4–9} Redox polymers are ideal candidates for this purpose because they are reversibly switchable between insulating and conducting states via oxidation or reduction.¹⁰ These molecules typically consist of alternating double and single bonds and would be metallic, but the strong electron–lattice coupling leads to lattice deformation that creates an energy gap between the conduction and valence bands (known as Peierls instability¹¹). One may expect a sensitive dependence of the conductance of these molecules on lattice deformation induced by an external force, which leads to an interesting electromechanical response.

Here we report on the electromechanical and redox switching properties of single oligothiophene molecules (Figure 1). These molecules have been studied using different techniques under various conditions because of their novel electronic properties.^{12–14} We focus here on the oligothiophenes with three and four thiophene rings (abbreviated as 3T1DT and 4T1DT, respectively). The molecules are terminated with thiol groups on both ends so that they can covalently bind to Au electrodes. To measure the electromechanical properties of a single oligothiophene molecule, we used a combined conducting AFM and electrochemical STM break junction method.¹⁵ We prepared conducting AFM

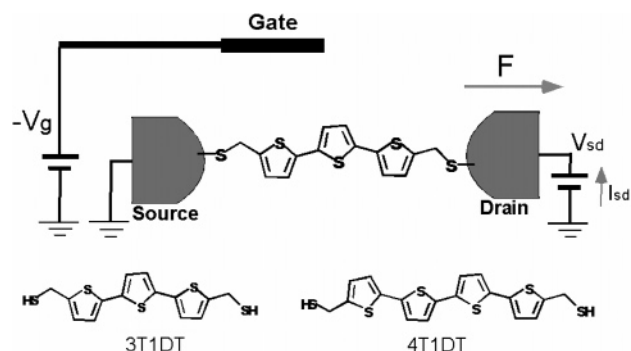


Figure 1. Schematic illustration of the experimental setup. The current through the molecule and the force applied to the molecule are measured using a modified conducting AFM. To study the electrochemical gate effect, we used an STM setup using an Ag wire reference electrode inserted in 0.1 M NaClO₄ as the electrochemical gate. The gate is used to switch the molecules between oxidized and reduced states, allowing us to control the current through single molecules. Note that the gate voltage cited here is the potential of the source electrode with respect to the quasi reference electrode, so the sign convention is opposite to the solid state FET. The quasi reference electrode was calibrated against the more commonly used Ag/AgCl (in 3.5 M KCl) reference electrode.

probes by coating commercially available Si AFM cantilevers with 20-nm Cr first and then with 70-nm Au with a sputtering coater. The spring constants of the cantilevers were 40 N/m. We fabricated gold substrates by thermally evaporating 100-nm gold on mica in a UHV chamber. We created individual molecular junctions by repeatedly moving a gold-coated AFM tip into and out of contact with a gold substrate in toluene containing 1 mM of the molecules, which is shown

* Corresponding author. E-mail: nongjian.tao@asu.edu.

[†] Arizona State University.

[‡] Shizuoka University.

