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Electron transport of oligothiophene derivative molecular device at varied temperature and light illumination

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ABSTRACT

The charge transport of thiol-functionalized thiophene molecular wire incorporated with an α-hydroxyphenyl pyridine group was investigated by a soft stamp-printing approach. Current–voltage characteristics were measured from 95 up to 299 K under both dark and light conditions. The molecular junction exhibits asymmetric conducting characteristics and reversible optoelectronic switching; the on/off ratio at 95 K is of 3 orders of magnitude. The experimental data was analyzed using the Simmons and Fowler–Nordheim tunneling models. The effective barrier height of device is greatly affected by substrate temperature, light illumination and bias polarity. The degree of electronic coupling between the top electrode and molecule has a great impact on the junction charge transport. Reproducible negative differential resistance was also observed at low temperature in dark. The first-principle calculations show that the conduction mainly takes place through the lowest unoccupied molecular orbital of the molecular wire, and the negative differential resistance may result from effect of resonant tunneling.

1. Introduction

One of the current research focuses is metal-molecule-metal junctions exhibiting nonlinear electron transport owing to their potential application as the basic units in molecular electronics [1,2]. So far, a number of molecular devices with intriguing properties such as diode rectification [3], optoelectronic switching [4], dual-conductance transport [5] and negative differential resistance (NDR) [6] have been reported. Of special interests are the switching and NDR behaviors as they may be used for nanoscale memories and logics [7]. For example, van der Molen et al. observed reproducible optoelectronic switching in devices based on diarylethene triggered by light-controlled isomerization [8]. The electrical property of a molecular junction depends largely on the charge transport through either single molecule [9–11] or self-assembled monolayers (SAMs) [12]. To implement molecular devices, a deep understanding of the conduction mechanism is necessary [13–15]. To date, numerous approaches have been developed to investigate the electron transport [16]. The critical factors are shown to include the electrode/molecule interfaces and the molecule itself [17–19]. Engelkes et al. studied asymmetric junctions of the SAMs of alkanethiols or alkane isonitriles by the conducting probe atomic force microscopy (CAFM), and found that low-voltage contact resistance is dependent of the electrode work function [18]. Kaun et al. [20,21] investigated alkanethiols with different length and indicated that the junction transport is largely affected by the molecule itself. The groups of Luo and Frisbie [22] and Tao et al. [23] observed a transition from tunneling to hopping, as the molecular length increases, when studying oligophenylenetriazole and oligothiophene molecules. On the other hand, the intramolecular conformation and inter-molecular interaction

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may also affect the junction charge transport to a large extent [17,24]. For example, molecular wires with different number of thiophene rings were shown to possess high tunneling efficiency [23,25–27]. The energy mismatch between the molecular orbital and the electrode Fermi level can impede the long-range charge transport [28]. To tackle this problem, the incorporation of functional components into the thiophene rings is of considerable interest. For instance, the study of oligothiophene wires integrated with the α-hydroxyphenyl pyridine showed that the intramolecular hydrogen bonding may substantially improve the molecular conductivity [29]. Though such finding is encouraging, the charge transport mechanism still remains an open question.

Generally, temperature-dependence investigations on junction charge transport are crucial not only for understanding but also for undisputed assigning the conduction mechanism of the current–voltage (I–V) characteristics [30,31]. Kim et al. [32] measured the I–V curves of a 1,4-benzene dimethanethiol junction from 30 to 300 K. They indicated that the electrode/molecule contact and subsequently the charge transport are significantly temperature-dependent. Ratner et al. reported that the charge transport of conjugated SAMs junctions changes as the substrate temperature and/or the bias voltage varies [33]. Another important factor that influences the charge transport is light illumination. Although Lehmann et al. [34,35] theoretically studied the electron transport through molecules coupled to leads under the stimulation of external laser signals, few experimental work was focused on the charge transport at various low temperatures and different light conditions.

