Electron Transport Properties of a Carotene Molecule in a Metal-(Single Molecule)-Metal Junction

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Using a recently developed method for tethering gold contacts to single molecules, we have measured current versus voltage (I-V) data for single carotenedithiol molecules with a total length of 28 carbons (18 in the conjugated alkene chain). The molecules are inserted into a docosanethiol monolayer (C₂₂H₄₅SH) on Au(111), and a Au nanoparticle is tethered to each molecule via the protruding thiol group. Electrical contact is made by placing a gold-coated AFM probe in contact with the nanoparticle. The I-V curves are relatively insensitive to contact probe force and cluster around integer multiples of a fundamental curve, suggesting that members of the smallest set correspond to data obtained from a single molecule. First principles calculations based on tunnel transport yield results that are remarkably close (within a factor of 4) to the measured data. The remaining small discrepancy can be well accounted for by taking account of the effects of charging caused by a probeto-gold particle contact resistance. Thus, it appears that electron tunneling dominates transport even in this 3-nm-long molecule. The carotenoid is a better conductor than a saturated *n*-alkane of equivalent length by a very large factor and is significantly more conductive than 2,5-di(phenylethynyl-4'-thioacetyl)benzene, another candidate "molecular wire".

Introduction

Despite the demonstration of promising molecular-electronic devices,^{1–4} questions remain about the nature of the contact between molecules and electronic conducting materials.^{5,6} We have shown previously that the conductivity of *n*-alkanes is enhanced enormously when metal "contact pads" are covalently bonded to each end of the molecule and a conducting atomic force microscope (c-AFM) probe is used to contact the top metal contact (a gold nanoparticle).^{7,8} By using an insertion process⁹ to support and separate the target molecules, single-molecule measurements were made.⁷ The data were highly reproducible and gave currents much closer to those predicted by first principles theoretical simulations⁷ than was the case for mechanically contacted molecules.⁸ Despite these successes, discrepancies between theory and experiment remained.¹⁰ Subsequent (unpublished) work indicates that electrical resistance between the nanoparticle and gold AFM probe can play an important role and might account for these remaining discrepancies.

The conductivity of the *n*-alkane chains bonded into an electrical circuit now appears to be well enough understood to justify a systematic comparison with other molecules that are candidates for molecular electronic materials. We recently completed an initial study of 2,5-di(phenylethynyl-4'-thioacetyl)-benzene,¹¹ a molecule specifically designed as a "molecular wire" (i.e., the molecule is used in its deprotected thiol form

for measurements). The measured conductance of this molecule in the gold–molecule–gold junction was surprisingly low. Carotenoid polyenes appear to be excellent candidates for molecular wires because of their conjugated nature and the planar conformation of the alkene chain, which maximizes the overlap of the π electrons. In earlier work,¹² we showed that carotenoids are orders of magnitude more conductive than alkanes of the same length, but quantitative information was difficult to obtain because these data were acquired by conducting atomic force microscopy in which one contact was not covalently bonded. We have now examined this topic using the contact pad approach developed by Cui et al.⁷ to contact carotene molecules, and the results are reported here.

The carotenoids are intrinsically interesting molecules. Their electronic delocalization is manifested in their optical properties and used in their biological functions.^{13,14} Their electronic properties are still a matter of some debate, but the current understanding may be summarized as follows: The π -electron system of the carotenoid pigment available to assist tunneling (or actually to accept/donate electrons) can be obtained from an analysis of the molecular orbital description of the low-lying electronic excited states. As is usual for organic compounds having large conjugated π -electron systems, the ground state is well described by a set of occupied bonding molecular orbitals and unoccupied antibonding orbitals. A strongly allowed electronic transition gives rise to the intense light absorption in the visible that is characteristic of carotenoids. Although this is not the lowest-energy electronic transition, it is well described in terms of promoting an electron from the HOMO to the LUMO.^{15,16} In carotenoids having C_{2h} symmetry, this state is designated $1^{1}B_{u}^{+}$, and the absorption band onset is at ca. 2.4

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Figure 1. Sample preparation. (a) 7,7'-Bis(4-thiomethylphenyl)-7,7'diapocarotene (**3**), the dithiolated carotenoid used in this work. (On the structure, all double bonds should be on the same side of the backbone—preferably the lower side.) Arrows point to the bonds most susceptible to cis—trans isomerization during synthesis. (b) A schematic of the c-AFM experiment. A dithiolated carotene molecule is inserted into a monolayer of the alkane monothiol $C_{22}H_{45}$ —SH. The free thiol group of the carotene is tethered with an Au nanoparticle, which is then contacted by an AFM tip coated with gold. (c) Reverse-phase HPLC of a sample of **3** synthesized showing 20% cis isomer content (see text).

