Universal Temperature Crossover Behavior of Electrical Conductance in a Single Oligothiophene Molecular Wire

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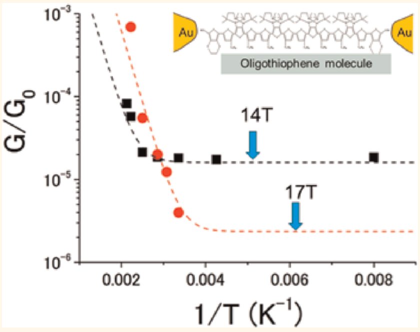
ABSTRACT



We have observed and analyzed a universal temperature crossover behavior of electrical conductance in a single oligothiophene molecular wire. The crossover between the Arrhenius-type temperature dependence at high temperature and the temperature-invariant behavior at low temperature is found at a critical molecular wire length of 5.6 nm, where we found a change from the exponential length dependence to the length-invariant behavior. We have derived a scaling function analysis for the origin of the crossover behavior. After assuring that the analysis fits the explanation of the Keldysh Green's function calculation for the temperature dependence, we have applied it to our experimental results and found successfully that our scaling function gives a universal description of the temperature dependence for all over the temperature range.

KEYWORDS: molecular electronics · temperature dependence of molecular conductance · tunneling · hopping · oligothiophene

Quite often, parallel discussions of charge migration mechanisms have been made on the problems of single molecular electronics and electron transfer reactions.[1−4] The mechanisms have been discussed in terms of coherent tunneling process and incoherent hopping process. Both of the processes are supposed to work in the two problems, whose relative importance may depend on the length of the molecule and the temperature. The former and the latter are described in terms of two completely different mechanisms, *i.e.*, superexchange tunneling and thermally induced hopping (TIH).[1−4] Length dependences of electron transfer rate and single molecular conductance have been actively studied experimentally.[5−16] A change from the exponential length dependence to the length-invariant behavior has been found in both problems. The origin of the change has been discussed in terms of the competition between the superexchange and the TIH processes, which are dominant at shorter length and longer length, respectively.

Two different temperature dependences were also observed in conductance measurements. While temperature-invariant behavior is found for shorter wires, Arrhenius's activation-type temperature dependence is obtained for longer ones.[15,16] Matters of interest here may be summarized as a question asking whether the type of temperature dependence is decided uniquely by the wire length or we may observe both temperature dependences in the same single molecular wire. This problem has been pioneered by Selzer *et al.* using a relatively short molecule.[17,18] They observed both temperature dependences with an interesting crossover behavior between them in the same 1-nitro-2,5-di(phenylethynyl-4-mercapto)benzene molecule. However, the mechanism of the crossover remained largely unresolved. There are wide varieties of the mechanism discussed in the literature ranging from the mechanism based on the Fermi distribution of metallic electrons in electrodes[19] to that between the TIH and the superexchange tunneling processes.[18]

In this article, we will discuss the charge migration mechanism of single molecular wires based on the direction discussed above. First, we describe our experimental details. One of the merits of our experimental

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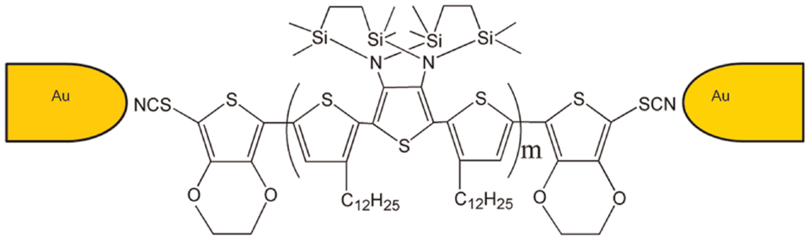

Figure 1. Structure of oligothiophene molecules used in the present study; *m* = 1, 4, and 5.

effort is that we have made the scanning tunneling microscopy (STM) break junction measurements and statistical analysis using histograms.[14] We have also studied the problem at the critical length between the exponential decaying length dependence region and the length-invariant region. Thus our experiments are well-defined, which is very suitable for detailed theoretical analyses. We used an oligothiophene wire with a critical length of 5.6 nm, where we found a change between two charge migration regimes.[12,13] We investigated the temperature dependence of the electrical conductance of the metal/single molecule/metal (MMM) junction in an effort to address the issues above. Figure 1 shows the structure of the oligothiophene molecules with different lengths. The molecules are described as $(2 + 3m)$T-di-SCN where $m = 1, 4$, and 5, *i.e.*, 5T-di-SCN, 14T-di-SCN, and 17T-di-SCN, respectively. In our previous study, we observed that the MMM junctions with molecules up to 14T-di-SCN ($m = 1$ to 4) showed exponential decaying length dependence at room temperature, while length-invariant behavior was observed for 17T-di-SCN ($m = 5$) and longer molecules.[12,13] The critical length was thus determined.