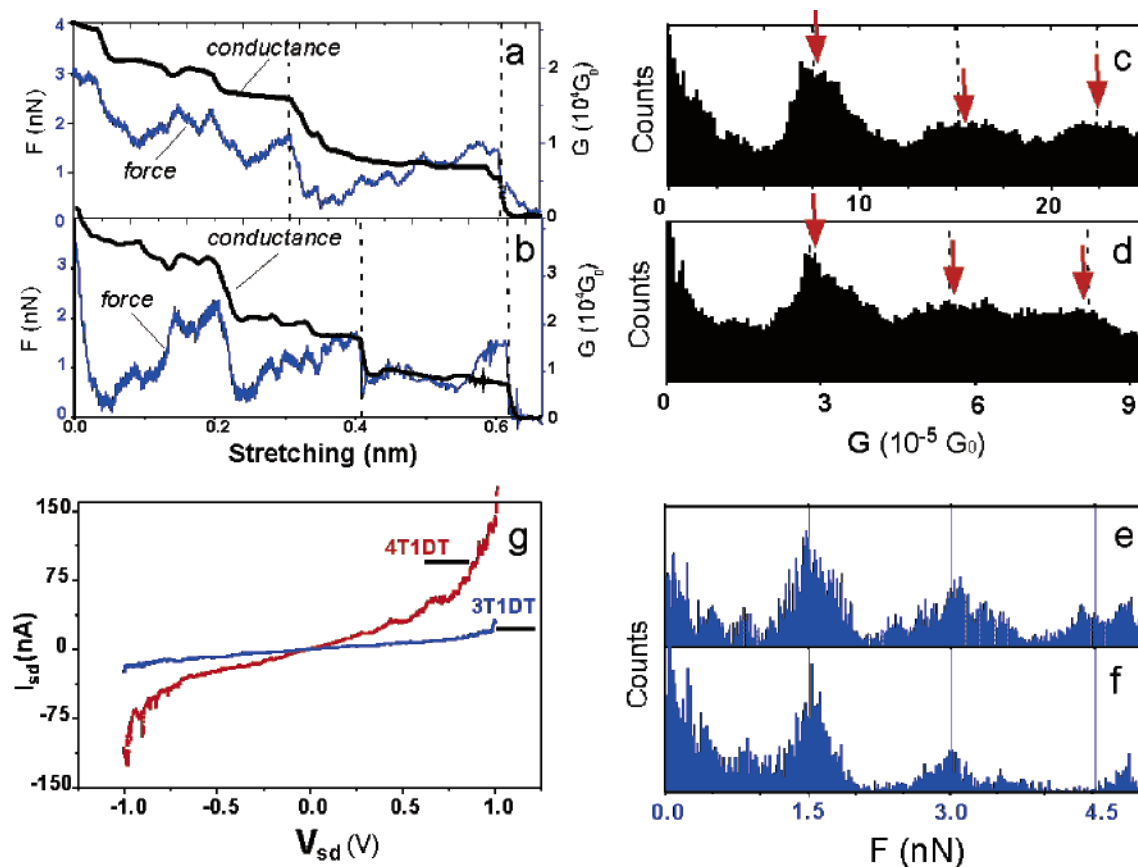


Figure 2. (a–b) Simultaneously measured conductance and force curves during individual stretching processes (stretching rate 40 nm/sec.) for 4T1DT in toluene solution. (c–d) Conductance histograms of 4T1DT (c) and 3T1DT (d) constructed using ~ 500 such curves as shown in a and b. (e–f) Breakdown force histograms of 4T1DT (e) and 3T1DT (d) constructed using ~ 500 such curves as shown in a and b. (g) I – V characteristic curves of 3T1DT and 4T1DT.

as a series of steps in the conductance (Figure 2a–b). For each molecule, the conductance histogram constructed from ~ 500 individual measurements reveals peaks located near integer multiples of a fundamental conductance value. The fundamental conductance value is identified with the conductance of a single molecule (Figure 2c–d).^{16,17} The corresponding conductance values for 4T1DT and 3T1DT are $7.5 \times 10^{-5} G_0$ and $2.8 \times 10^{-5} G_0$, respectively, where $G_0 = 2e^2/h \approx 77 \mu\text{S}$, with e as the electron charge and h as Planck's constant. It is surprising and interesting that the longer molecule (4T1DT) is more conducting than the shorter one (3T1DT). We will return to this later.

Once the conductance of a single molecule is determined, we measured the I – V_{sd} characteristic curves using the following procedures. We first pulled the source and drain electrodes apart until the conductance dropped to the lowest step, corresponding to the value of a single 3T1DT or 4T1DT conductance. We then froze the electrodes and recorded the current (I_{sd}) while sweeping the source–drain voltage (V_{sd}). We will refer to these procedures as the pull–hold–measure method. The I – V_{sd} curves show that 4T1DT is not only more conducting but also deviates from linear ohmic behavior at a lower voltage than 3T1DT (Figure 2g).

The simultaneously recorded force and conductance in Figure 2a–b show that each discrete conductance decrease is accompanied by an abrupt decrease in the force, corre-

sponding to the breakdown of a molecule from contacting the electrodes. Similar to the conductance histogram described above, the force histogram also reveals well-defined peaks at multiples of a fundamental force quantum, which is the force required to break a single molecule at the junction (Figure 2e–f). Unlike the conductance, which takes different values for 3T1DT and 4T1DT, the breakdown forces are similar for both molecules, which are 1.5 ± 0.2 nN. This force is about the same as that to break an Au–Au bond under the same condition,¹⁸ which indicates that the breakdown is likely to occur at Au–Au bonds near the molecule–electrode contacts.