eV. The lowest singlet excited state is designated $2^{1}A_{g}^{+}$ and corresponds to electronic configurations that include promoting two electrons from the HOMO to the LUMO and configurations in which an electron is promoted from HOMO-1 to the LUMO and from the HOMO to LUMO+1. Strong electron correlation lowers the energy of this state below that of $1^{1}B_{u}^{+}$. The energy of this electric-dipole-forbidden $2^{1}A_{g}^{+}$ state is uncertain in these carotenoids but is thought to be in the vicinity of 1.7 eV. A second forbidden state having ${}^{1}B_{1u}^{-}$ symmetry has also been reported to lie between the allowed ${}^{1}B_{1u}^{+}$ state and the $2{}^{1}A_{g}^{+}$ level.^{17–19} Its energy has not been determined. Nevertheless, within the framework of modern molecular orbital treatments, the electronic energy of the ground state-to- ${}^{1}B_{u}^{+}$ transition, ca. 2.4 eV, corresponds approximately to the HOMO-LUMO gap in these systems. Spectroscopic studies on a wide range of carotenoids indicate that this assignment of excited states is not dependent upon strict C_{2h} symmetry.

Experimental Section

Molecular Films. The dithiolated carotenoid 7,7'-bis(4thiomethylphenyl)-7,7'-diapocarotene (3) see Figure 1a) was synthesized as described below. Samples for this study were prepared by placing freshly annealed Au(111)-on-mica²⁰ surfaces in 1 mM solutions of docosanethiol (C22H45-SH) in toluene for 12-16 h. This process forms a uniform monolayer of the alkanethiol on Au(111). After rinsing the monolayer in toluene, the film was incubated in a fresh 0.022 mM solution of the freshly thawed carotenedithiol (see below) for 6 h. Subsequently, the film was rinsed in toluene and incubated in a suspension (1 to 2 mg in CH₂Cl₂) of triphenylphosphinestabilized ~1.5-nm-diameter gold nanoparticles²¹ for 12 h.^{7,10} Prior to experiments, samples were rinsed with freshly distilled dichloromethane and toluene several times. The carotene solutions were frozen until immediately prior to use. All rinsing and depositions involving the carotene were performed in the dark. Optical spectra collected before and after use of the carotene solutions did not show any observable degradation or oxidation.

Synthesis of the Carotenedithiol. Thioacetic Acid (S)-(4-Bromomethylbenzyl) Ester (1). α, α' -Dibromo-*p*-xylene (5.0 g, 0.019 mol) was dissolved in 10 mL of tetrahydrofuran (THF) and heated to ~50 °C. A solution of 2.0 g (0.018 mol) of potassium thioacetate in 20 mL of THF was added dropwise. The mixture was kept well stirred under a nitrogen atmosphere overnight. After that time, the reaction mixture was diluted with dichloromethane and extracted with water three times. The organic solvent was distilled at reduced pressure, and crude **1** was purified by column chromatography on silica gel (5% ethyl ether/hexane) to yield 0.81 g (17%) of the desired compound. ¹H NMR (300 MHz, CDCl₃): δ 7.29 (4H, m, ArH), 4.46 (2H, s, -CH₂Br), 4.10 (2H, s, -CH₂S-), 2.35 (3H, s, -CH₃).

4-Acetylthiomethylbenzyltriphenylphosphonium Bromide (2). Ester 1 (0.81 g, 3.1 mmol) was dissolved in 30 mL of toluene. To this solution was added 1.0 g (3.8 mmol) of triphenylphosphine. The reaction mixture was stirred in an oil bath at 110 °C overnight. After that time, it was cooled to 0 °C and filtered, and the filter cake was washed two times with toluene and two times with hexanes. The expected salt remained as white crystals (1.5 g, 94% yield). ¹H NMR (300 MHz, CDCl₃): δ 7.7 (15H, m, ArH), 7.04 (4H, m, ArH), 5.37 (2H, m, -CH₂P-), 4.01 (2H, s, -CH₂S-), 2.34 (3H, s, -CH₃); MS (MALDI-TOF) *m/z*: 441.15 (calcd for C₂₈H₂₆OPS⁺, 441.14).