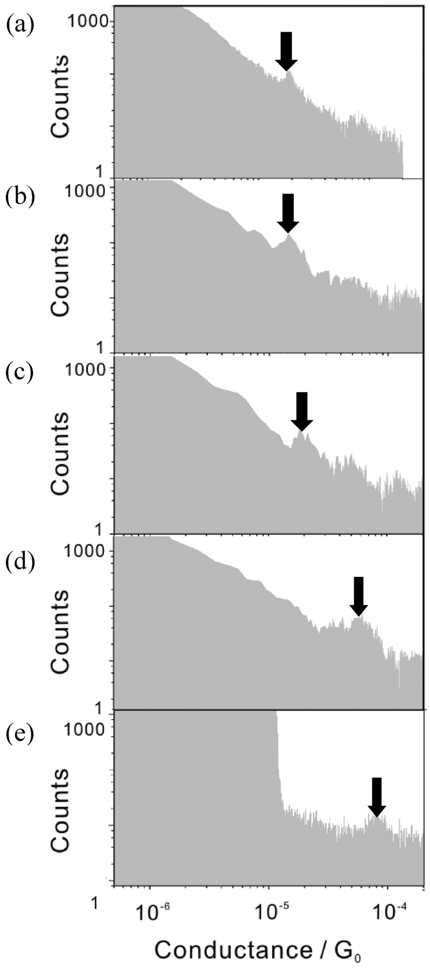

Figure 2. Conductance histograms of the 14T-di-SCN oligothiophene molecule at (a) 125 K, (b) 350 K, (c) 400 K, (d) 450 K, and (e) 470 K.

RESULTS AND DISCUSSION

Figure 2a–e show the conductance histograms for the 14T-di-SCN molecule taken at 125, 350, 400, 450, and 470 K, respectively. The arrows in the figures indicate the peak positions assigned as the molecular conductance values. One can clearly see that the conductance of the 14T-di-SCN molecule remains unchanged at the value of $1.8 \times 10^{-5}\ G_0$ for temperatures up to 350 K and then increases up to $7.9 \times 10^{-5}\ G_0$ at 450 K, which is almost 5 times larger than that at 350 K. We can observe the crossover of electrical conductance behavior clearly in the 14T-di-SCN molecule, as shown in the Arrhenius graph in Figure 3. This behavior was not observed in the other molecules used in the experiment.

Before examining experimental results, here we describe our theory. First, we calculated $I-V$ curves considering the contact effects to the electrodes, temperature effects, and the electron–phonon (e–ph) coupling effects using the extended Su–Schrieffer–Heeger (SSH) model. Theory is given in terms of Keldysh Green's functions, whose details are found in refs 20 and 21. Some descriptions of the model and the parameter values are given in the Supporting Information. Fully self-consistent calculations between electron and phonon transports under e–ph couplings were done including phonon damping due to its coupling to electron–hole excitation, inelastic heat generation, and heat dissipation to the thermalized electrodes. This makes our theory sophisticated enough to cover all the scenarios discussed in the literature.[18,19] The e–ph coupling effect was taken into account within the self-consistent Born approximation (SCBA). We calculated the temperature dependence of $dI/dV|_{V=0}$ from the $I-V$ result, shown in Figure 4. It is

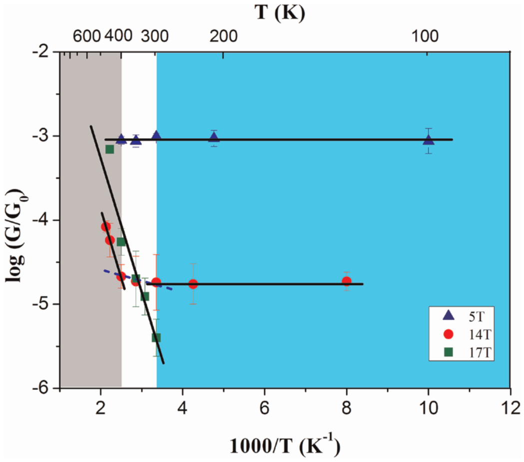

Figure 3. . Arrhenius plot of the conductance for 5T- (▲), 14T- (●), and 17T- (■) di-SCN oligothiophene molecules-based MMM junctions. The line fitted to the plot of 17T-di-SCN is drawn.