In this article, we systematically studied the charge transport of addressable crossbar junctions of a thiophene molecule incorporated with an α-hydroxyphenyl pyridine group. I–V characteristics were measured at varied low temperatures under both dark and light conditions, which were analyzed based on the Simmons and the Fowler–Nordheim (FN) tunneling models. Theoretical calculations were also carried out using the Gaussian 09 and the ATK12.2.2 programs for further understanding of the observations [36–37].

2. Experimental details

The crossbar junctions of the oligothiophene derivative were fabricated using a soft polymer stamp-printing method as detailed elsewhere [38,39]. The fabrication started with a silicon (100) wafer covered with 250 nm thermal oxide on both sides. Firstly, conventional photolithography and thermal vapor deposition were carried out to obtain the bottom Au electrode patterns (50 nm-thick). Subsequently, the molecules of interest were self-assembled on the Au electrode surface. The top Au electrode bars were then printed from an elastomeric poly(dimethylsiloxane) (PDMS) stamp pre-coated with a thin Au layer (20 nm-thick). Finally, the sample was placed in a vacuum chamber where low frequency (0.002 Hz) AC I–V characteristics were measured by a HP 3325A synthesizer/function generator and a Keithley 619 electrometer, respectively, from 95 up to 299 K with/without light illumination. The light source used is a florescent light with the intensity of 3.11 cd/m^2 and the wavelength ranging from 400 to 700 nm, respectively. Fig. 1(a) shows the schematic structure of a molecular junction comprised of the oligothiophene molecule with a side chain. The chemical structure of the target molecule, 4-(4-hydroxy-3-(6-(5‴-mercapto-3′,3″,3‴,4-tetramethyl-[2,2′:5′,2″:5″,2‴-quaterthiophen]-5-yl)-3-(5‴-mercapto-3,4′,4″,4‴-tetramethyl-[2,2′:5′,2″:5″,2‴-quaterthiophen]-5-yl)pyridin-2-yl)styryl)benzonitrile (THPT), is shown in Fig. 1(b). Clearly asymmetric electrode/molecule interfaces can be expected in our crossbar junctions: the top electrode softly printed onto the SAMs leaves a physisorbed contact, while the SAMs are anchored to the bottom Au electrode via strong Au–S chemical bonds.

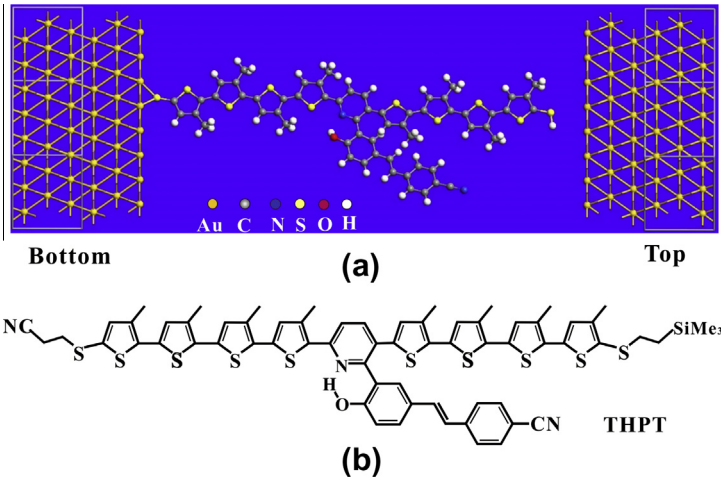

Fig. 1. (a) Schematic molecular junction used in our calculation, where the conjugated molecule is connected to the top and bottom Au electrodes via physisorption and chemisorption, respectively. The terminal sulfur atom is chosen to locate at the threefold site of the Au (111) surface with a distance of 1.71 Å, which gives an Au–S distance of 2.39 Å. The distance between the THPT molecule and the top Au electrode is determined to be 5 Å. (b) Chemical structure of the as-studied THPT molecular wire.