7,7'-Bis(4-thiomethylphenyl)-7,7'-diapocarotene (3). A portion of crocetindial (0.10 g, 0.34 mmol) and 0.44 g (0.84 mmol) of 2 were mixed with 10 mL of tetrahydrofuran, and enough methanol was added to dissolve the salt (~ 2 mL). An excess of sodium methoxide (0.23 g, 4.2 mmol) was added to this solution, which was kept well stirred in an inert atmosphere overnight. The reaction mixture was diluted with dichloromethane and extracted with a dilute solution of citric acid and then with water. The solvent was distilled from the organic phase at reduced pressure, and column chromatography on silica gel with 20% hexane/dichloromethane produced 23 mg (23% yield) of the desired dithiol. Reverse-phase HPLC of this product indicated that it consisted of a mixture of two major isomers in an approximate ratio of 80:20 (Figure 1c), which is ascribed to cis-trans isomerism in the carotene. (The arrows in Figure 1a indicate the most likely position where cis isomerism would occur as a consequence of the nonstereospecific Wittig-type reaction used to expand the polyenic chain.) ¹H NMR and COSY experiments were consistent with the proposed structure. ¹H NMR (500 MHz, CDCl₃, major isomer): δ 7.39 (d, J = 8 Hz, ArH), 7.27 (d, J = 8 Hz, ArH), 6.89 (d, J = 16 Hz, 8-CH), 6.68 (m, 11-CH), 6.65 (m, 15-CH), 6.57 (d, J = 16 Hz, 7-CH), 6.42 (d, J = 15 Hz, 12-CH), 6.37 (d, J = 15 Hz, 10-CH), 6.30(m, 14-CH), 3.74 (d, J = 8 Hz, $-CH_2-$), 2.05 (s, 19-CH₃), 1.97 (s, 20-CH₃), 1.76 (br m, -SH); MS (MALDI-TOF) m/z: 536.24 (calculated for C₃₆H₄₀S₂, 536.26); UV-vis (toluene) 379, 454 (sh), 477, 505 (sh) nm.

Scanning Probe Microscopy. For c-AFM experiments (shown schematically in Figure 1b), microfabricated contactmode silicon cantilevers with a spring constant of 0.35 N/m (MikroMasch, CSC11) were coated with an underlayer of 50 Å Cr/100 Å Au followed by a second coating of 50 Å Cr and 400 Å of gold. The tips were cleaned in ozone-UV prior to use. Measurements were made with a PicoSPM conducting atomic-force microscope (Molecular Imaging, Phoenix) using a hermetically sealed sample chamber flushed with argon to reduce oxygen and water-vapor contamination. Contamination was reduced by keeping the sample submerged in freshly distilled toluene during measurement. This also serves to minimize adhesion between the AFM tip and the sample, permitting controlled contact between the tip and gold nanoparticles. All STM images were obtained with electrochemically

Figure 2. STM images of the steps in insertion and contact tethering. (a) STM image of the $C_{22}H_{45}$ -SH alkane monothiol monolayer prior to insertion of the dithiolated carotenoids. (b) Similar image after insertion of the carotenoid and (c) after the carotenoid is subsequently treated with a suspension of gold nanoparticles. The bright spots in b correspond to the carotenedithiols, which are more conducting than the alkanethiol matrix. These spots are rather broad, probably because of the significant protrusion of the top of the inserted molecule (see text), so the increase in width owing to the tethering of gold contacts in c is not obvious. However, the apparent height of the spots increases significantly after gold particles are attached. (A height scale is listed below each image.) All images were obtained under toluene in an Ar environment at a bias of -1.25 V and a set-point current of 18 pA.

etched PtIr tips using a PicoSPM with the sample under toluene and operating in a dry argon environment. The operating setpoint current was between 12 and 20 pA with tip biases between -0.8 and -1.2 V.

Experimental Results

The insertion process can be followed in STM images as illustrated in Figure 2, which shows the docosanethiol monolayer (a), the monolayer with inserted carotenoids (b), and the assembly with tethered gold particles (c) all at the same magnification. The insertion density (about 10 to 100 molecules per $100 \times 100 \text{ nm}^2$) is typical. In contrast to our earlier work^{7,10} where the inserted molecule and surrounding matrix were nearly identical, here the images of the inserted dithiolated carotenoids (Figure 2b) are much broader (ca. 3-nm diameter), presumably as a consequence of the ca. 4-Å overhang of the inserted

molecules above the surrounding matrix. In consequence, images with Au particles attached are only somewhat broadened relative to those taken without the Au particles. However, the apparent height of the "spots" associated with the inserted molecules is more than doubled when Au particles are attached (Figure 2c). (The apparent height in an STM image is only indirectly related to true topographic changes when comparing images of samples of different chemical composition.)

Current-voltage curves were obtained by lowering the goldcoated c-AFM probe onto a gold particle and recording the current as the probe bias was swept (typically at a rate of 3 V/s). Both the sweep rate and the range of the sweep were varied to ensure that reproducible data were obtained and that the data were free from hysteresis. A maximum bias of ± 1.5 V could be applied without bias-dependent changes of the currentvoltage characteristics from sweep to sweep.

In the case (studied earlier) of alkanedithiol molecules inserted into alkanethiol monolayers, the current measured via the nanoparticle contact was found to be largely independent of applied force,⁷ in contrast to measurements made without bonded^{8,12} contact pads. It proved to be difficult to make a similar measurement (measuring current while sweeping contact force) in the present case, presumably because of the less rigid molecular arrangement owing to the height difference between the inserted molecule and the surrounding matrix. Nonetheless, we were able to record a series of I-V curves as the force setpoint was changed, avoiding the problems of programming a scan in the height of the probe at a fixed position in the plane of the film (as would be required to record current vs force change continuously). The I-V curves also served as an internal control, becoming distorted if the tip moved during the voltage scan. The quantity I/I_0 (plotted in Figure 3a) was found by obtaining the divisor that minimized the variance between each I-V curve and the initial one, just as was done in the analysis of the I-V curves (see below). It can be seen that the curves