very remarkable that an activation-type temperature dependence is obtained within the weak coupling SCBA. We derived the scaling function to describe the temperature dependence of the conductance using this result. We also used, for that purpose, a result of the strong coupling expansion theory where electric current I was derived to be[22]

$$I(V) = \mathrm{Re}[\sigma(eV)]V/d \tag{1}$$

$$\mathrm{Re}[\sigma(\omega)] \propto [(1 - e^{-\beta\omega})/\omega]U(\omega) \tag{2}$$

$$U(\omega) = (\pi/\gamma)^{1/2} \exp[-\sum_q |u_q|^2 \tanh(\beta\omega_q/4)]e^{\beta\omega/2} \times \exp(-\omega^2/4\gamma) \tag{3}$$

where $\beta = 1/k_BT$, and T and k_B are temperature and the Boltzmann constant. We have used the same notations as those in ref 22. On the basis of this result, we propose the following scaling function to describe the temperature dependence of phonon contribution to the conductance, *i.e.*, $\delta G = \mathrm{d}\delta I/\mathrm{d}V|_{V=0}$:

$$S(T) = A \exp(-\tanh(B/T)) + C \tag{4}$$

where A, B, and C denote the scaling parameters. B originally comes from the phonon energy in the strong coupling expansion theory, while parameter A gives a correction to adjust for the difference in conductance values between the high and the low temperature limits. C gives a correction to match with the low-temperature conductance value. A and C are closely related with the low-temperature conductance value and therefore depend much on the length of the molecular wire. More details are discussed in the Supporting Information.

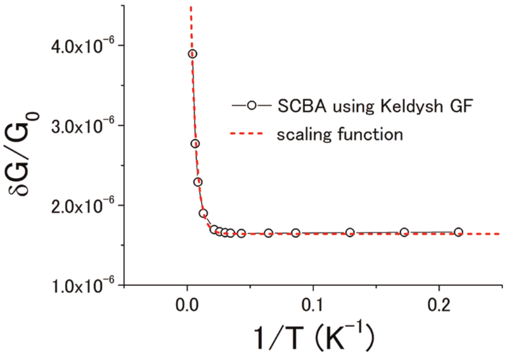

Figure 4. Scaling analysis of the theoretical result obtained by using SCBA based on Keldysh Green's function. The scaling function is given by eq 4, and the scaling parameter values were determined to be $A = 8 \times 10^{-6}\ G_0$, $B = 120$ K, and $C = -1.3 \times 10^{-6}\ G_0$, respectively, where G_0 denotes unit conductance.

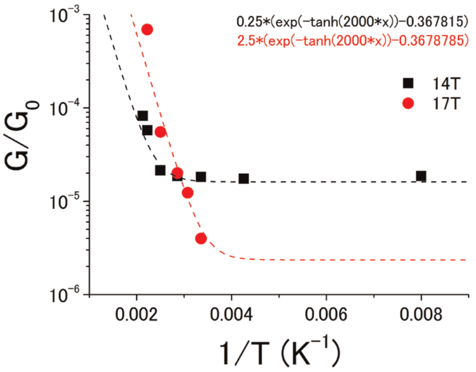

Figure 5. Scaling analyses of the experimental result of the 14T-di-SCN and 17T-di-SCN oligothiophene molecules. The scaling function is given by eq 4, and the scaling parameter values were determined to be $A = 0.25\ G_0$, $B = 2000$ K, and $C = -0.09195375\ G_0$ and $A = 2.5\ G_0$, $B = 2000$ K, and $C = -0.91969625\ G_0$ for 14T-di-SCN and 17T-di-SCN, respectively.

To check the usefulness of our scaling function, we fit our Keldysh Green function calculation results with the scaling function. The result is summarized in Figure 4. We found that the activation energy expressed by B is estimated to be 10.3 meV, which corresponds to the lowest phonon energy value. The phonon mode is calculated to be active in inelastic tunneling spectroscopy, ensuring that the scaling function works well.

We apply this scaling function to analyze the experimental temperature dependence of the conductance. Figure 5 shows the results of 14T-di-SCN and 17T-di-SCN oligothiophene molecules. A fair fit is obtained by using the same value of B, *i.e.*, $B = 172.3$ meV for the two molecules. Using the same value for B, we could also fit the experimental results of the oligothiophene molecules given in Figure 3 by changing the values of A and C. A and C are more strongly dependent on the length of the molecule than B and thus are responsible for the length dependence effect on the conductance. The parameter values for A and C for 14 and 17 thiophenes are given in the caption of Figure 5. C depends on the length in such a way that the low-temperature limit of the conductance

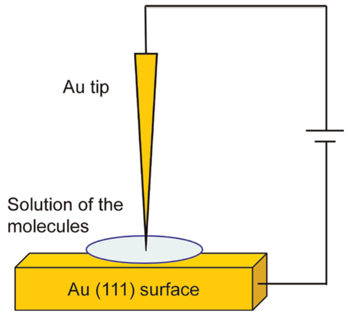

Figure 6. Schematic illustration of STM-break junction experiment.

follows the exponential decay law. The length dependence of *A* is somewhat interesting, as it takes a larger value for 17 thiophene than 14 thiophene. This is seemingly curious, but it may be possible because the number of low-energy states would be larger for 17 thiophene than 14 thiophene. It is very interesting to note that a similar behavior was discussed in ref 15. In Figure 4 of ref 15, the high-temperature conductance of 3-mer and 4-mer is larger than that of 2-mer. This behavior may be understood similarly. Since our scaling function is obtained from the strong coupling formula of the conductance generalized to include a temperature-independent component additionally mimicking the elastic conductance, it will be capable of describing the competition between the TIH and the superexchange tunneling mechanisms. On the other hand, because it gives a good fit to our Keldysh Green's function results, the scaling function successfully covers the possibility of the contact and Fermi distribution effects of metallic electrodes discussed in ref 19 as well.

