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Fine-Tuning of Single-Molecule Conductance by Tweaking Both Electronic Structure and Conformation of Side Substituents

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Abstract: Herein, we describe a method to fine-tune the conductivity of single-molecule wires by employing a combination of chemical composition and geometrical modifications of multiple phenyl side groups as conductance modulators embedded along the main axis of the electronic pathway. We have measured the single-molecule conductivity of a novel series of phenyl-substituted carotenoid wires whose conductivity can be tuned with high precision over an order of magnitude range by modulating both the electron-donating character of the phenyl substituent and its dihedral angle. It is demonstrated that the electronic communication between the phenyl side groups and the molecular wire is maximized when the phenyl groups are twisted closer to the plane of the conjugated molecular wire. These findings can be refined to a general technique for precisely tuning the conductivity of molecular wires.

There is an increasing interest in understanding the electrical properties of single molecules, both from a fundamental point of view and for potential applications in nanoscale electrical circuitry.^[1–5] An important aim in the development of such molecular circuits is to create chemically stable molecular scaffolds possessing well-defined configurations that can be systematically varied to control the magnitude of the conductance output. Possessing such capability is vital to mimic some aspects of conventional electronics, such as the design of resis-

tors with precise resistance values and limited tolerance. Achieving a comparable degree of control in single-molecule circuits involves simultaneously controlling a variety of molecular parameters, for example, length, conjugation, substitutions, conformation, alignment of the highest occupied/lowest unoccupied (HOMO/LUMO) molecular frontier orbitals to the electrode Fermi energy level, and anchoring chemical groups to the electrodes.^[6–12] This, in turn, confers a great degree of freedom to tune the conductance magnitude of organic molecules. In the last decade, several of these parameters were individually explored. For instance, the conductance of a single-molecule electrical contact has been explored as a function of the chemical anchoring groups to the electrodes,^[6,7,13–15] the molecular wire length,^[8,9,16] the chemical substituents,^[10,17–21] and the molecular conformation.^[11,12,22,23] All these parameters allow alignment of the HOMO/LUMO frontier orbitals to the Fermi energy level of the junction electrodes, thus controlling the electron transport through the nanoscale molecular wire. Despite the significant knowledge acquired on single-molecule conductivity, and on ways to improve their performance and reproducibility, the search for a molecular platform that meets all the above criteria is yet to be achieved.

In this study we turn our attention to carotenoids, which are excellent candidates for molecular wires. Their conjugated nature and planar conformation of the alkene chain maximizes the overlap of the π -orbitals, opening channels for electron transport at large distances. In fact, nature chooses carotenoids to allow pathways for electron transfer in basic biological processes such as photosystems.^[24] We have previously developed synthetic routes for these naturally occurring molecules with exquisite control over their geometry and chemical stability, and we have recently demonstrated their utility as single-molecule wires.^[25,26]

Here we report the chemical synthesis and single-molecule conductivity measurements of a new series of carotenoid molecular wires whose conductivity can be fine-tuned by inserting multiple phenyl substituents and by controlling both their chemical composition and conformation. This multiple control of the phenyl substituents imbedded in the carotenoid backbone allows for fine-tuning of the single-molecule wire conductance over an order of magnitude, and establishes a novel methodological platform to achieve a desired conductance output in a nanoscale molecular circuit. We further present molecular models that describe the experimental findings based on DFT-optimized structures and the distribution of the frontier molecular orbitals through the molecular wires.