Figure 3. Current–voltage data from inserted molecules. (a) Contact-force dependence of the current. The I-V curves were recorded as the set point was systematically increased. Every point on each curve was divided by the corresponding point on the first (lowest force) curve, and the corresponding set of current ratios was averaged to produce the quantity I/I_0 plotted here. Currents remained relatively constant until the contact force exceeded 6 nN. (b) Current–voltage curves representative of the groups centered around 1, 2, and 3 units of conductance (see text). The data shown here are averages of the curves selected using the divisor distribution shown in d, and error bars correspond to ± 1 standard error. (c) Curves 1, 2, and 3 from b divided by 1, 2, and 3 at each point. (d) Histogram of the value of a divisor chosen to minimize the variance between any pair of measured curves and normalized so as to be 1 or greater. Clear peaks are seen at 1 (± 0.22) and 2 (± 0.22). There is also evidence of a peak at 3.04 (± 0.41). The number of curves under each peak is in the ratio of 1:1.4:0.4.

are quite stable up to contact forces of about 6 nN with this particular tip (end radius ca. 30 nm).

Some typical I-V curves taken in the lower contact-force range are shown in Figure 3b. These data are actually averages of curves belonging to clusters selected as described below. The curves are, within experimental uncertainty, symmetrical about zero bias.

Curves were observed to cluster around certain values of current at a given bias, as observed in our earlier work with *n*-alkanedithiols.^{7,10} To characterize this variability, we analyzed these curves in the following way. One of the curves with the smallest current at the highest bias was arbitrarily assigned as the "standard curve" for the complete data set (N = 230). Then the value of a divisor, X, was found for each of the other curves such that dividing all points on the curve by X minimized the variance between it and the standard curve. The resulting histogram of X values shows two distinct peaks (Figure 3c) with evidence of a third, implying that the currents cluster around 1X, 2X, and 3X of a fundamental current. (The first peak actually occurs at X = 1.04, reflecting the choice of a standard curve that was a bit smaller than the peak values associated with the first peak; numbers and widths have been rescaled in the Figure caption so that the first peak is at X = 1 to emphasize the integer separation between peaks.) The corresponding I-V curves were sorted according to the associated X value. Curves with $0.5 \leq$ X < 1.5 were assigned to the 1X group, curves with $1.5 \le X <$ 2.5 were assigned to the 2X group, and curves with $2.5 \le X \le$ 3.5 were assigned to the 3X group. The average of the curves within each group (and the associated standard errors, shown as the width of the lines) is plotted in Figure 3b. Dividing each curve by 1, 2, and 3 at each voltage point yields the "master curve" shown in Figure 3c.

The following conclusions can be drawn from this exercise: (a) The I = V curves cluster around integer multiples of a

(a) The I-V curves cluster around integer multiples of a fundamental curve. The evidence for this lies in the width of the peaks in the histogram of X values; the width of the first two peaks is substantially less than their separation (see Figure 3 caption). Peak 3 is not as convincing. (Note that the small error bars on curve 3 in Figure 3b reflect, in part, the exclusion of curves for $X \ge 3.5$ as well as the use of the standard error that understates the width of the distribution.)

(b) Curves from the three groups have essentially the same shape as shown by the superposition in Figure 3c. (Small but significant differences are noticeable at higher bias, and these contribute to the spread in X values for the 3X family of curves.)

Fits to the low-bias (linear I-V) region (Figure 5a) show that the resistance of the 1X family of curves is 4.9 ± 0.2 G Ω at low bias.

Theoretical Modeling

Calculations of the theoretical current-voltage curve for the carotene molecule were based on the Landauer-Buttiker formalism^{22,23} with the transmission function calculated using quantum mechanical scattering theory.^{24,25} The model system was an infinite 2D lattice (monolayer) of carotene molecules sandwiched between gold contacts made up of eight ideal Au(111) layers in a supercell structure, as discussed in detail elsewhere.²⁶ The self-consistent Kohn-Sham single-electron states were obtained for this system using Fireballs-2000,²⁷⁻²⁹ a local atomic-orbital density functional theory (DFT)-based method in the pseudopotential local density approximation (LDA). The present procedures have been previously found to give similar results using the related Siesta method.³⁰ Green's



Figure 4. Contact geometry for the simulations. The terminal sulfur sits in a 3-fold hollow on the gold surface with the molecular axis inclined 30° to the surface normal, the C–S–Au (hollow site) angle constrained to lie between 90 and 100°, and the S–C–C bond maintained at 110°. The S–Au bond energy is relatively insensitive to the rotations of S about the surface normal, so I-V curves were calculated for the full range of values of this angle. The cis isomer cannot be positioned on the surface within these constraints, and a minimum-energy configuration was found with the Au–S–C bond angle at 110°.

