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Combined Effect of Polar Substituents on the Electronic Flows in the Carotenoid Molecular Wires

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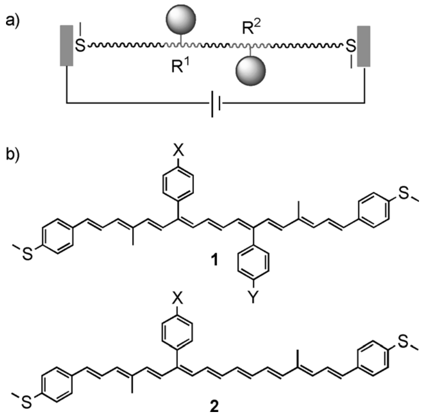
Fabrication of the electric circuits of organic molecular wires with variable conductance is one of the urgent goals in molecular electronics. A plethora of organic molecular wires has been devised, and the measurements of their conductance values were reported.[1] Even though the conductance of a single molecule varies from measurement to measurement, being especially dependent on the geometry of contacts between metal electrodes and the organic molecule, the peak values of the conductance distribution generally agree reasonably when adequate statistical data are collected.[2] The conductance value of the organic molecular wire is a manifestation of the intrinsic bonding nature within the organic molecule. In this context, the carotenoid, which consists of extensive π conjugation, is an ideal organic molecular wire of potentially high electric conductance.[3] The exponential decay of the conductance according to the increased chain length of the carotenoids indicates that the molecular wires with variable conductance could be obtained by the use of carotenoids of different chain length.[4] However, we are concerned herein with the potentially more useful approach of modulating the conductance of a wire of fixed length by inserting conductance modulators (R^1, R^2, etc.) into a carotenoid molecule of a specific chain length (Scheme 1a). Some theoretical and experimental reports on the variation of conductance of molecular wires by a substituent have appeared in the literature;[5] however, no systematic study on the combined effects of the substituent groups on the conductance modulation of organic molecular wires was reported to date. Herein, we report our efforts for the preparation and the conductance measurement of the carotenoid wires with variable conductance by implantation of the polar aromatic substituents to the conjugated polyene chain, and most importantly the combined effect on conductance exerted by the implanted conductance elements.



Scheme 1. a) Conceptual design of the circuit consisting of the carotenoid wires with polar substituents R^1 and R^2 as conductance modulators. b) Carotenoid molecular wires **1** and **2** with the aromatic substituent(s) X of different electronic nature.

Recently, we reported the carotenoid wires **1** (Y = X) and **2** containing the polar aromatic substituent(s) (p-X-C_6H_4-) of different electronic nature (X = OMe, Me, H, and Br) as the conductance (or resistance) element(s) to provide the carotenoid wires with diverse conductance values (Scheme 1b).[6] The difference of the conductance values between **1** (Y = X) and **2** is the quantitative contribution of each aromatic substituent (p-X–C_6H_4-) to the conductance of the molecular wire, which may give an insight in designing the carotenoid wires of any specific conductance values within the range over which conductance can be modulated. The initial conductance measurement has been carried out by conducting atomic force microscopy (cAFM) with a gold-coated probe on the self-assembled carotenoid wires between Au(1,1,1) substrate and an Au (2 nm diameter) particle.[7] The methylsulfide terminal group was utilized as an anchor to gold electrodes for the reasons of stability and synthetic convenience.[6] The measurements of the current/voltage (I/V) characteristics by this method were consistent, and the conductance of each carotenoid wire was obtained as the gradient of the fundamental I/V curve at a low bias region.[7] The quantitative contribution of each polar group