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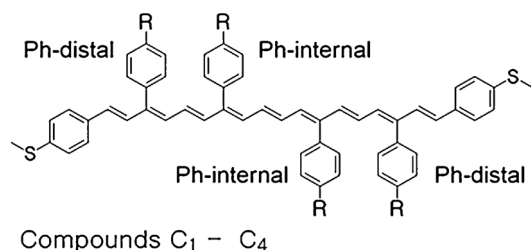
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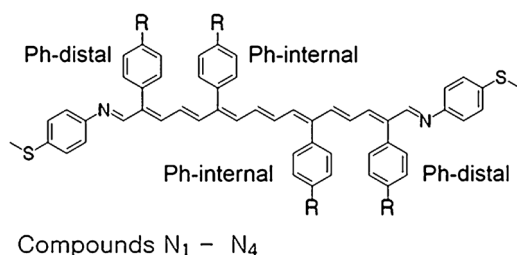
[⁺] These authors contributed equally to this work.

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a) C series



b) N series



c)

-R	C Series	N Series
-Cl	C ₁	N ₁
-H	C ₂	N ₂
-CH ₃	C ₃	N ₃
-O-CH ₃	C ₄	N ₄

Figure 1. Molecular structure for a) C series: C₁–C₄, and b) N series: N₁–N₄, with distal and internal phenyls labelled as “Ph-distal” and “Ph-internal”, respectively. c) Definition of the R groups.

A key design feature in both molecular series investigated in this study (Figure 1 a,b) is the cementing of phenyl substituents along a rigid, structurally well-defined polyene chain bearing a –SCH₃ group at each end to allow attachment to gold electrodes. The –SCH₃ as anchoring groups allow for the formation of robust single-molecule junctions with limited variation of the contact configuration and narrow conductance distributions.^[6,7,15] The phenyl substituents along the polyene backbone have a dual function: the first is to ensure chemical stability of the highly conjugated system.^[25,26] Chemical stability is one of the key shortcomings of many highly conjugated molecular wires, but their conductance is much higher than their saturated counterparts, making them more attractive for molecular electronic applications. The second function of the phenyl substituents is to systematically vary the electron donating/withdrawing character of the substituents from less electron-donating (Ph–Cl) to more electron-donating (Ph–OCH₃) groups. In the C-series, the polyene chain is composed of all carbon atoms, while in the N-series the distal carbons of the polyene chains are replaced by nitrogen atoms (Figure 1). The two series are identical in terms of the position of the phenyl substituents in the polyene chain, but differ in the

twist angle of the distal phenyl rings relative to the plane of the conjugated polyene backbone. Figure 2 shows the B3LYP/6-31G(d) geometry-optimized structures of a representative molecule of each series (for computational details, see section 7 of the Supporting Information). As a consequence of the presence of the nitrogen atom, the distal phenyl rings in the N-series are twisted by at least 10° closer to the plane of the polyene chain, while the internal phenyl rings have comparable twists angles throughout both series (Supporting Information, section 3).

Using an STM break-junction approach, we measured the single-molecule conductivity of both the C- and N-series of the carotenoid wires. Details about the STM break-junction technique have been published elsewhere.^[2,27] Briefly, in a typical break-junction experiment, the STM tip is first brought to a tunnelling distance over a flat, clean Au(111) surface area. The STM feedback is then turned off and the tip is driven in and out of contact with the substrate. During the contact process, carotenoid molecules dissolved in the working medium can eventually bridge the tip and the Au(111) surface electrodes via the S–CH₃ contact groups at the distal ends of the molecule. All measured current traces displaying well-defined plateaus (Figure 3 a,b) that evidence the formation of a single-molecule bridge were used to build the conductance histograms (see section 2 in the Supporting Information for details). The S–CH₃ contact groups and the rigid structure of the carotenoid backbone confer low variability in the single-molecule conductance (Figure 3), a necessary requirement to resolve conductance differences among the different molecules studied.