functions that are needed to compute the current versus voltage curves were calculated from the Hamiltonian and overlap matrix elements. Though the electronic structure calculation was performed with gold slabs of finite thickness, we extended Green's functions to include semi-infinite contacts using a block-recursion technique. Full details are given,³¹ and related descriptions are available.^{26,10}

The current is calculated as

$$I(V) = \frac{2e}{h} \int T(E, V) \left[f\left(E - \frac{eV}{2}\right) - f\left(E + \frac{eV}{2}\right) \right] dE \qquad (1)$$

where T(E, V) is the transmission function,^{24,25} *f* is the Fermi function, and *V* is the voltage. We have assumed that the electron energies in the electrodes are shifted symmetrically by +eV/2 and -eV/2 for the left and right electrodes, respectively. The calculations of the metal-molecule-metal system are fully self-consistent at zero bias and thus include charge-transfer effects at the interface; however, the effects of bias and the electric field are approximated simply by shifts in the Fermi levels of the left and right contacts.

The calculated conductance of the carotene molecule (3) is sensitive to its geometric structure, particularly the alternating double and single bonds in the molecule's polyene (polyacetylene-like) segment connecting the phenyl rings. The degree of bond alternation, or "dimerization", is characterized by α , which is defined as the ratio of the single-bond length to the double-bond length in the polyene backbone connecting the phenyl rings. With no dimerization ($\alpha = 1$), the HOMO– LUMO gap of the polyene chain goes to zero as its length increases in the same way that the spacing between levels for a particle-in-a-box goes to zero as the length of the box increases. For short segments of an H–(CHCH)_n–H chain containing 2*n* carbon atoms, the HOMO–LUMO gap with α being unity is given approximately by

$$\Delta E = 4t \sin\left[\frac{\pi}{2(2n+1)}\right] \tag{2}$$

This equation is derived from a simple tight-binding model where *t* is an interaction Hamitonian matrix element. Dimerization of the polyene chain ($\alpha > 1$) leads to a substantial (~1.8 eV) HOMO–LUMO gap—the limit is approached as the length of the chain increases—exactly analogous to the band gap of a semiconductor. Tunneling current through an energy barrier generally goes as $I = I_0 e^{-\beta L}$, where *L* is the length of the barrier (here polyene) and the decay constant β due to tunneling goes



Figure 5. Comparison of theory and experiment. (a) Calculated currents for the trans (1 - -) and doubly cis (- -) geometries with error bars showing the range owing to possible orientations with respect to rotations of the S-Au bond normal to the gold surface. The experimental data for a single molecule are shown on the same scale as the solid line. The inset (lower right) shows the ohmic region at low bias with linear fits that yield low-bias conductances of 0.2 nS (experimental), 0.45 nS (doubly cis, calculated), and 0.83 nS (trans, calculated). The corresponding resistances are 4.9, 2.2, and 1.2 G Ω . (b) Coulomb-blockade-corrected I-V curves showing improved agreement at low bias (-, experiment; O, theory) with further improvement when the bias dependence of the tunneling rate is accounted for (Δ). The inset (lower right) shows the two-junction model.

to zero for energies near the HOMO and LUMO and reaches a peak (most rapid decay), usually near the middle of the gap. The tunneling current is "exponentially" sensitive to α because a higher α leads to a larger HOMO–LUMO gap and a corresponding increase in β .

Structural optimization of the carotene molecule using density functional theory was found to produce far too little dimerization $(\alpha = 1.03)$, resulting in 1.40 and 1.36 Å for the single- and double-bond lengths, respectively. This results in a HOMO-LUMO gap that is too small (about 1.0 eV) compared to the experimental value, which is near 2.4 eV. (See the introductory discussion.) It is known that Hartree-Fock (HF) calculations generally do much better than LDA-DFT in predicting the correct dimerization in the case of polyacetylene.32 Our Hartree-Fock structural optimization³³ of the carotene molecule yields $\alpha = 1.10$ with 1.46 and 1.33 Å for the single- and double-bond lengths, respectively, in excellent agreement with experiment.³⁴ The resulting energy-optimized carotene geometry from HF is then input into the DFT calculation, and a HOMO-LUMO gap of around 1.8 eV is found. This value is in accord with existing experimental data (2.4 eV).

To calculate the electronic current, we use the HF-optimized carotene structure in DFT calculations of the carotene-gold system. For testing purposes, we also performed current-voltage calculations using carotene structures optimized by DFT and found significant differences in the current compared to experiment. The lower dimerization and resulting smaller HOMO-LUMO gap predicted by DFT, for example, result in much higher current values and a dramatic turn-on in current at around 0.5 V when conduction electrons access the HOMO and LUMO levels.