We have found that 4T1DT is more conducting than 3T1DT. To understand this observation, we have estimated the gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the two molecules from the UV–Vis spectra (inset of Figure 3a) and found that the HOMO–LUMO gaps of 4T1DT and 3T1DT are about 3 and 3.4 eV, respectively. So the longer molecule has a smaller HOMO–LUMO gap, which agrees with the theoretical calculations.¹⁹ Although the smaller HOMO–LUMO gap for 4T1DT favors a higher conductivity, the conductance also depends on the position of the LUMO and HOMO relative to the Fermi energy of the electrodes. We have studied the HOMO and LUMO positions by measuring the redox properties of the molecules

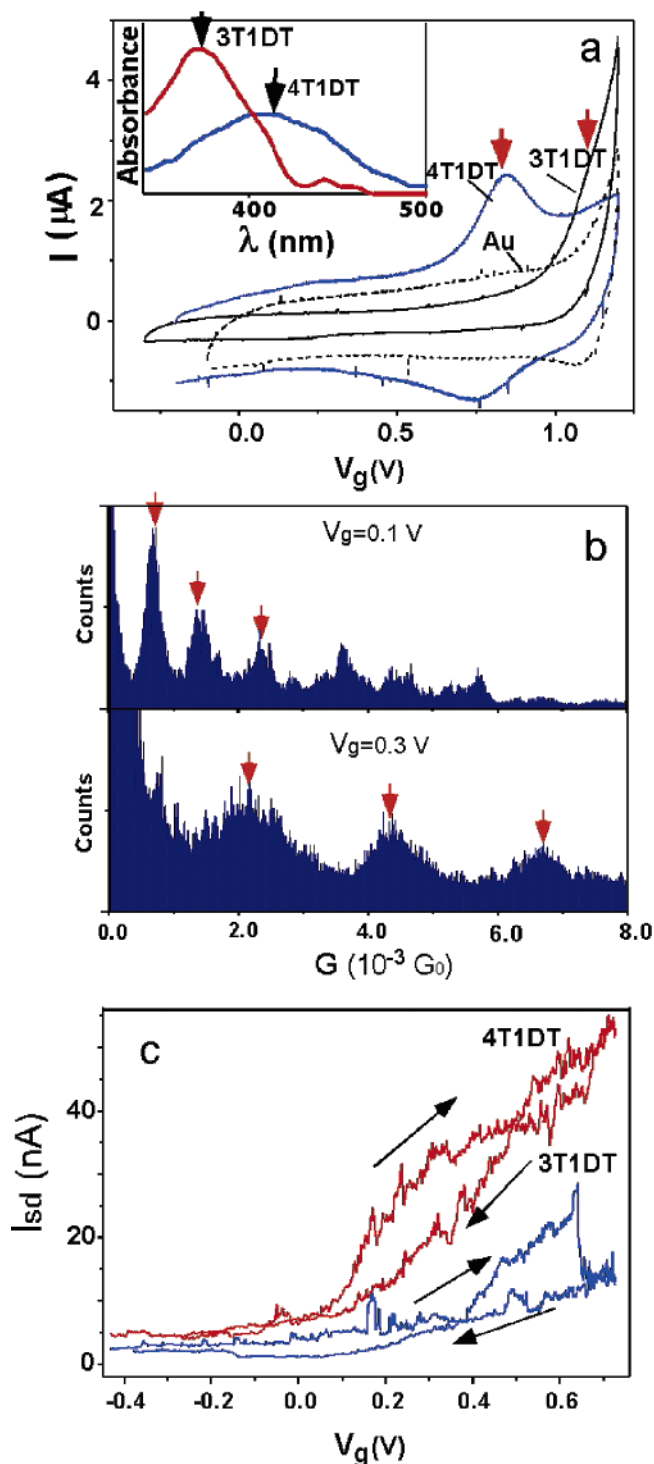


Figure 3. (a) Cyclic voltammograms of 3T1DT (black line) and 4T1DT (blue line) adsorbed on a gold electrode in 0.1 M HClO₄. The potential sweep rate is 0.2 V/sec. The arrows point to the reduction and reoxidation peaks of the two redox processes. For comparison, the voltammogram of a bare gold electrode is also shown (dashed line). Inset of (a) UV-vis spectroscopy of 3T1DT and 4T1DT molecules. (b) Conductance histograms of the 4T1DT molecule conductance in 0.1 M NaClO₄ at different gate voltages. (c) Source-drain current vs gate voltage for single 3T1DT and 4T1DT molecules obtained by recording the source-drain current while sweeping the gate voltage in 0.1 M NaClO₄.

