NANO LETTERS

2008
Vol. 8, No. 4
1237-1240

Electrical Conductance of Oligothiophene Molecular Wires

Ryo Yamada,[†] Hiroaki Kumazawa,[‡] Tomoharu Noutoshi,[‡] Shoji Tanaka,[§] and Hirokazu Tada*[,†,||]

Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan, School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan, Research Center for Molecular-Scale Nanoscience, Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan, and CREST, Japan Science and Technology Agency, Honcho, Kawaguchi 333-0012, Japan

Received December 7, 2007; Revised Manuscript Received January 27, 2008

ABSTRACT

A break junction method using a scanning tunneling microscope has been applied to electrical conductance measurement of newly designed oligothiophene molecules terminated with a thiocyanate group. The tunneling conduction was evident from an exponential decay of the conductance as a function of the molecular length up to ca. 6 nm. The tunneling decay constant was estimated to be 0.1 Å^{-1}. The pre-exponential factor was 1.3 $\times$ 10^{-6} S, which was smaller than that observed for alkanedithiols.

π-Conjugated molecules are expected to form high conductive wires[1] because molecular orbitals of them are connected through the molecular framework. In addition, the small energy gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) is favorable for injection and tunneling of charged carriers. The potential ability of π-conjugated molecules as conductive wires is evident from the studies on photoinduced and electrochemical charge transfer rate through molecules.[2–5] It has been shown that the tunneling decay constant of π-conjugated molecules ($\sim$0.2 Å^{-1}) is smaller typically by 1 order of magnitude than that observed for σ-bonded ones ($\sim$1.0 Å^{-1}). Among a variety of π-conjugated molecules, α-linked oligothiophenes are promising molecules as frameworks of molecular electronics because the α-position and β-positions of the molecules can be used to attach linkers and modulators of electronic states, respectively. The length of the oligothiophenes can be precisely controlled and elongated to nanometer range.[2,6,7] Nowadays, 96-mer, which reaches 37 nm long, is synthesized.[8] Although electrical conductance measurements of oligothiophenes with 3 and 4 thiophene units were reported,[9,10] the length dependence has not been investigated. It is essential and interesting to study the length dependence using highly π-conjugated molecules for detail discussion on conduction mechanisms.

In this study, we have measured electrical conductance of oligothiophenes of 5-, 8-, 11-, and 14-mer by a break junction method using a scanning tunneling microscope (STM). In the STM break junction method, a tip of STM is repeatedly brought into and out of contact with a substrate in a solution containing molecules.[11] When the tip is pulled up from the contact, conductance changes in a stepwise manner at an integer multiple of quantum conductance $G_0 = 2e^2/h$ (= 77.4 μS) due to the formation of a single atomic contact of the metal electrodes. After the single atomic contact of the metal electrodes is broken, a new sequence of conductance steps is observed. These conductance steps are attributed to formations of molecular junctions between the tip and the gold substrate. The conductance value of the single molecular junction is determined from a histogram created from hundreds−thousands of measurements. The STM break junction method is convenient and reliable because measurements are readily possible by a commercial STM. In addition, integration of a large amount of data enables researchers to find conductance values of stable junction structures, resulting in high reproducibility. While this technique has been applied to conductance measurement of alkanedithiols,[2] alkyldiamines,[13] phenyldithiols,[14] oligophenylene ethynylene,[15] oligoaniline,[16] carotenoid polyenes,[17] short oligothiophenes,[10] and other molecules,[18] the length of the longest molecule measured in these studies was ca. 4 nm.[17] 14-mer oligothiophene prepared in the present study enabled us to investigate the conduction mechanism up to 6 nm.

The molecules were prepared according to the general synthetic protocols described previously.[18] Purification of all

* Corresponding author. E-mail: tada@molectronics.jp. Address: Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan.

[†] Graduate school, Osaka University.

[‡] School of Engineering, Osaka University.

[§] Institute for Molecular Science.

[||] CREST.