The details of the molecule-metal contact are also important (see Figure 4), and they were investigated as follows: The Au-S-C bond angle was fixed at 90°, and the S-C-C angle was fixed at 110°, resulting in an angle between the two sulfur endgroups and the normal to the gold substrate of 30°, as might be expected for insertion into the tilted docosanethiol matrix. There are uncertainties concerning exactly how the carotene molecule fits into the decosanethiol film. For the all-trans isomer, the interaction between C and the Au surface was not strong enough to identify a highly preferred orientation. On the basis of these considerations, I-V curves were therefore computed for all arrangements in which the molecule was rotated about the surface normal on a fixed conical surface oriented 30° with respect to the surface normal (see Figure 4). The doubly cis isomer was more difficult to accommodate between two gold slabs, and the Au-S-C bond angle had to be distorted to 110°.

I-V curves were computed for all allowed rotational arrangements of this molecule as well. The rotationally averaged computed I-V curves are shown in Figure 5a. The long-dashed line is the calculated result for the trans isomer, the short-dashed line is for the doubly cis isomer, and the solid line is the single-molecule experimental curve. The theoretical "error bars" indicate the range in currents spanned by rotating the molecule about the Au-S bond. A magnified inset shows the low-bias ohmic region with results for the doubly cis isomer and for the all-trans isomer shown by solid triangles and open squares, respectively. The corresponding resistances are 2.2 G Ω (cis) and 1.2 G Ω (trans).

Discussion

Origin of Quantized Molecular Conduction. By analogy with our previous results for alkanedithiols,^{7,10} the simplest and most reasonable explanation for the clusters of I-V curves observed for the carotenedithiol is that the three curves in Figure 3b correspond to 1, 2, and 3 molecules bridging the gap between the top gold contact and the underlying gold substrate, resulting in resistance ratios R_0 , $R_0/2$, and $R_0/3$. However, a second possibility should be considered. Approximately 20% of the carotenedithiol preparation was a minor isomer. This most likely has the cis configuration at a double bond adjacent to one aryl ring because the method of synthesis produces a mixture of cis and trans bonds at this location. Alternatively, the isomerization of the all-trans carotene about any of its alkene double bonds could have happened in solution or on the gold substrate because such isomerizations are known to occur via chemical agents, the carotenoid radical cation, and the carotenoid triplet state. The theoretical calculations given above suggest that a carotene with two cis double bonds is less conductive than an all-trans carotene by about a factor of 2. Perhaps the first peak in the histogram in Figure 3d represents a cis carotenedithiol, and the second peak, a trans carotenedithiol (rather than two carotenedithiol molecules).

Although this latter interpretation cannot be totally excluded, there are several factors that suggest that it is unlikely. In the first place, there are approximately equal numbers of curves under peaks 1 and 2 in Figure 3d, whereas the isomer ratio in the solution used to form the monolayer was 4 trans/1 cis (Figure 1c). The observed ratio would therefore require either the cis isomer to insert preferentially into the monolayer of docosanethiol or the trans isomer to isomerize preferentially to cis after it has entered the monolayer. These possibilities seem unlikely, given that the trans form is thermodynamically more stable in solution and that the trans form would be expected to be less disruptive of the close packing of the alkanethiols in the monolayer (by analogy with the similar packing in long-chain carboxylic acid and phospholipid monolayers). Second, the theoretical simulations suggest that dramatic differences in the shapes of the I-V curves at higher bias should exist for the cis and trans isomers (Figure 5a), but this is not observed (Figure 3c). Finally, the calculations show that a carotenoid with two cis double bonds is almost exactly half as conductive as one with none. The synthetic procedure is such that the formation of a carotenoid with cis double bonds at both ends is highly improbable. Presumably, a carotenoid with one double bond would have a resistance somewhere between that of all-trans and doubly cis. However, the histogram in Figure 3d clearly shows a factor of 2 in conductivity difference between the two families of curves. For these reasons, we favor the interpretation that the curves in Figure 3b correspond to 1, 2, or 3 molecules bridging the gap between gold contacts. It should be noted that even if the other interpretation were correct the curve of lowest conductivity would *still* represent the conductivity of a single carotenoid molecule.

Magnitude of Molecular Conductance. The experiment and theory agree remarkably well, as shown in Figure 5a. It is important to stress that neither experimental data nor calculated data are scaled in any way: the absolute values of current are shown. Given the uncertainties in the simulation, this means that the measured currents may be accounted for by electron tunneling. This degree of agreement in the absolute magnitude of tunnel current is unusual and was only recently achieved for the simple *n*-alkanedithiols.⁷

Role of Contact Resistance. A close inspection of the experimental and calculated curves (for the trans isomer where the overall shape agreement is better) shows small but significant differences in shape when the theory is scaled to give a best fit to experiment (not shown): the experimental current in the ohmic region is too small (compared with theory), and the experimental curve grows less rapidly than the calculated curve at high bias. This suppression of current in the low-bias region and a smaller-than-expected growth as resonance is approached are both possible consequences of contact resistance between the AFM probe and the gold nanoparticle. The nanoparticles are ligand-stabilized, and it is not clear whether the contact stresses used in this work are adequate to penetrate the ligand layer. The large tip radius (ca. 30 nm) and the relatively large cluster diameter (~1.5 nm) should result in a significant contact area (when compared to a tip-singlemolecule contact). Nonetheless, the contact may not be formed from metallic bonds because of the possibility of an intervening ligand layer.