bound to gold electrodes using cyclic voltammetry (Figure 3a). The cyclic voltammograms show that both molecules can

be reversibly oxidized, but the redox potential of 4T1DT is about 0.3 V lower than that of 3T1DT, indicating that the HOMO of 4T1 is closer to the Fermi energy of Au than that of 3T1DT. This is also consistent with the observation that the I - V curve of 4T1DT deviates from linear behavior at a lower bias. On the basis of the evidence described above and further experimental data shown below, we attribute the unusual length-dependent conductance of oligothiophenes to the length-dependent electronic states of the molecules.

If the conductance is indeed associated with the relative position of the HOMO to the Fermi energy, then we expect that the conductance can be changed by shifting the HOMO relative to the Fermi energy using the electrochemical gate (V_g). This was carried out using an electrochemical STM breaking junction setup¹⁷ in which an Apiezon wax-coated gold Au STM tip was used. The thiophene molecules were self-assembled onto the gold substrate by exposing the substrate to toluene containing 4T1DT or 3T1DT overnight. The electrochemical STM experiment was performed in 0.1 M NaClO₄ aqueous electrolyte with a Pt counter electrode and Ag quasi reference electrode. The quasi reference electrode was calibrated against the more commonly used Ag/AgCl (in 3.5 M KCl) reference electrode. The source potential (tip) was varied relative to the reference electrode (electrochemical gate) while fixing a small bias voltage ($V_{sd} = 0.1$ V) between the source and drain (substrate) electrodes with a bipotentiostat. Figure 3b plots the conductance histograms of 4T1DT at $V_g = 0.1$ and 0.3 V. The histogram analysis shows that the average conductance of a single oligothiophene molecule averaged over a large number of measurements increases with the electrochemical gate voltage.

We have also measured the source-drain current through individual molecular junctions by sweeping the gate voltage using the pull-hold-measure method. We note that the highest gate voltage had to be kept below 0.7 V to avoid oxidation of Au. The current through 4T1DT starts to increase with V_g quickly at ~ 0.2 V (Figure 3c). The current through 3T1DT also increases with V_g , but it starts to increase quickly at a higher potential (~ 0.4 V). This observation is consistent with the observation that 4T1DT is oxidized at a lower potential than 3T1DT. This electrochemical gating behavior resembles a p-type field effect transistor (the sign convention here is opposite of that in solid-state electronics), but the mechanism is different. We believe that the gate-controlled current in 4T1DT and 3T1DT is due to the oxidation of the molecules because of the following two considerations. First, the I_{sd} versus V_g behavior in single oligothiophenes observed here is rather similar to that of bulk films, which are known to switch between insulating and conducting states upon oxidation.¹⁰ Second, the large hysteresis present in the I_{sd} versus V_g curves is consistent with oxidation-induced structural relaxation in the molecules.

The force measurement described earlier confirms that the measured molecules are covalently linked to both electrodes and also allows us to study the electromechanical properties of the molecules. An important observation is that the conductance decreases significantly upon stretching until the bond breaks at the contacts (Figure 4a). The amount of