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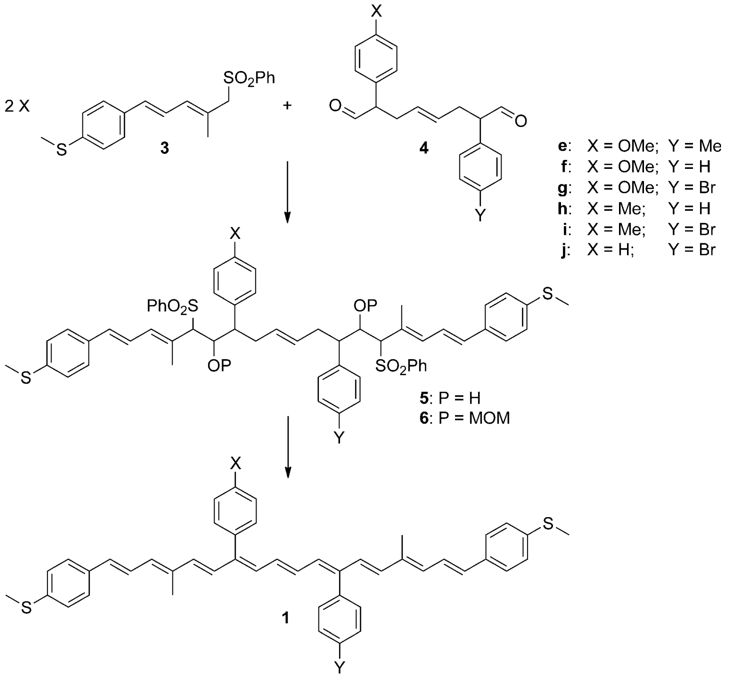
to the conductance of the carotenoid wire **1** was measured to be 15.38 nS for anisyl (X = OMe), 3.56 nS for tolyl (X = Me), 1.53 nS for phenyl (X = H), and −0.90 nS for bromophenyl (X = Br) groups.[6] However, it is crucial to figure out the combined effect on conductance of each element (R^1 and R^2 or *p*-X–C_6H_4-) to design the carotenoid molecular wires with a specific conductance value. It was thus necessary to prepare the carotenoid wires **1** ($X\neq Y$) with different combinations of the two polar aromatic substituents and to measure the conductance values to find out the underlying trend of conductance modulation.

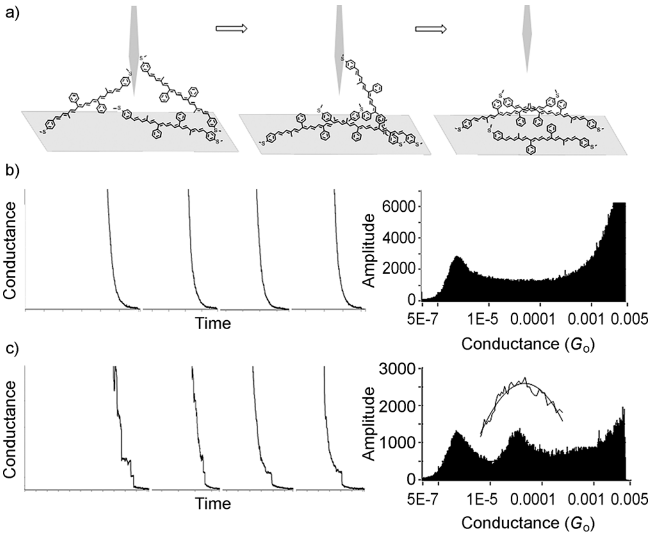
The synthesis of the carotenoid molecular wires **1** ($X\neq Y$) containing two different polar aromatic substituents is presented in Scheme 2. The allylic sulfone **3**, which has been specially designed for the terminal part of the carotenoid wires, was coupled with the key 4-octenedials **4** that contained two different polar aromatic groups at 2- and 7-positions.[8] Six 4-octenedials **4e–j** can been prepared by the selection of two groups out of the four different X substituents (MeO, Me, H, Br). The detailed synthesis of dialdehydes **4** is described in the Supporting Information. The coupling has been carried out at −78 °C by deprotonation of allylic sulfone **3** with *n*-butyllithium, followed by the addition of dialdehydes **4**, and then quenching with 1 M HCl at that temperature to prevent the retro reaction. It is neither suggestive nor necessary to separate the stereoisomeric coupling products, because six new chiral centers are generated by the coupling reaction, which will be destroyed eventually in the final elimination step. The hydroxyl groups of the coupling products **5** were protected under a solvolytic condition in dimethoxymethane with P_2O_5 to give the methoxymethyl (MOM) ethers **6**. A couple of the double elimination of MOM and SO_2Ph groups produced the desired carotenoid wires **1**, which were easily purified by recrystallization from CH_2Cl_2 and MeOH to give all-*trans*-carotenoid chains (7-(*Z*),12-(*Z*)-carotenoids according to the IUPAC naming rule).[9]



Scheme 2. Synthesis of the carotenoid molecular wires **1e–j** ($X\neq Y$) with the aromatic substituents of different electronic nature as the conductance (or resistance) elements.

