

Conductance Control in Stabilized Carotenoid Wires

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A study of molecular electronics of organic nanowires has been a popular research topic in the past decade not only because of a booming atmosphere of nanoscience and engineering but also a need for the smaller, faster, and flexible substitutes for the conventional metallic wires.^[1–5] The self-assembly of organic molecules containing a terminal thiol group on a gold substrate allows the measurement of electric conductance of the organic molecules using conducting Atomic Force Microscopy (c-AFM).^[6,7] Reproducible measurement of molecular conductance is possible by through-bond contacts (e.g., S–Au bond) between the organic molecules and metal electrodes.^[8,9] However, materialization of high and controllable conductance in organic nanowires up to the level of metallic ones has been an elusive dream. Nevertheless, several nanometer-sized organic molecules such as *p*-phenylene-ethylene oligomers,^[10] *p*-phenylene-ethynylene oligomers,^[11] and especially carotenoids showed somewhat promising properties as a conducting molecular wire.^[12,13] It was pointed out that the existence of conjugated unsaturated carbon–carbon bonds, reflecting delocalized π -electron system, was essential for high conductance of organic molecular wires.^[14]

Carotenoids, natural products known as a strong antioxidant as well as a harmless red pigment, also play an important role of transferring electrons in biological processes

such as visual action and photosynthesis.^[15,16] The potential of these ideal molecular wires was not fully elucidated but rather limitedly investigated under carefully controlled conditions mainly due to their thermal and photochemical instabilities.^[12,13] The molecular conductance of the carotene dithiol **1** with typical nine C=C bond conjugation (Figure 1), submerged in toluene under argon atmosphere was only 0.28 nS (nano-Siemens) even though it was still 6–7 orders of magnitude higher than that of *n*-alkane of equivalent chain length.^[13,17] The molecular conductance of the carotenoid wires decreased exponentially with a small decay constant ($\beta = 0.22 \text{ \AA}^{-1}$) as the number of double bonds in conjugation increased.^[17] Our experience in synthesizing carotenoids guided us to design the conceptually new and seemingly stable carotenoids to challenge the possibility of improving and diversifying the molecular conductance of carotenoids of the same size, so that the electric circuits of the stable carotenoid wires with various conductances (or resistances) may be realized in practical sense.

The instability of carotenoids is an inevitable consequence of their antioxidant activities in quenching singlet oxygen and scavenging reactive radical species.^[18,19] The synergistic protective effect of carotenoids in combination with vitamin E containing the aromatic phenyl group against photodynamic cell damage has been reported.^[20] The enhanced antioxidant efficiency of carotenoids was explained by the prevention of free radical-mediated carotenoid degradation or repair of the semi-oxidized carotenoid molecules by vitamin E. We thus devised the novel carotenoid wires **2** so as to provide the labile conjugated polyene chain with stability as well as various conductances by attaching the aromatic phenyl groups containing the *para*-substituent X (OMe, Me, H, and Br) of diverse electronic natures to the polyene chain at C-13 and C-13' (Figure 1). The stability of carotenoids **2** by the phenyl groups might be expected from the repulsive steric interactions with attacking nucleophiles and/or the reversible trapping of incoming radicals (e.g., reactive oxygen species) that would cause fragmentations of the conjugate polyene chain. The benzene rings containing a *para*-

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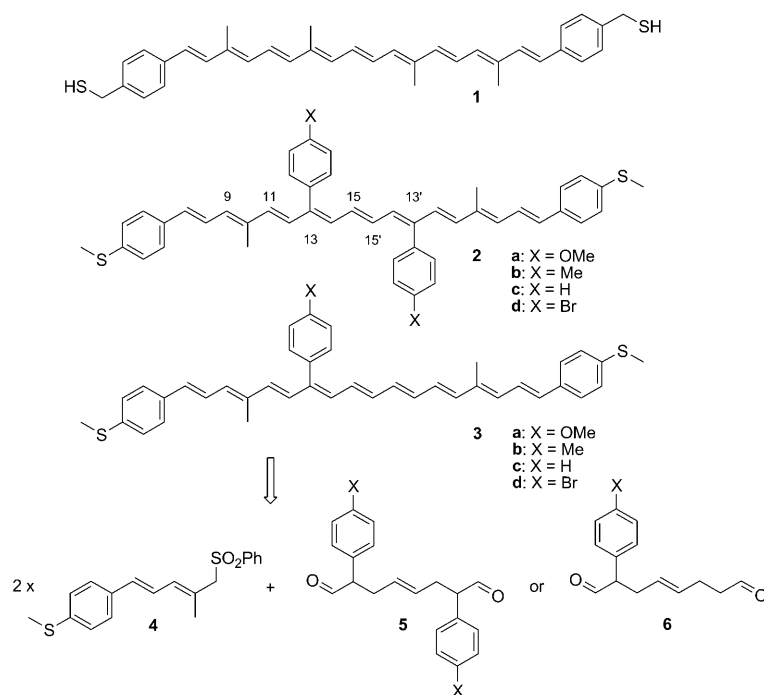