10.1021/nl0732023 CCC: $40.75
Published on Web 03/01/2008

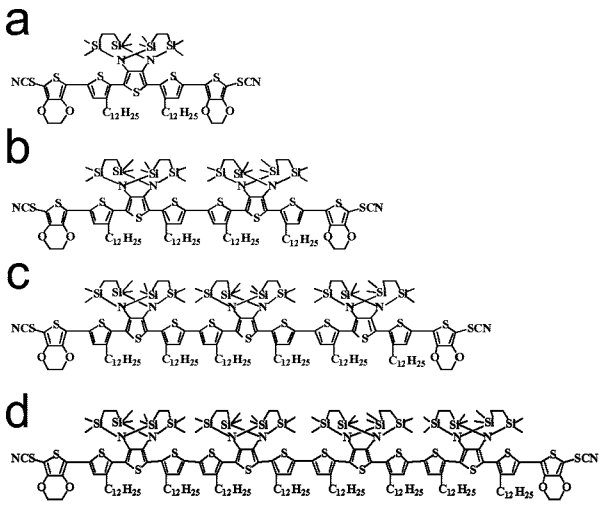

Figure 1. Structures of molecules used in this study: (a) 5T-di-SCN, (b) 8T-di-SCN, (c) 11T-di-SCN, and (d) 14T-di-SCN.

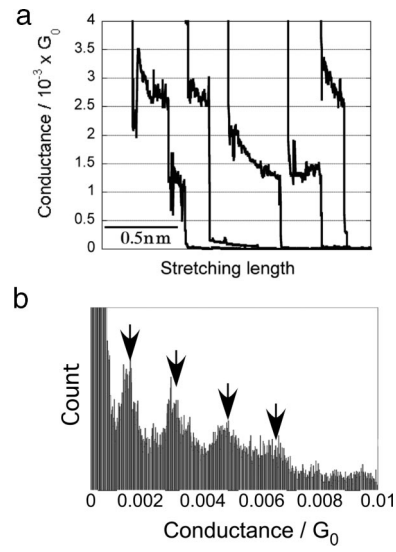

Figure 2. (a) Conductance measured during the stretching process at 30 nm/s in 5T-di-SCN solution. Bias voltage was 100 mV. (b) Conductance histogram of 5T-di-SCN. Arrows indicate a fundamental conductance value interpreted as the conductance of single 5T-diSCN molecule and its multiples.

oligomers was achieved by gel permeation chromatography. The purity of the obtained oligomers was clearly revealed by MALDI-TOF mass spectroscopy using dithranol as matrix. The STM break junction measurement was carried out at room temperature by using mechanically cut gold tips on Au(111) surfaces in ca. 1 mM solution of the molecules in hexadecane. The break junction process was repeated until the conductance of G_0 was frequently observed to ensure the formation of atomically sharp tips. Then, the stretching−current curves were recorded. Conductance histograms were constructed from the 500−1000 individual measurements.

Figure 1 shows structures of a series of oligothiophene molecules used in this study. The thiophene framework was surrounded by an alkylsilyl group, which works as insulating spacers between molecules. *n*-Alkyl chains increase the solubility and obstruct the twisting along the molecular axis. Thiocyanate group was used as an anchor to the electrodes instead of thiols to prevent the polymerization of molecules through the S−S bond formation.

Parts a and b of Figure 2 show typical stretching−current curves and conductance histogram, respectively, obtained in 1 mM solution of 5T-di-SCN. The stretching−current curve shows plateaus that were not observed in pure hexadecane. The peaks indicated by arrows in Figure 2b were integer multiples of a fundamental conductance $G = 1.4 \times 10^{-3}\ G_0$ (1.1×10^{-7} S). We conducted measurements using the molecule with a SCN group only at the one end of the oligothiophene (5T-mono-SCN). No plateaus nor peaks were observed in stretching−current curves and conductance histogram in the same conductance range. Thus, we concluded the plateaus observed in Figure 2a are attributed to the conductance of 5T-di-SCN molecules bridged between the electrodes at the both ends of the molecules and the fundamental value of the peaks in the conductance histogram is the conductance of single 5T-di-SCN. The plateaus sometimes had a slope and decreased by 40% during a stretching process. Similar phenomenon was reported for 3- and 4-mer oligothiophenes.[10] As discussed later, the observed decrease in the conductance is attributed to the change of the LUMO−HOMO gap energy upon stress.

Parts a−d of Figure 3 show a conductance histogram of 5T-di-SCN, 8T-di-SCN, 11T-di-SCN, and 14T-di-SCN. Note that Figure 3a is identical to Figure 2b except that the horizontal axis is drawn in a logarithmic scale. The peaks indicated by arrows were revealed to be integer multiples of fundamental conductance that are ascribed to the conductance of single molecules. The conductance values determined for 8T-di-SCN, 11T-di-SCN, and 14T-di-SCN were 7.0×10^{-4}, 1.5×10^{-4}, and $4.0 \times 10^{-5}\ G_0$, respectively.