The main observed trend in both series is the increase in single-molecule conductance as a function of the increasing electron-donating capability of the phenyl substituents (Figure 3). This implies that the HOMO level is closer to the Fermi energy and that it is the orbital dominating the electron transport in the carotenoid molecular junction studied.^[1,2,6,20,28] The second finding from the single-molecule conductance measurements is the amplified evolution of the conductance with the electron-donating character of the substituents in the N-series. When comparing both C- and N-series, the insertion of Ph–Cl substituents led to an indistinguishable conductivity in both series (initial data point in Figure 4); this result implies that the insertion of the nitrogen atom in the N-series is not directly involved in the electron transport through the carotenoid backbone. However, the conductance trend deviates between the two series as the electron-donating character of the phenyl substituents increases, being larger for the N-series (Figure 4). This fact evidences the indirect role of the N by allowing more involvement (coupling) of the distal phenyl groups with the polyene backbone due to their twisted phenyls of lower dihedral angle versus the polyene plane (Figure 2). The larger electron-donating ability of the distal functionalized phenyls in response to the decrease in the dihedral angle is translated into an amplified upward shift in the HOMO level for the N-series as the phenyl para substituent is progressively changed from low to high electron-donating character.

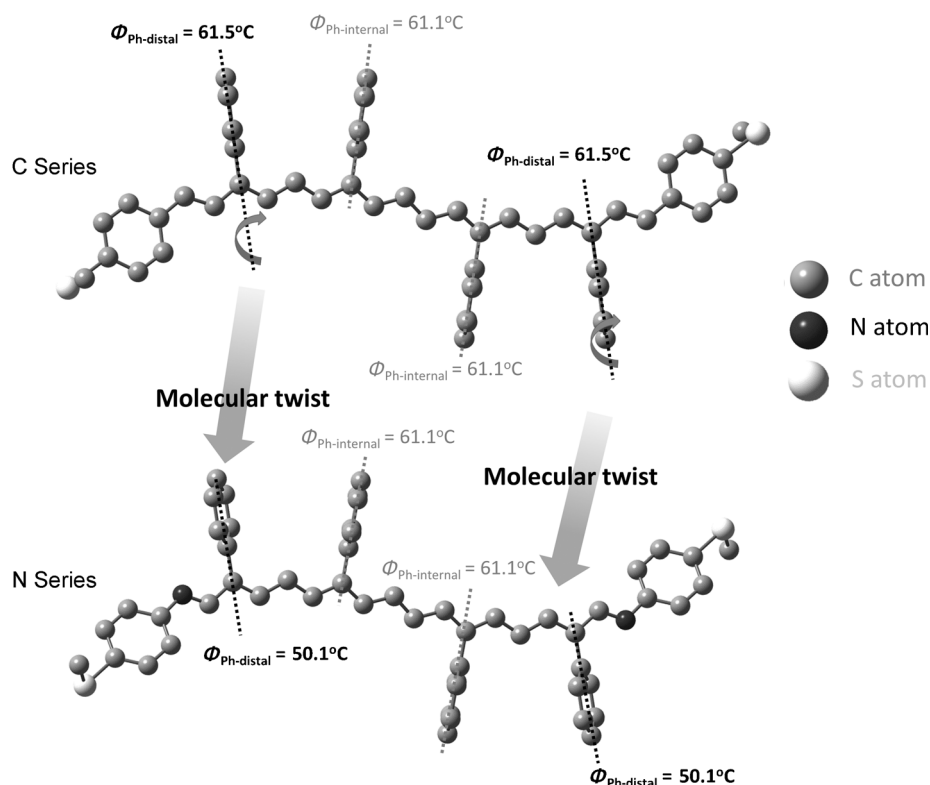


Figure 2. B3LYP/6-31G(d)-optimized structures of Ph-H-substituted C-series and N-series. Dihedral angles (ϕ) of the phenyl substituents are depicted. Dihedral angles of the other phenyl substituents, Ph-O-CH₃, Ph-CH₃ and Ph-Cl, are summarized in Table S3 (see section 3 of the Supporting Information).