Figure 1. Conventional carotenoid wire **1**, and the novel carotenoids **2** and **3** as a single-molecular wire with conductance control, and their retro-synthetic method.

methylthio group instead of methylenethiol of **1** are connected to the conjugated polyene chain at both ends in order to establish the fully delocalized π -electron system and to prevent the oxidation of thiol to disulfide.^[21] It was reported that the conductance of benzenedithiol was 20 times bigger than that of benzenedimethanethiol,^[22] and that thioethers also formed a stable self-assembled monolayer (SAM) on a gold substrate.^[23,24] Carotenoids **3** have been devised in order to quantitatively evaluate the electronic effect of each phenyl group containing the *para*-substituent X (OMe, Me, H, and Br) on the conductance of the carotenoid wires **2** (Figure 1). The difference between the conductivity values of the carotenoid wires **2** and **3** with the same X would reveal the contribution of each phenyl substituent, so that designing of the carotenoid wires of a specific conductance (or resistance) may be possible.

Contrary to the typical synthesis of the carotenoids of natural origin which utilized the Wittig reactions of crocetin dialdehyde or its higher (or lower) homologues,^[13,17] the synthesis of the carotenoids **2** and **3** containing phenyl substituents was not a trivial event. After several years' trial and errors, we finally completed the synthesis of the novel carotenoids **2** and **3** by the application of the double elimination protocol to the coupling product between the newly proposed dialdehyde **5** or **6** and two equivalents of allylic sulfone **4** (Figure 1).^[25–28] The carotenoids were purified by recrystallization and characterized to be all-*trans* configuration. These carotenoids were stable enough to be stored at 0°C in the dark over a year without any decomposition. The

experimental details are included in Supporting Information.

An electric circuit has been assembled by embedding the carotenoids in an insulating and supporting monolayer of methyl(octadecyl)sulfane on a gold surface (Figure 2).^[29] Methyl sulfide of octadecane instead of the thiol itself was utilized to form the monolayer in order to allow the comparable bond strength to gold with those of the carotenoids **2** and **3** containing the terminal methylthio groups. It is noteworthy that the formation of pits on a gold surface which is an indication of a strong S–Au bond is also observed in this case (Figure 2B).^[30] Adsorptions of methyl(octadecyl)sulfane and the carotenoid **2c** (X = H) on a gold substrate were also confirmed by XPS (see Figures S2 and S3 in the Supporting Information). The self-assembly of 2 nm-size gold particles on top

of the other methylthio group of the embedded carotene wires completed the electric circuit.^[31] Even though the use of a large gold particle (e.g., 5.4 nm in diameter) is reported to be advantageous by eliminating the distortions in I–V curves both through Coulomb blockade and the intrinsic electronic gap in a small particle,^[32] we utilized 2 nm gold particles in order to fairly compare the conductance of our carotenoid wires with the literature values. A gold-coated AFM probe was used as an electrode to contact the carotenoid molecule through a gold nanoparticle.

The c-AFM measurements were carried out under inert nitrogen atmosphere. However, the measurements obtained under air were practically the same. It was not necessary to submerge the sample and probe in an insulating liquid in order to obtain reproducible results, which partly demonstrated the stability of the novel carotenoid wires. The force exerted by the cantilever on the sample may produce artifacts in the current measurement, and was controlled to be less than 3 nN (nano-Newton) to give reliable and reproducible results. No hysteresis was observed according to the direction of the voltage sweep. A maximum bias of ± 0.8 V could be applied without bias-dependent changes of the current–voltage characteristics from sweep to sweep. Current–voltage (*I*–*V*) curves were measured on 1000 sample contacts for each carotenoid, and obtained as several distinct groups of curves (see Figures S4–S11 in Supporting Information). Each curve was divided by the appropriate integer, a continuous divisor, to lie on the fundamental curve which represents a single carotenoid molecular electronics.^[8] Histo-