Even though the measurement of *I*/*V* curves of the molecular wires by using cAFM was consistent, it was somewhat tedious and laborious, because it required not only to prepare well-defined self-assembled monolayers of the molecular wires, but also the statistical treatments of several thousands of data sets for each molecular wire to find out the fundamental *I*/*V* curve.[7] Instead, we decided to use the repeated break-junction method developed by Xu and Tao for the fast and efficient measurement of the conductance of the carotenoid molecular wires.[10]

A highly diluted solution (0.5 μM) of the carotenoid molecule in mesitylene was prepared and placed on a gold substrate. When the gold STM probe was pushed into the gold substrate (current set point 300 pA; bias −0.3 V; ramp rate 8 V s^{-1}; pre-amplification 10 nAV^{-1}), it makes contacts with the carotenoid molecules in the solution; as it is pulled away from the substrate, the contacts are subsequently broken (Scheme 3 a). Several control curves in mesitylene and the resulting control histogram are shown in Scheme 3 b. Discrete steps were observed in the sample current curves over time, which correspond to an integer number of molecular



Scheme 3. Conductance measurement of the carotenoid wire **1c** (X = Y = H in Scheme 2) by the repeated break-junction method. a) Making and breaking contacts between the STM probe and the carotenoid wires anchored to the gold substrate when the probe is pushed into and pulled away from the substrate. b) Control conductance curves over time and the control histogram. c) Steps in the sample conductance curves over time, which indicate the number of carotenoid molecules that make contacts to the STM probe and the histogram of the conductance value of the carotenoid wire (Gaussian fit to the conductance histogram is also shown above).

wires bridging the substrate and the probe (Scheme 3c). Thousands of measurements can be completed within an hour, and the results were plotted in a histogram to give the conductance value of the single-carotenoid wire in G_0. The conductance value at the maximum count of the Gaussian fit around the histogram of the first local maximum after that from the base line in the conductance curve was selected as the conductance of a single-carotenoid wire in G_0. The dispersion of the conductance values is presumably due to the different contact geometries between the molecular wires and the probe (and the substrate).[11]

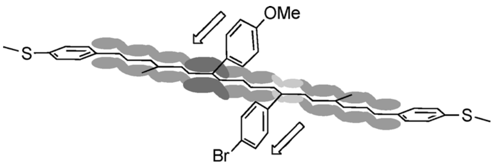
The conductance values of the original four carotenoid wires **1a**–**d** (X = Y) were first measured by the break-junction method to compare with those obtained from the *I*/*V* measurement on the carotenoids between metal contacts (Table 1, entries 1–4). Once again, the electron-releasing anisyl group provided the highest conductance value (17.07 nS), whereas the electron-withdrawing bromophenyl group gave the lowest one (1.15 nS) among the series. There was a good correlation between the two measurement methods, and the values obtained by the break-junction method were roughly half of those by the *I*/*V* measurement, which presumably reflected the geometrical differences of the same carotenoid molecule according to the measurement method: compression of the chain molecule in the AFM versus elongation of the chain molecule in the STM. The conductance measurement on the new carotenoid wires **1e**–**j** with two different substituent combinations was then carried out by the break-junction method (Table 1, entries 5–10). We found a very interesting relationship between the conductance of the asymmetric wires **1e**–**j** and that of the symmetric ones **1a**–**d**. The conductance value of the wire **1e** containing anisyl and tolyl substituents was very close to that of the symmetric wire **1b** containing two tolyl groups. The conductance values of the asymmetric wires **1f** and **1h** containing a phenyl group, as the lower conductance element, were almost same as that of the symmetric wire **1c** containing two phenyl groups. The same trend was observed for the wires **1g**, **1i**, and **1j** containing a bromophenyl group as the lower conductance element, conductance values of which were not much different from the symmetric wire **1d** with two bromophenyl groups. The total conductance of the carotenoid wires containing two polar aromatic substituents is controlled mainly by the more electron-withdrawing substituent, whereas the more electron-donating one contributes to the fine tuning: the conductance values of **1f** (MeO, H) and **1h** (Me, H) are 3.44 and 3.09 nS, respectively, and those of **1g** (MeO, Br), **1i** (Me, Br), and **1j** (H, Br) are 1.50, 1.49, and 1.37 nS, respectively.