If the probe-to-cluster contact resistance is significantly higher than the quantum of resistance $(h/2e^2 \approx 12.9 \text{ k}\Omega)$, then the current will be dominated by a sequential electron-transport process in which electrons transfer one at a time across the probe-to-cluster and cluster-to-substrate junctions. This will result in a suppressed current flow for biases below that required to overcome the Coulomb charging energy (i.e., "Coulomb blockade") of the cluster.³⁵

This possibility can be treated by considering the junction as a resistance (proportional to the inverse tunneling rate) in parallel with a capacitor to represent the AFM-to-gold particle contact and a second parallel resistor—capacitor combination in series with the first to represent the gold particle-to-gold substrate contact. (See the inset in Figure 5b.) Such an arrangement has been treated in detail by Averin and Likharev³⁶ and by Hanna and Tinkham.³⁷

With R_1 corresponding to the probe-to-particle tunnel junction resistance, C_1 corresponding to its capacitance, R_2 corresponding to the particle-to-substrate tunnel junction resistance, and C_2 corresponding to its capacitance and allowing for a charge accumulation Q_0 on the nanoparticle, the current is obtained from

$$I(V) = -e \sum_{n=-\infty}^{\infty} \sigma(n) [\Gamma_{2}^{+}(n) - \Gamma_{2}^{-}(n)] = -e \sum_{n=-\infty}^{\infty} \sigma(n) [\Gamma_{1}^{-}(n) - \Gamma_{1}^{+}(n)]$$
(3)

where $\sigma(n)$ is the steady-state probability that the nanoparticle is charged with *n* electrons. Here,

$$\Gamma_j^{\pm}(n) = \frac{1}{R_j e^2} \left(\frac{-\Delta E_j^{\pm}}{1 - \exp\left(\frac{\Delta E_j^{\pm}}{k_B T}\right)} \right) \qquad j = 1, 2 \qquad (4)$$

and

$$\Delta E_1^{\pm} = \frac{\mp e}{C_1 + C_2} \left(-\left(n \pm \frac{1}{2}\right) e + Q_0 + C_2 V \right)$$
(5)

$$\Delta E_2^{\pm} = \frac{\pm e}{C_1 + C_2} \left(\left(n \pm \frac{1}{2} \right) e - Q_0 + C_1 V \right)$$
(6)

The superscripts + or - refer to an electron hopping on or off the nanoparticle, respectively, through the junction.

The residual charge on the nanoparticle, Q_0 , was set equal to zero in the fits that follow because nonzero values give asymmetric I-V curves, contrary to experiment. In eq 3, the electron distribution abides by detailed balance

$$\frac{\sigma(n)}{\sigma(n+1)} = \frac{\Gamma_1^-(n+1) + \Gamma_2^-(n+1)}{\Gamma_1^+(n) + \Gamma_2^+(n)}$$
(7)

and normalization of probability

$$\sum_{n=-\infty}^{\infty} \sigma(n) = 1 \tag{8}$$

We can estimate C_2 as being of the same order of magnitude as the free-space capacitance of a sphere, $4\pi\epsilon_0 R$, where $R \approx$ 1.5 nm, giving 0.08 aF (1 aF = 10^{-18} F). Previous fits of data for a number of different *n*-alkanes using the same gold spheres showed that good results are obtained with $C_1 = 0.318$ aF and $C_2 = 0.085$ aF (J. Tomfohr, unpublished data). Therefore, we started with these values for the capacitance and used a value for R_2 of 1.2 G Ω calculated quantum mechanically for the trans isomer (inset, Figure 5a). We found that the resulting I-V curves were essentially independent of R_1 so long as $R_1 \ll R_2$. The results of a calculation for $R_1 = 1$ M Ω are shown as circles in Figure 5b. Given that, with the exception of the unimportant R_1 , the parameter values were obtained independently, and the fit at low bias is quite striking.

We previously found that the approach outlined above worked well in accounting for I-V curves measured for various *n*-alkanes over the entire range of biases. Here, it clearly fails at higher bias. However, this is not surprising because of the assumption of a fixed value for R_2 . This approximation (i.e., a constant resistance R_2) is valid for the alkanes that have a very large HOMO-LUMO gap; however, it fails for carotene when the applied bias begins to approach the HOMO–LUMO gap separation energy. We therefore introduced a bias-dependent R_2 in an ad hoc manner by modifying eq 4 for the transfer rate across junction 2 as

$$\Gamma_{2}^{\pm}(n) = \frac{I(V_{a}) + I(V_{b})}{2e} \frac{1}{1 - e^{\Delta E_{2}^{\pm}/kT}}$$
(9)

where I(V) is the current at voltage V determined from the calculated I-V curve for the trans isomer and V_b and V_a are the (*n*-dependent) voltages across junction 2 before and after the electron transfer. Physically, the voltage across the junction will change (from V_b to V_a) during an electron transfer, and we use the average of currents $I(V_b)$ and $I(V_a)$ from the I-V calculation for the molecule to approximate the average transfer rate. For an ohmic junction I(V) = V/R, we recover eq 4 because ΔE is given by the electron charge multiplied by the average voltage $(V_b + V_a)/2$. The I-V curve resulting from this modification fits the experimental data quite well (triangles in Figure 5b). A better fit is obtained if we increase R_1 to 10 M Ω .