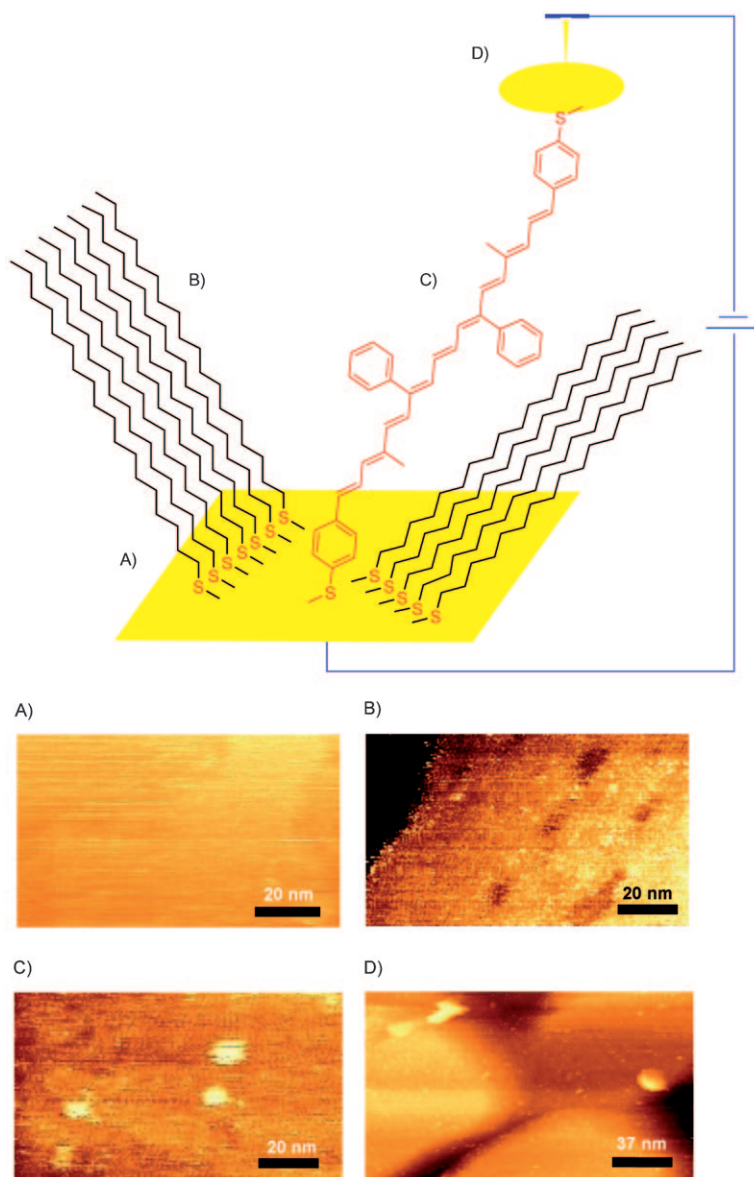


Figure 2. Schematic diagram of the electric circuit assembly (top) and STM image of the film at each stage (bottom). The circuit was assembled by embedding the carotene wire C) in a self-assembled methyl(octadecyl)sulfane monolayer B) on a gold surface A). A 2 nm diameter gold particle D) was then placed on the top of the carotene wire. The dark spots in B) correspond to pits. Images were taken in constant current mode at 47 pA and +1.4 V using a Pt/Ir (80:20) probe.

gram of the current divisor showed peaked values at integer 1, 2, 3, and 4, which signified that mostly 1–4 molecules of the carotenoid assembled below a gold particle. The representative I – V curves of each single carotenoid wire containing different *para*-phenyl substituent X are plotted together (Figure 3). The representative I – V curves of each carotenoid are not the average of the fundamental curves, but selected from them so as to closely match with the average conductance value obtained from the fundamental curves. Conductance of a molecular wire can be obtained as the gradient of the I – V curve at the ohmic region at low-bias (Table 1).^[7] The conductance values of the carotenoid wires were ob-

tained statistically from the gradients of the fundamental curves which gave the linear regression coefficient R^2 of 0.98 or higher at low bias region.

The I – V curves are mostly symmetrical for the carotenoids **2** and slightly asymmetrical for the carotenoids **3**, and show steep slopes for the wires with electron releasing groups. The carotenoid **2a** containing two electron-releasing *para*-anisyl groups (X=OMe) gives the highest conductance of 33.46 nS, which is 120 times bigger than that of the carotenoid **1**. One *para*-anisyl group of **3a** is more potent in giving higher conductance than two *para*-tolyl groups (X=Me) of **2b**. The carotenoids **2c** and **3c** (X=H) behave unexpectedly: the wire **2c** containing two phenyl groups gives bigger current values than the wire **3c** containing one from –0.12 to +0.22 V, but it is reversed in the other regions. An electron-withdrawing *para*-bromophenyl group (X=Br) provides more resistance rather than conductance. Although the most resistive carotenoid among the series is the wire **2b** containing two *para*-bromophenyl groups, its conductance value of 3.37 nS is still 12 times bigger than that of the carotenoid **1**, which explains the importance of the connecting group (methylated benzenethiol versus benzenemethanethiol) between the conjugated polyene chain and gold metal.