It should be noted that the parameter *B* plays an important role in determining the crossover temperature, in addition to *A* and *C*. The correspondence of the *B* value to the lowest phonon energy discussed for the theoretical result given in Figure 4 gives a clear reason to support that the phonon energy is involved in determining the crossover temperature. The *B* value of 172.3 meV explaining the experimental result in Figure 5 may be too small for the electronic gap scenario.[19] Actually, the energy gap $\Delta E = E_F - \varepsilon_C$ is estimated from the exponent of the length dependence of the conductance at low temperature for our series of molecules[12] by $\Delta E/t_C \approx 2.5$ where E_F denotes the Fermi level. ε_C and t_C represent the site energy and the transfer integral of the Hamiltonian given by eq S1 in the Supporting Information. Because $t_C \approx 2$ eV, ΔE is estimated to be 5 eV, which is much larger than the *B* value. This is also quite different from the estimate used in ref 19, where a value of the energy gap around 100−200 meV was supposed. Our system is largely different from that discussed in ref 19. This suggests that a purely electronic mechanism[19] is unlikely to explain the temperature crossover behavior. Because we do not have to change the values of *A* and *C* to get a fair fit to the whole experimental temperature dependence of the same single molecular wire, *i.e.*, the 14T-di-SCN oligothiophene molecule, naive interpretation using the competition scenario between the TIH and the superexchange tunneling processes may have to be reconsidered. Special attention, in this regard, may have to be paid to the implication of our results that the competition between the superexchange and TIH processes depends not only on wire length but also on temperature. We may be able to control the competition between two charge transport mechanisms in the same molecular wire by temperature. That is, it should be stressed that the critical length for the change in the length dependence depends on temperature.

CONCLUSION

In summary, we have observed and analyzed temperature crossover behavior of electric conductance in a single oligothiophene wire both experimentally and theoretically. We found that the temperature crossover is determined by the universal temperature scaling function derived and checked here. Our results imply that the competition between the superexchange and TIH processes depends not only on wire length but also on temperature.

METHODS.

Materials. The oligothiophene molecules were synthesized according to the general synthesis protocols described previously.[23−25] Two ends of a molecular wire were terminated with thiocyanate (−SCN) groups, which act as anchors to the Au electrodes.[18,26,27] The 100 nm thick Au layer was prepared by thermal evaporation of 99.999% Au onto a freshly cleaved mica. The substrate was then flame annealed in order to obtain a clean surface and was immersed in a 1 mM toluene solution of the molecules at room temperature.[12,13] After the substrates were removed from the solution, the solvent was evaporated. Gold tips for scanning tunneling microscopy were prepared by mechanically cutting a 0.25 mm Au wire (99.99%).

STM Break Junctions. The electrical conductance of oligothiophene-based MMM junctions was determined using a STM break junction (BJ) method.[28−32] In the STM-BJ method, an Au tip was repeatedly brought into contact with and retracted from a substrate (Figure 6). When the tip is pulled up after contact with the substrate, the measured conductance changes in a stepwise manner at integer multiples of quantum conductance G_0 owing to the formation of a quantum point contact of Au. When molecules are present between the two electrodes (STM tip and substrate), conductance steps are observed below 1 G_0 after further retraction of the two contacts. The conductance steps that appear after the contacts of the two electrodes are attributed to the formation of stable MMM junctions. The conductance of the molecule is determined from the conductance histogram created from five hundreds to thousands of conductance traces measured during the tip retracting processes. Curves showing exponential decay were not chosen to construct the histogram. The bin width was changed to confirm the peak position so that different conductance regions could be analyzed in detail. The full width at half-maximum of the peaks was found by fitting each conductance peak to a

Gaussian distribution. Measurements below and above 300 K were carried out by using homemade instruments equipped with a cryostat (Helitran, Advanced Research Systems) under vacuum conditions ($<1 \times 10^{-4}$ Pa) and commercial STM equipped with a temperature stage (Agilent Technology) in an Ar atmosphere, respectively. The thermal drift after the temperature stabilized was ~0.2 nm/s. The junctions were pulled apart at the fixed speed of 15 nm/s.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Description of the theory for the scaling function analysis. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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