Comparison with Other Measurements. Comparative studies of conduction through saturated and unsaturated complexes^{38,39} show evidence of enhanced transport in the unsaturated systems, together with a significant decrease in the inverse electronic decay length,³⁸ as might be expected given the enhanced overlap and delocalization in the unsaturated molecular systems. To date, however, the only published study of carotenoids appears to be our earlier conducting AFM work on a monothiol derivative, contacted mechanically (i.e., no chemical bonding between the probe and the molecule).¹² In the case of *n*-alkanes, we found a very large (3 orders of magnitude) difference between similar sets of measurements when mechanical and bonded contacts were compared.^{7,8} In the case of the carotenoid, it is surprising that the resistance measured for the ohmic region in both the early work (mechanical contact) and the present work (bonded contact) is about 5 G Ω ! However, the earlier (mechanical contact) measurements on inserted carotenoids were made in quite a different manner from the mechanical contact measurements on n-alkane monolayers. In the work of Letherman et al.,12 current images were obtained at a series of fixed biases, and the maximum current was extracted by fitting the "image" of the conducting molecule so as to remove uncertainties associated with the relative tip-tomolecule positioning. Clearly, this tedious procedure was successful (but it yielded much noisier data than the procedure presented here).

In the earlier study,¹² we were unable to distinguish between tunnel transport and hopping conduction based on the oxidation of the carotene, using the shape of the I-V curve as a test. Given our increased confidence in the absolute value of both measured and calculated currents, the relatively close agreement between tunneling theory and experimental curves suggests that transport is in fact dominated, or at least contributed to significantly, by tunneling, even in this long (3 nm) molecule.

Comparison with Other Molecular Conductors. We have now studied six dithiolated molecules using gold nanoparticles as contact pads, and it is interesting to compare some of them. Table 1 summarizes the low-bias resistance values as obtained from published data^{10,11} and from this work. As a rough guide, we have also listed an estimated resistance based on an ideal contact and a β (inverse decay length) of 1.0 per carbon. The *n*-alkanes are less conductive than this idealized model and appear to have smaller β^{10} discrepancies that are lessened when contact resistance and the consequent Coulomb blockading are

 TABLE 1: Measured Resistances at Low Bias for Various Dithiolated Molecules Contacted with Gold Nanoparticles^a

molecule	Ν	R(low bias) G Ω	12.9 $\exp(\beta N)$ k Ω G Ω
octanedithiol	8	$\begin{array}{c} 0.965 \pm 0.02 \\ 2.89 \pm 0.5 \\ 8.26 \pm 1 \\ 52 \pm 18 \\ 4.9 \pm 0.2 \end{array}$	0.038
decanedithiol	10		0.277
dodecanedithiol	12		2.05
TPE ^b -dithiol	16		112
carotenedithiol	28		1.8×10^{7}

^{*a*} Variances are estimated from repeated attempts to fit the linear portions of the curves near zero bias. *N* is the minimum number of carbons in a direct path through the molecule. For comparison, an estimated resistance based on a β of 1.0 per carbon is shown. ^{*b*} TPE-dithiol is 2,5-di(phenylethynyl-4'-thioacetyl)benzene.

taken into account (unpublished work). In contrast, the unsaturated molecule 2,5-di(phenylethynyl-4'-thioacetyl)benzene has a resistance close to that predicted using a β of unity, even though β has been expected to be much smaller for this molecule.^{38,39} The carotenoid is by far the longest molecule studied using bonded contacts, yet its low-bias resistance is less than that of dodecanedithiol!

In conclusion, we have now obtained current versus voltage data for single carotene molecules with a total length of 28 carbons (18 in the conjugated chain). Despite some uncertainty about the role of isomers, the data give, at worst, an estimate of the single-molecule resistance for all-trans carotenedithiol 3 to within a factor of 2. At best, the single-molecule I-V curve for all-trans 3 in a gold-molecule-gold junction has been determined to within the width of the measured single-molecule distribution (i.e., about $\pm 20\%$). These data are in remarkable agreement (factor of 4) with the results of a theory based on tunnel transport, and the agreement can be made almost complete when some reasonable corrections for contact resistance are made. This suggests that the conductance can be accounted for largely by tunnel transport, despite the electroactive nature of this molecule. Overall, the molecule is an excellent mediator of tunneling, having a conductance similar to that of an *n*-alkane of less than half its length.

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