In addition to the peaks indicated by arrows, a peak indicated by a gray band was observed around 2.0×10^{-4} G_0 in all histograms. To clarify the origin of this conductance, the control experiment was carried out in 1 mM solution of CH_3SCN. Figure 3e shows the conductance histogram obtained in the control experiment. A single broad peak around $2.0 \times 10^{-4}\ G_0$ (1.6×10^{-8} S) was evident. This result implies that the same junction was formed in the solutions of CH_3SCN and the molecules used in the present experiment. We suppose that the conductance peak around $2.0 \times 10^{-4}\ G_0$ is attributed to a Au-CN:Au junction formed by the residual CN on the gold surface produced by the following chemical reaction.[20]

$$\text{R-SCN} + 2\text{Au} \rightarrow \text{R-S-Au} + \text{Au(CN)}_{\text{ads}}$$

The current–voltage characteristics of the molecules were obtained from the conductance histogram at various voltages from –0.1 to 0.1 V. Plateaus were hardly observed over this potential range. The correlation factors of the linear line fitted to the obtained results were better than 0.95 for all the molecules, and thus the conductance of the molecules was evaluated from the slope of the fitted lines. As shown in Figure 4, the conductance exponentially decreased as a function of the number of the thiophene ring except for 5T-

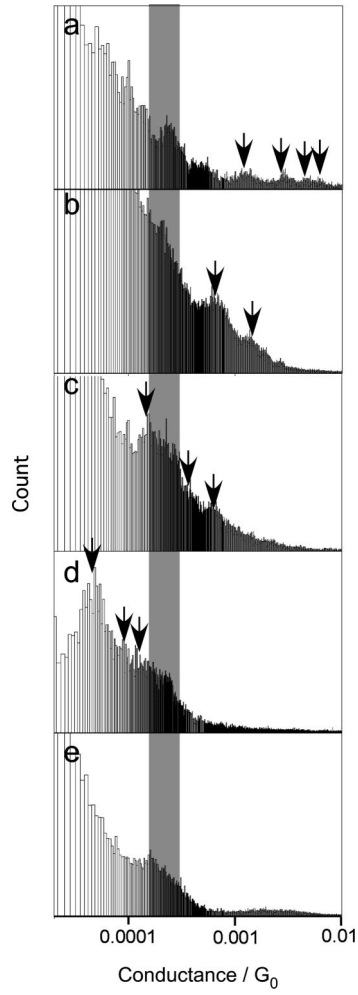

Figure 3. Conductance histogram of 5(a), 8(b), 11(c), 14T-di-SCN(d), and CH_3SCN (e). Arrows indicate fundamental conductance values and their multiples.

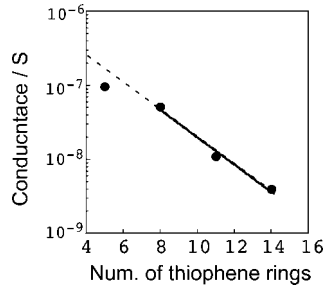

Figure 4. Conductance as a function of the number of thiophenes.

di-SCN. The conductance for the molecules longer than 8T-di-SCN was, therefore, described as $G = G_p \exp(-\beta n)$ where G_p represents the conductance through the contacts, β is a decay constant, and n is the number of thiophene rings or the length of the conduction channel. The decay constant, $\beta = 0.1$ Å^{-1} ($0.42\ n^{-1}$)[21] and $G_p = 1.3 \times 10^{-6}$ S were obtained from the slope of the line fitted to the conductance of 8, 11, and 14T-di-SCN. The observed β was in good agreement with that of porphyrin-thiophene-C_{60} molecules, 0.11 Å^{-1}.[22] This result shows that oligothiophene is a good molecular wire allowing an long-range electric conduction.

The observed $G_p$was smaller than that of Au/alkyldithiols/Au (6×10^{-5} S)[12] although S−Au bond formation was expected for both thiocyanate and thiol groups.[19] The small G_p was reported for diamines [13,23] and dicarboxyl acids[23] and correlated to the strength of the bond to the Au electrode. The magnitude of G_p was also correlated to the bias voltage window for the stable current–voltage measurement, which was –0.4 to 0.4 V for Au/NH_2 and Au/COOH junctions while Au/S junction was stable over +1 V and under –1 V.[23] Considering these trends, the small G_p and bias voltage window, –0.1 to 0.1 V, observed in the present experiment indicated that the bond formed between the molecule and the Au electrode was weaker than that of Au/alkyl-dithiol/Au junctions. There are two possible explanations for the weak bond formation in the present experiment. One is that the molecules adsorbed with the electrodes through nitrogen atoms by forming R-SCN:Au junctions without cleaving the S-CN group. The other possibility is differences in electronic states of the S−Au bonds between alkandithiol and thiocyanated-thiophenes. Considering the fact that the rate of reaction 1 is slow,[20] the formation of R-SCN:Au junction is plausible.