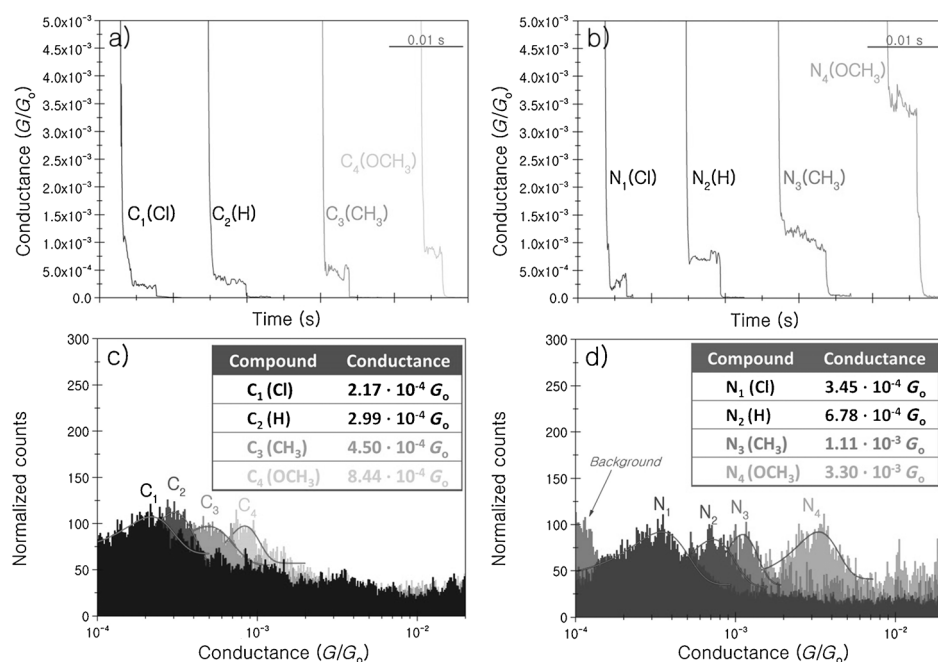


Figure 3. Representative individual current traces for a) C₁–C₄ and b) N₁–N₄ molecules. Semi-log conductance histograms for c) C₁–C₄ and d) N₁–N₄ compounds. The conductance values are extracted from Gaussian fits of the peaks. Insets in figures c and d summarize the average conductance magnitude for each compound. The applied bias was set to 50 mV.

The experimental findings are supported by the distribution and the calculated energy of the HOMO levels involved in the electron transport for these molecular systems. The distribution of the HOMO frontier orbitals (Figure 5) clearly shows that in the C-series, the nearly orthogonal configuration (dihedral angle of 60°) of all the phenyl substituents prevents proper electronic communication between them and the carotenoid backbone, thus suppressing major involvement of the phenyl substituents in the electron transport. Hence, the molecular orbitals for all four phenyls in the C-series chain are only mildly mixed with those of the polyene backbone. On the contrary, the molecular orbitals in the more twisted distal phenyls (dihedral angle of 50°) of the N-series present a more effective hybridization with the polyene chain. The differences in the observed hybridization of the phenyl substituents for both C- and N-series results in a shallower increase of the HOMO energy in the former, 0.37 eV, versus a sharper increase in the latter, 0.48 eV, when going from Ph-Cl to Ph-OCH₃ (see DFT-calculated energies in section 4 of the Supporting Information). These differences explain the amplified trend of conductance versus the electron-donating character observed for the N-series (Figure 4).

In conclusion, we have synthesized a series of carotenoid molecular wires with the ability to fine-tune their conductance using a series of side-phenyl substituents with controlled conformation. The comparison of the single-molecule conductance for the two studied carotenoid series shows that a slight twist of the phenyl substituents towards a more planar conformation greatly enhances their electron-donating role in the molecular wire. With such fine compo-