Table 1. The conductance values of the carotenoid wires **1** with the substituents C_6H_4–X and C_6H_4–Y.

Entry	**1** (X, Y)	Conductance [*I*/*V*][a] [nS]	Conductance (break junction)[b] [nS]	G_o (stand. error)
1	**1a** (MeO, MeO)	33.46 ± 5.19	17.07 ± 0.17	2.202×10^{-4} (2.151×10^{-6})
2	**1b** (Me, Me)	10.41 ± 0.94	5.56 ± 0.07	7.174×10^{-5} (8.721×10^{-7})
3	**1c** (H, H)	7.45 ± 2.17	2.86 ± 0.03	3.692×10^{-5} (3.318×10^{-7})
4	**1d** (Br, Br)	3.37 ± 1.30	1.15 ± 0.01	1.483×10^{-5} (1.194×10^{-7})
5	**1e** (MeO, Me)	–	5.63 ± 0.10	7.257×10^{-5} (1.230×10^{-6})
6	**1f** (MeO, H)	–	3.44 ± 0.04	4.442×10^{-5} (5.370×10^{-7})
7	**1g** (MeO, Br)	–	1.50 ± 0.04	1.937×10^{-5} (4.565×10^{-7})
8	**1h** (Me, H)	–	3.09 ± 0.02	3.987×10^{-5} (3.079×10^{-7})
9	**1i** (Me, Br)	–	1.49 ± 0.03	1.919×10^{-5} (4.435×10^{-7})
10	**1j** (H, Br)	–	1.37 ± 0.02	1.768×10^{-5} (2.961×10^{-7})

[a] Conductance calculated as the gradient of the fundamental current/voltage (*I*/*V*) curve at a low bias region. [b] Conductance measured by the break-junction method at the maximum peak height of the Gaussian fit to the conductance histogram.

It may not be easy to explain the theoretical background for the combined effect of the two different polar aromatic substituents on the conductance of the carotenoid wire. The orthogonal disposition of the aromatic substituents to the conjugated polyene chain surely does not alter the HOMO–LUMO gap of the carotenoid series **1**,[6,12] which is supported by the almost identical UV absorption data (see the Supporting Information). The electron-releasing anisyl substituent would increase the near-by π-electron density along the conjugated polyene chain, whereas the electron-withdrawing bromophenyl group would decrease it (Scheme 4). The flow of π electrons along the carotenoid wire is controlled by the more electron-withdrawing group of the two. In other words, there is a "bottle-neck effect" by an electron-withdrawing substituent on the conductance of the carotenoid wires: the more resistive contributor controls the total conductance of the carotenoid wires. The overall effect after quantum interference of the two polar substituents was lowering the HOMO of the carotenoid relative to the gold Fermi level by the resistive modulator, thereby lowering the total conductance of the wire. The conductance of the carotenoid wire containing the anisyl and the bromophenyl groups is obviously controlled by the more resistive bromophenyl substituent.



Scheme 4. Control of the electronic flow in the carotenoid wire by the resistive substituent: a "bottle-neck" effect in the π-electron density by the electron-withdrawing substituent.

In summary, the carotenoid molecular wires containing two different polar aromatic substituents as the conductance (or resistance) modulators were synthesized, and the electric conductance of the wires was measured by the repeated break junction method. The combined effect on the electronic flows by each polar substituent of the carotenoid wire was disclosed. The conductance of the carotenoid molecular wire is mainly controlled by the electron-withdrawing substituent, whereas a fine tuning is allowed by the electron-donating element. We are currently investigating the effect of multiconductance elements and their (direct or paralleled) connectivity on the total conductance of the carotenoid wires.