The quantitative effect of each phenyl group containing the *para*-substituent X (MeO, Me, H, and Br) on the conductance of the carotenoid wires **2** was obtained by subtracting the conductance values of **3** from those of **2** with the same X (Table 2). The *para*-anisyl group (X=OMe) increases the conductance by 15.38 nS, and the groups of *para*-tolyl (X=Me) and phenyl (X=H) contribute to the conductance by 3.56 and 1.53 nS, respectively. The *para*-bromophenyl group (X=Br), on the other hand, decreases the conductance by 0.90 nS. This trend of increasing conductance generally coincided with the electron-donating ability of each substituent X, and thus the conductance values contributed

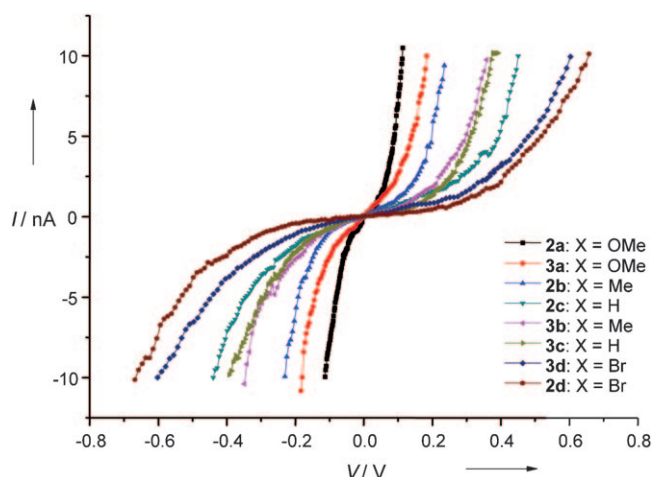


Figure 3. I - V curves of the novel carotenoids **2** and **3** showing different conductance values according to the electron donating or withdrawing ability of the substituent group X .

Table 1. Conductance of the carotenoid wires **2** and **3**, and their $\lambda_{\max}$ values in UV spectra.

Carotenoid, X	Low bias region	Conductance [nS] ^[a]	$\lambda_{\max}$ [nm]
2a : MeO	-0.05 – +0.05	33.46 ± 5.19	464, 492, 526
3a : MeO	-0.05 – +0.05	18.08 ± 2.85	457, 484, 517
2b : Me	-0.10 – +0.10	10.41 ± 0.94	464, 491, 526
3b : Me	-0.10 – +0.10	6.85 ± 1.93	457, 484, 517
2c : H	-0.15 – +0.15	7.45 ± 2.17	462, 490, 524
3c : H	-0.05 – +0.05 ^[b]	5.92 ± 0.55	457, 483, 517
2d : Br	-0.20 – +0.20	3.37 ± 1.30	465, 490, 524
3d : Br	-0.20 – +0.20	4.27 ± 0.76	457, 483, 517

[a] The values were obtained as the average and the standard deviation of the gradients of I - V curves, which gave the linear regression coefficient R^2 of 0.98 or higher in the low bias region indicated. [b] A relatively narrow voltage region was selected due to the unsymmetrical shape of the I - V curves for **3c**.

Table 2. Effect of each phenyl group with *para*-substituent X on the conductance of the carotenoid wires **2** and the Hammett constant of X .

Phenyl group (X)	Conductance [nS] ^[a]	Hammett constant (σ)
anisyl (MeO)	15.38	-0.27
tolyl (Me)	3.56	-0.17
phenyl (H)	1.53	0
bromophenyl (Br)	-0.90	0.23

[a] The values were obtained by the difference of the conductance values between di- and monosubstituted carotenoid wires **2** and **3** with the same substituent X .

by each phenyl group with a *para*-substituent X were plotted over the Hammett constant (σ) for each X (Figure 4), which was originally developed to correlate the substituent effect of aromatic compounds with their chemical reactivity.^[33] Contrary to the theoretical prediction in a related study, it did not show a linear relationship between the conductance and its Hammett constant.^[34]

We believe the phenyl groups at C-13 and C-13' of the carotenoids practically do not participate in the conjugation