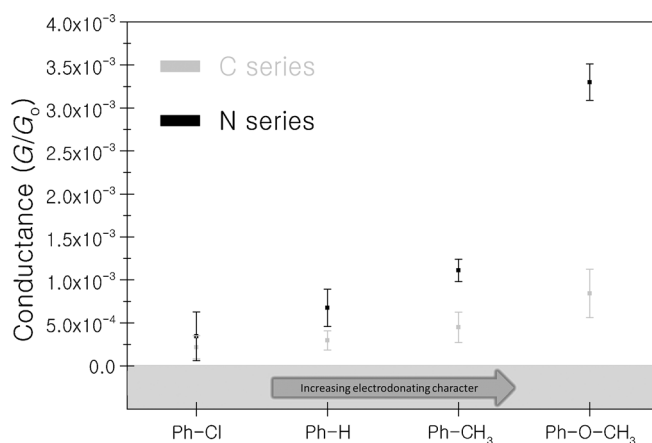


Figure 4. Evolution of the conductance values versus the electron-donating character of the phenyl substituents. The error bars represent the standard deviation of the conductance values and are derived from the full width at half maximum (FWHM) values of the conductance peaks in the histograms of Figure 3 c,d.

sitional and geometrical adjustments of the phenyl substituents, we managed to increase the conductivity of a polyene wire over an order of magnitude, starting from $2.1 \times 10^{-4} G_0$ (conductance quantum: $G_0 = 77.4 \mu S$) conductance and reaching a significantly high value of $3.5 \times 10^{-3} G_0$ for a ≈ 3 nm long molecular wire. This study offers a general method to fine-tune the conductivity of a molecular wire with high precision in a wide conductance range, combining both the electronic character and the conformation of the side-group substituents.

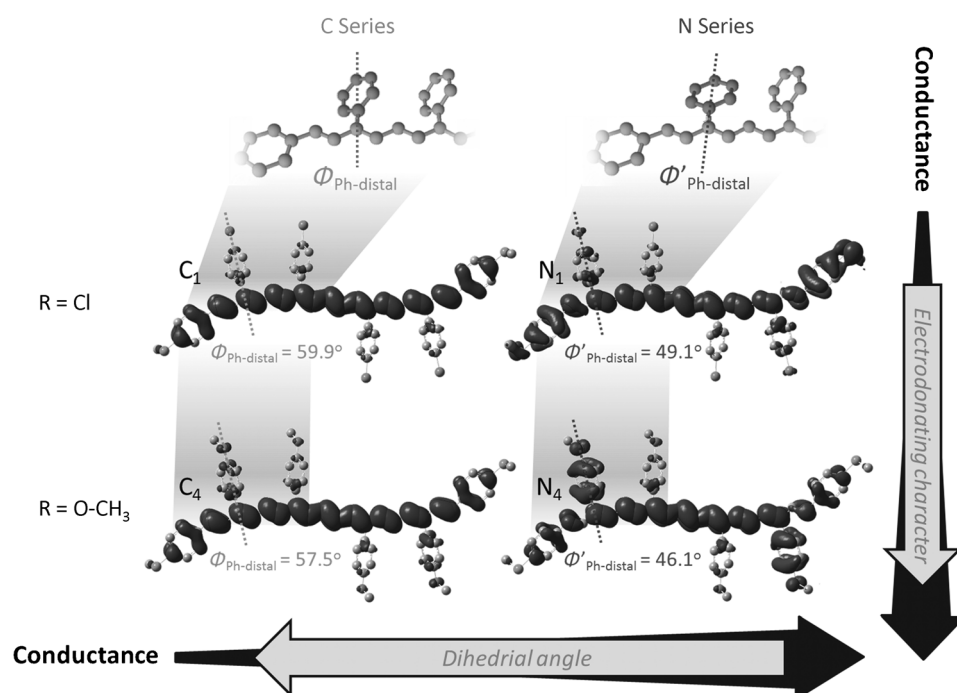


Figure 5. Distribution of the HOMO + HOMO-1 frontier orbital versus the electron-donating character of the phenyl substituents for both C- and N- series. Arrows indicate the evolution of the conductance as a function of the phenyl dihedral angle (x-axis) and phenyl electrodonating character (y-axis).

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