The conductance of 5T-di-SCN was smaller than that expected from the fitting line drawn in Figure 4. One of the possible reasons for this discrepancy is a change of the LUMO−HOMO gap energy as a function of molecular length. It is well-known that the LUMO−HOMO gap energy is approximately proportional to the reciprocal number of thiophene rings.[24] Therefore, conductance is expected to become higher as the number of thiopene units increases if the LUMO−HOMO gap energy is considered. In fact, the conductance of a 4-mer thiophene was reported to be higher than that of a 3-mer thiophene.[10] We measured UV−vis absorption spectra of 5, 8, 11, and 14T-di-SCN in hexadecane solutions to estimate the LUMO−HOMO gap energy. All molecules exhibit absorption around 430 nm, which indicates that conjugation of the π electron is limited to 5-thiophene units, in the longest, in the solutions due to the rotation of thiophene ring. On the contrary, the small β value obtained in the experiment indicates the long order conjugation of π electron. We suppose that the stretching of the molecule enhances the conjugation of π electron during the break junction process.

As mentioned above, the conductance plateau sometimes had a slope as shown in Figure 2a. The decrease in the conductance upon stretching reached 40%. The decrease of the conductance can be caused by elongation of the conducting path, increment of the LUMO−HOMO gap energy of the molecule and that of contact resistance.[10] The distance required to cause the observed decrease in conductance was estimated to be 0.5 nm on the basis of $\beta = 0.1$ Å^{-1}. Although the elongation distance of 0.5 nm seems comparable to the plateau length observed in Figure 2a, the elongation of 0.5 nm requires the extension of 5T-di-SCN by 123%, which is not likely to occur. In addition, the molecules are usually considered to be much more rigid than the gold electrode.[10] Thus, the plateau length is explained by the extension of gold electrodes. Considering the fact that the slopes in

plateaus reported for alkane-dithiols,[10] amines[13,23] and carboxylic acids[23] were much smaller than that observed in the present experiment, the change of contact resistance upon stress does not have strong influence on the change of conductance upon stretching. Thus, we attribute the conductance decrease upon stretching to the change of the LUMO−HOMO gap energy.

In summary, we have measured the electrical conductance of a series of oligothiophene molecular wires terminated with −SCN. The dependence of the conductance on the molecular length up to 14-mer, ca. 6 nm long, showed an exponential behavior with a decay constant $\beta = 0.1$ Å^{-1}. The preexponential factor was 1.3×10^{-6} S, which was much smaller than that observed for alkanedithiols and close to that of alkyldiamines.

Acknowledgment. This work was supported by Grant-in-Aid for Scientific Research on Priority Areas "Science of Ionic Liquids" and "Electron transport through a liked molecule in nanoscale" from the Ministry of Education, Culture, Sports, Science, and Technology of Japan..