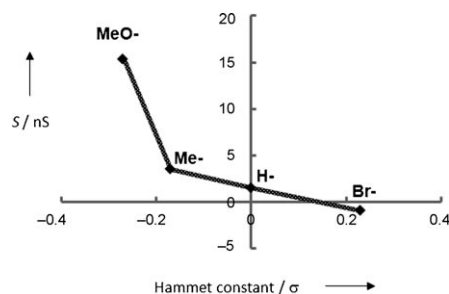


Figure 4. Conductance (S)-Hammett constant (σ) relationship of the group X in the carotenoids **2** and **3** containing the p - X - C_6H_4 group.

with the conjugated polyene based on the analysis of the UV spectra of the carotenoids **2** and **3** (column 4, Table 1). Attachment of one more phenyl group to the C-13' position of the carotenoids **3** allows the bathochromic shifts of $\lambda_{\max}$ only by 7–9 nm (the difference between **2** and **3**), which are a little bigger than the value observed by an alkyl substituent (e.g., 5 nm) but significantly smaller than the one observed by a conjugated carbon-carbon double bond (e.g., 30 nm).^[35] The phenyl groups at C-13 (and C-13') of **2** and **3** could not take the coplanar position to the plane of the polyene presumably due to a steric reason. Comparison of the 1H NMR spectrum of the 13,13'-diphenyl carotene **2c** with that of the 13,13'-dimethyl carotene analogue also supports the above idea: the chemical shifts of H-11, H-15, and H-9 are up-field shifted by 0.97, 0.59, and 0.28 ppm, respectively due to the ring current effect of benzene, which manifests that these protons are placed on top (or bottom) of the benzene ring at C-13 (see Table S2 in Supporting Information).^[36]

It is believed that electron transport of a molecular wire proceeds through the frontier orbitals of the molecule, which are closest to the Fermi levels of the electrode,^[1,2] and that the electronic effect of the substituents may shift the frontier molecular orbitals and alter the electron-transport efficiency through the molecule.^[37] Since the $\lambda_{\max}$ of the UV spectra of **2** or **3** are not different from each other according to the substituent X but almost identical within the carotenoid series **2** or **3**, the energy gaps between the HOMO and the LUMO of the carotenoids **2** or **3** would be almost the same. The electron-donating substituent (X) may increase the electron density of the polyene chain and places the LUMO of the carotenoid closer to the Fermi level of gold electrode than the electron-withdrawing substituent does, and thereby facilitates the electron transport process.

In summary, we were able to synthesize the stabilized carotenoid molecular wires with tunable conductance by introduction of the phenyl substituents of diverse electronic natures into the conjugated polyene chain. The conducting capability of the carotenoid wires generally coincides with the electron-donating ability of the substituent in the phenyl groups, while an electron-withdrawing substituent provides the carotenoid wires with resistance. The contributing value of each functional group (p - X - C_6H_4 -) on the conductance of the carotenoid wires **2** was obtained experimentally, which

would be utilized in designing the carotenoid wires of a specific conductance, though the positional effect of the groups on the conductance should be clarified. Our new concept in designing the stabilized carotenoid wires to improve and diversify the conductance would pave a way to the materialization of the organic molecular wires. Attachment of more phenyl groups and the combination of different phenyl groups of diverse electronic natures to further improve and diversify the conductance of the carotenoid wires are currently underway.

Experimental Section

Sample preparation for the AFM measurement of carotenoids: Fresh flame-annealed films of Au(111) on mica were treated with piranha solution (a 7:3 mixture of conc. H_2SO_4 and 30% H_2O_2) for 5 min, and then rinsed thoroughly with freshly distilled H_2O and toluene, respectively. A 1.0 mm solution of methyl(octadecyl)sulfane in toluene was placed on the gold plates and left to adsorb for 4 h. The samples were rinsed with toluene. The samples of a uniform monolayer of methyl(octadecyl)sulfane were then submerged in a 10 μM solution of carotenoids in toluene for 2 h, and rinsed with toluene. Finally, gold nanoparticles were placed on top of the methylthio group of carotenoids by immersing the above sample in a suspension of 2 nm-size gold particles (BBInternational, UK) in toluene for 12 h. The samples were rinsed several times with freshly distilled toluene prior to the AFM measurement. Samples were imaged under nitrogen atmosphere. The AFM (NanoFocus Inc., Korea) has a force-sensing conducting cantilever, and the current flows between the AFM tip with a spring constant of 0.15 N m^{-1} (MikroMasch, CSC17) and the samples, which can be measured in the constant force contact mode.

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