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Keywords: carotenoids · conductance · electrochemistry · molecular electronics · molecular wire

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[1] a) C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, *408*, 541–548; b) J. M. Tour, *Acc. Chem. Res.* **2000**, *33*, 791–804; c) F. Giacalone, J. L. Segura, N. Martin, J. Ramey, D. M. Guldi, *Chem. Eur. J.* **2005**, *11*, 4819–4834; d) R. M. Metzger, *J. Mater. Chem.* **2008**, *18*, 4364–4396; e) D. K. James, J. M. Tour, *Chem. Mater.* **2004**, *16*, 4423–4435.

[2] S. M. Lindsay, M. A. Ratner, *Adv. Mater.* **2007**, *19*, 23–31.

[3] a) G. Leatherman, E. N. Durantini, D. Gust, T. A. Moore, A. L. Moore, S. Stone, Z. Zhou, P. Rez, Y. Z. Liu, S. M. Lindsay, *J. Phys. Chem. B* **1999**, *103*, 4006–4010; b) G. K. Ramachandran, J. K. Tomfohr, J. Li, O. F. Sankey, X. Zarate, A. Primak, Y. Terazono, T. A. Moore, A. L. Moore, D. Gust, L. A. Nagahara, S. M. Lindsay, *J. Phys. Chem. B* **2003**, *107*, 6162–6169.

[4] J. He, F. Chen, J. Li, O. F. Sankey, Y. Terazono, C. Herrero, D. Gust, T. A. Moore, A. L. Moore, S. M. Lindsay, *J. Am. Chem. Soc.* **2005**, *127*, 1384–1385.

[5] a) E. Leary, S. J. Higgins, H. van Zalinge, W. Haiss, R. J. Nichols, *Chem. Commun.* **2007**, 3939–3941; b) F.-R. F. Fan, J. Yang, L. Cai, D. W. Price Jr., S. M. Dirk, D. V. Kosynkin, Y. Yao, A. M. Rawlett, J. M. Tour, A. J. Bard, *J. Am. Chem. Soc.* **2002**, *124*, 5550–5560; c) Y. Li, G. Yin, J. Yao, J. Zhao, *Comp. Mater. Sci.* **2008**, *42*, 638–642; d) T. A. Papadopoulos, I. M. Grace, C. J. Lambert, *Phys. Rev. B* **2006**, *74*, 193306/1–193306/4.

[6] J. Maeng, S. B. Kim, N. J. Lee, E. Choi, S.-Y. Jung, I. Hong, S.-H. Bae, J. T. Oh, B. Lim, J. W. Kim, C. J. Kang, S. Koo, *Chem. Eur. J.* **2010**, *16*, 7395–7399.

[7] X. D. Cui, A. Primak, X. Zarate, J. Tomfohr, O. F. Sankey, A. L. Moore, T. A. Moore, D. Gust, G. Harris, S. M. Lindsay, *Science* **2001**, *294*, 571–574.

[8] a) J.-H. Min, S.-Y. Jung, B. Wu, J. T. Oh, M. S. Lah, S. Koo, *Org. Lett.* **2006**, *8*, 1459–1462; b) S.-Y. Jung, J.-H. Min, J. T. Oh, S. Koo, *J. Org. Chem.* **2006**, *71*, 4823–4828; c) S. B. Kim, H. Kim, B. Lim, J. Meang, S.-H. Bae, E. Choi, J. T. Oh, I. Hong, S.-Y. Jung, J. E. Yeo, S. Koo, *Pure Appl. Chem.* **2011**, *83*, 613–620.

[9] a) S. K. Guha, S. Koo, *J. Org. Chem.* **2005**, *70*, 9662–9665; b) E. Choi, J. E. Yeo, S. Koo, *Adv. Synth. Catal.* **2008**, *350*, 365–369.

[10] B. Xu, N. J. Tao, *Science* **2003**, *301*, 1221–1223.

[11] X. Li, J. He, J. Hihath, B. Xu, S. M. Lindsay, N. J. Tao, *J. Am. Chem. Soc.* **2006**, *128*, 2135–2141.

[12] K. Golibrzuch, F. Ehlers, M. Scholz, R. Oswald, T. Lenzer, K. Oum, H. Kim, S. Koo, *Phys. Chem. Chem. Phys.* **2011**, *13*, 6340–6351.

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