References

(1) (a) Salomon, A.; Cohen, D.; Lindsay, S.; Tomfohr, J.; Engelkes, V. B.; Frisbie, C. D. *Adv. Mater.* **2003**, *15*, 1881–1890. (b) Linday, S M.; Ratner, M. A. *Adv. Mater.* **2007**, *19*, 23–31. (c) Joachim, C.; Ratner, M. A. *Nanotechnology* **2004**, *15*, 1065–1075.
(2) Otsubo, T.; Aso, Y.; Takimiya, K. *J. Mater. Chem.* **2002**, *12*, 2565–2575.
(3) Holten, D.; Bocian, D. F.; Lindsey, J. S. *Acc. Chem. Res.* **2002**, *35*, 57–69.
(4) Sikes, H. D.; Smalley, J. F.; Dudek, S. P.; Cook, A. R.; Newton, M. D.; Chidsey, C. E. D.; Feldberg, S. W. *Science* **2001**, *291*, 1519–1523.
(5) Sachs, S. B.; Dudek, S. P.; Hsung, R. P.; Sita, L. P.; Smalley, J. F.; Newton, M. D.; Feldberg, S. W.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1997**, *119*, 10563–10564.
(6) Bäuerle, P. In *Electronic Materials: The Oligomeric Approach*; Mullen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998; pp 198–234.
(7) Otsubo, T.; Aso, Y.; Takimiya, K *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1789–1801.
(8) Izumi, T.; Kobashi, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2003**, *125*, 5286–5287.
(9) Kergueris, C.; Bourgoin, J.-P.; Palacin, S.; Esteve, D.; Urbina, C.; Magoga, M.; Joachim, C. *Phys. Rev. B* **1999**, *59*, 12505–12513.
(10) Xu, B. Q.; Li, X. L.; Xiao, X. Y.; Sakaguchi, H.; Tao, N. J. *Nano Lett.* **2005**, *5*, 1491–1495.
(11) For recent review, see: He, J.; Sankey, O.; Lee, M.; Tao, N.; Li, X.; Lindsay, S *Faraday Discuss.* **2006**, *131*, 145–154.
(12) (a) Xu, B.; Tao, N. J. *Science* **2003**, *301*, 1221–1223. (b) Li, X.; He, J.; Hihath, J.; Xu, B.; Lindsay, S. M.; Tao, N. J. *J. Am. Chem. Soc.* **2006**, *126*, 2135–2141.
(13) Venkataraman, L.; Klare, J. E.; Tam, I. W.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L. *Nano Lett.* **2006**, *6*, 458–462.
(14) Xiao, X.; Xu, B.; Tao, N. J. *Nano Lett.* **2004**, *4*, 267–271.
(15) Xiao, X.; Nagahara, L. A.; Rawlett, A. M.; Tao, N. J. *J. Am. Chem. Soc.* **2005**, *127*, 9235–9240.
(16) (a) Chen, F.; He, J.; Nuckolls, C.; Roberts, T.; Klare, J. E.; Lindsay, S. *Nano Lett.* **2005**, *5*, 503–506. (b) Chen, F.; Nuckolls, C.; Lindsay, S. *Chem. Phys.* **2006**, *324*, 236–243.
(17) (a) He, J.; Chen, F.; Li, J.; Sankey, O. F.; Terazono, Y.; Herrero, C.; Gust, D.; Moore, T. A.; Moore, A. L.; Lindsay, S. M. *J. Am. Chem. Soc.* **2005**, *127*, 1384–1385. (b) Visoly-Fisher, I.; Daie, K.; Terazono, Y.; Herrero, C.; Fungo, F.; Otero, L.; Durantini, E.; Silber, J. J.; Sereno, L.; Gust, D.; Moore, T. A.; Moore, An. L.; Lindsay, S. M. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 8686–8690.
(18) (a) Tanaka, S.; Yamashita, Y. *Synth. Met.* **2001**, *119*, 67–68. (b) Tanaka, S.; Yamasita, Y. *Trans. Mater. Res. Soc. Jpn.* **2001**, *26*, 739. (c) Tanaka, S.; Yamasita, Y. *Synth. Met.* **1999**, *101*, 532–533.
(19) (a) Miura, S.; Kiguchi, M.; Murakoshi, K. *Surf. Sci.* **2007**, *601*, 287–291. (b) Kiguchi, M.; Miura, S.; Hara, K.; Sawamura, M.; Murakoshi, K *Appl. Phys. Lett.* **2006**, *89*, 213104. (c) Ishizuka, K.; Suzuki, M.; Fujii, S.; Takayama, Y.; Sato, F.; Fujihira, M *Jpn. J. Appl. Phys* **2006**, *45*, 2037–2040.
(20) (a) Ciszek, J. W.; Stewart, M. P.; Tour, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 13172–13173. (b) Ciszek, J. W.; Tour, J. M. *Chem. Mater.* **2005**, *17*, 5684–5690. (c) Dreesen, L.; Volcke, C.; Sartenaer, Y.; Peremans, A.; Thiry, P. A.; Humbert, C.; Grugier, J.; Marchand-Brynaert, J. *Surf. Sci.* **2006**, *600*, 4052–4057.
(21) The length of a thiophene unit is estimated to be 0.4 nm.
(22) (a) Nakamura, T.; Fujitsuka, M.; Araki, Y.; Ito, O.; Ikemoto, J.; Takimiya, K.; Aso, Y.; Otsubo, T. *J. Phys. Chem. B* **2004**, *108*, 10700–10710. (b) Ikemoto, J.; Takimiya, K.; Aso, Y.; Otsubo, T.; Fujitsuka, M.; Ito, O. *Org. Lett.* **2002**, *4*, 309–311.
(23) Chen, F.; Li, X.; Hihath, J.; Gyabg, Z.; Tao, N. J. *J. Am. Chem. Soc.* **2006**, *128*, 15874–15881.
(24) For a recent reciew, see: Giershner, J.; Cornil, J.; Egelhaaf, H.-J. *Adv. Mater.* **2007**, *19*, 173–191.

NL0732023