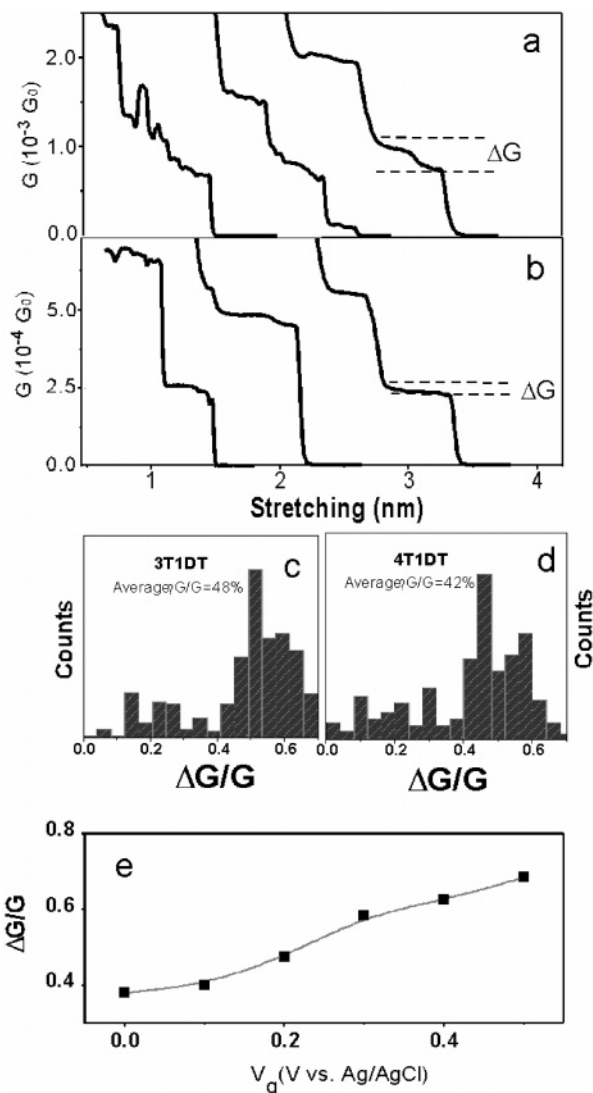


Figure 4. (a) Transient conductance curves recorded during the stretching of individual 4T1DT junctions. The force-induced conductance of the last molecule is marked by ΔG . (b) Transient conductance curves recorded during the stretching of individual 1,8'-octanedithiol junctions are shown for comparison. (c–d) Histograms of the force-induced conductance change, $\Delta G/G$, for 4T1DT (c) and 4T1DT (d) molecules. (e) The force-induced conductance change, $\Delta G/G$, vs electrochemical gate voltage for 4T1DT.

conductance decrease varies from run to run, but the statistical analysis shows that the average conductance decrease is about 48% and 42% per nN for 3T1DT and 4T1DT, respectively (Figure 4c–d). For comparison, we have measured force-induced conductance changes in 1,8'-alkanedithiol (C8), a linear molecule consisting of eight single C–C bonds (Figure 4b). The conductance change is $\sim 10\%$ per nN, which is much smaller than those of oligothiophenes.

A stretching force may change the conductance of a molecule in several ways. First, it can elongate the molecule, which increases the electron pathway. In the case of C8, the conduction mechanism via the saturated C–C bonds is described by electron tunneling or superexchange.^{17,20} Using the elongation length estimated from the spring constant of

the molecule and the tunneling decay constant ($\beta \approx 1 \text{ \AA}^{-1}$) determined experimentally,^{17,20} we estimated that the conductance would decrease by 10%, consistent with the measured conductance decrease. This shows that elongation alone can explain the stretching-induced conductance decrease in C8. However, oligothiophene molecules are made of rigid rings, which are stiffer than C8, and thus result in smaller elongations. Besides, the tunneling decay constant for conjugate oligothiophene molecules is smaller than that of alkanedithiols,^{21,22} so the simple elongation and tunneling model cannot explain the observed large force-induced conductance change in oligothiophenes. Second, stretching may affect the molecule–electrode contacts. Because both C8 and oligothiophene are bonded to electrodes via S–Au bonds, the contact contribution to the observed conductance changes in oligothiophene molecules should be less than $\sim 10\%$. Finally, stretching can distort the electronic states of the molecules. C8 has a large LUMO–HOMO gap, and the distortion in the electronic states is expected to be small, which explains the relative small stretching-induced conductance decrease. In contrast, oligothiophene molecules consist of conjugated double–single bonds, and the alternating double and single bond lengths due to Peierls instability give rise to the HOMO–LUMO gap.¹¹ Because the double bond is more rigid than the single bond, a stretching force will increase the difference in the single and double bond lengths. To the first-order approximation, the HOMO–LUMO gap is proportional to the difference in the single and double bond lengths, so the stretching will increase the HOMO–LUMO gap and decrease the conductance.

We have shown that the conductance increases with the electrochemical gate voltage as the HOMOs are shifted toward the Fermi levels. When shifting the HOMO closer to the Fermi levels, one expects a greater force-induced conductance change on the basis of the above Peierls instability argument. Figure 4e shows that indeed the force-induced conductance change increases from $\sim 40\%$ at 0 V to $\sim 60\%$ at 0.5 V.

In summary, we have studied the charge transport and electromechanical properties of single oligothiophene molecules, 3T1DT and 4T1DT. The longer 4T1DT is more conductive than the shorter 3T1DT. This unusual length-dependent conductance was attributed to a smaller HOMO–LUMO gap and a closer position of the HOMO to the Fermi levels of the probing electrodes for 4T1DT. This conclusion is supported by the UV–vis absorption, electrochemical measurements, and also by the dependence of the conductance on the electrochemical gate, which shifts the HOMO relative to the Fermi levels. Using the electrochemical gate, we have switched the conductance of the molecules between low and high conductance states via oxidation of the molecules. We have studied the electromechanical properties of Au–oligothiophene–Au junctions. A stretching force causes a large decrease in the conductance, which is attributed to an increase in the HOMO–LUMO gap upon stretching on the basis of the Peierls instability model. Both the 3T1DT and 4T1DT junctions break down when the force

is increased to ~ 1.5 nN (a loading rate 40 nm/sec.), corresponding to the breakdown of the Au–Au bond at the contacts.

Acknowledgment. We thank Stuart Lindsay for valuable discussions and DOE (DE-FG03-01ER45943) (B.X.), NSF (X.L.), and “JSPS (The 21st Century COE Program on Nanovision Science)” (H.S.) for financial support.

References

- (1) Aviram, A.; Ratner, M. *Chem. Phys. Lett.* **1974**, *29*, 277.
- (2) Carroll, R. L.; Gorman, C. B. *Angew. Chem. Int. Ed.* **2002**, *41*, 4379.
- (3) Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature* **2000**, *408*, 541.
- (4) Tao, N. J. *Phys. Rev. Lett.* **1996**, *76*, 4066.
- (5) Gittins, D. I.; Bethell, D.; Schiffrin, D. J.; et al., *Nature* **2000**, *408*, 67.
- (6) Tran, E.; Rampi, M. A.; Whitesides, G. M. *Angew. Chem. Int. Ed.* **2004**, *43*, 3835.
- (7) Haiss, W.; van Zalinge, H.; Higgins, S. J.; Bethell, D.; Hobenreich, H.; Schiffrin, D. J.; Nichols, R. J. *J. Am. Chem. Soc.* **2003**, *125*, 15294.
- (8) Xu, B.; Xiao, X.; Yang, X.; Zang, L.; Tao, N. *J. Am. Chem. Soc.* **2005**, *127*, 2386.
- (9) Chen, F.; He, J.; Nuckolls, C.; Roberts, T.; Klare, J. E.; Lindsay, S. *Nano Lett.* **2005**, *5*, 503.
- (10) Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 1441.
- (11) Kittel, C. *Introduction to Solid State Physics*; John Wiley & Sons: New York, 1996.
- (12) Kergueris, C.; Bourgoïn, J. P.; Palacin, S.; et al. *Phys. Rev. B.* **1999**, *59*, 12505.
- (13) Sakaguchi, H.; Hirai, A.; Iwata, F.; et al. *Appl. Phys. Lett.* **2001**, *79*, 3708.
- (14) Zhitenev, N. B.; Meng, H.; Bao, Z. *Phys. Rev. Lett.* **2002**, *92*, 186805/1.
- (15) Xu, B. Q.; Xiao, X. Y.; Tao, N. J. *J. Am. Chem. Soc.* **2003**, *125*, 16164.
- (16) Smit, R. H. M.; Noat, Y.; Untiedt, C.; et al. *Nature* **2002**, *419*, 906.
- (17) Xu, B. Q.; Tao, N. J. *Science* **2003**, *301*, 1221.
- (18) Rubio, G.; Agrait, N.; Vieira, S. *Phys. Rev. Lett.* **1996**, *76*, 2302.
- (19) Frère, P.; Raimundo, J.-M.; Blanchard, P.; Delaunay, J.; Richomme, P.; Sauvajol, J.-L.; Orduna, J.; Garin, J.; Roncali, J. *J. Org. Chem.* **2003**, *68*, 7254.
- (20) Wang, W.; Lee, T.; Reed, M. A. *Phys. Rev. B.* **2003**, *68*, 035416/1.
- (21) Magoga, M.; Joachim, C. *Phys. Rev. B.* **1997**, *56*, 4722.
- (22) Tomfohr, J. K.; Sankey, O. F. *Phys. Status Solidi B* **2002**, *233*, 59.

NL050860J