Topology-Driven Single-Molecule Conductance of Carbon Nanothreads

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Abstract

Highly conductive single-molecule junctions typically involve π -conjugated molecular bridges, whose frontier molecular orbital energy levels can be fine-tuned to best match the Fermi level of the leads. Fully saturated wires, *e.g.*, alkanes, are typically thought of as insulating rather than highly conductive. However, in this work we demonstrate *in silico* that significant zero-bias conductance can be achieved in such systems by means of topology. Specifically, caged saturated hydrocarbons offering multiple σ -conductance channels afford transmission far beyond what could be expected based upon conventional superposition laws, particularly if these pathways are composed entirely from quaternary carbon atoms. Computed conductance of molecular bridges based on carbon nanothreads, *e.g.*, polytwistane, is not only of appreciable magnitude; it also shows a very slow decay with increasing nanogap, similarly to π -conjugated wires. These findings offer a way to manipulate the transport properties of molecular systems by means of their topology, alternative to traditionally invoked electronic structure.

TOC image



Is π -conjugation mandatory to achieve efficient transport in molecular electronics? In this work we aim to address this question for a particular type of unimolecular electronics - molecular junctions,¹ which involve one or several, typically π -conjugated, molecules bringing a nanogap between the conductive electrodes. Molecular junctions provide invaluable insight into the intricate details of charge, spin, force and heat transport on a molecular level and hold great promise for applications as nanosensors, nanotransistors, etc. Conductance of such assemblies in great part depends on the extent to which the energy levels of the frontier molecular orbitals (MOs) of the bridge are aligned with the electrode's Fermi level, hence the π -conjugated systems with narrow HOMO-LUMO (i.e., highest occupied and lowest unoccupied MO) gaps are often chosen to achieve better transport. Beyond that, *topology* – broadly understood here as a relative arrangement of individual conducting blocks in the space between the contacts – can also affect conductance of the multicomponent junctions. Specifically, the conductance superposition law (also called the ohmic or Kirchhoff's superposition law, the superposition theorem, etc.)² states that the net conductance in a closed parallel circuit is equal to the sum of the conductances of its components, *i.e.* $G = \sum G_i$ (Eq. 1). In the case of molecular junctions, conducting block is a chain of atoms, *e.g.*, carbons, connecting the leads. Depending on the exact architecture of the junction (Figure 1),³ its conductance can either strictly obey Eq. 1,⁴ or, under dense coverage (great number of the parallel molecules separated by shorter distances) deviate from it taking the form of $G = nG_{eff}$ (Eq. 2, here *n* is the number of identical wires, G_{eff} is the effective single-wire conductance).^{5,6} This is due to electronic communication, i.e. overlap and energy level splitting of the frontier MOs, between adjacent π -conjugated wires, which results in a phase-dependent quantum interference⁷ (also called intermolecular crosstalk^{8,9,10} in systems in Figure 1A). In the case of intramolecular quantum interference between parallel π -conjugated branches (Figure 1B), the superposition law in Eq. 1 no longer holds:^{11,12} for two branches with conductances G_1 and G_2 , the net conductance is equal to $G_1 + G_2 + 2\sqrt{G_1 \times G_2}$ (Eq. 3); for *n* identical branches, the total conductance follows a quadratic superposition law n^2G_i (Eq. 4).³



Figure 1. Parallel circuit scenarios in SMJs: (A) multiple molecules, connected in parallel; (B) single molecule with parallel intramolecular paths. Orange areas schematically denote the electrodes.

However, all these examples of topological effects on conductance are essentially due to π orbital interactions. When the latter are ruled out - either due to their absence, as in the fully saturated wires, or due to the destructive quantum interference, as in a meta-anchored benzene, observed conductance arises from the through-bond σ -transmission channels.^{13,14} Destructive interference can still be harnessed in pure σ -systems, e.g., the bicyclo[2.2.2]octasilane, which affords an unprecedented molecular insulator - more insulating in fact than the vacuum it occupies.^{15,16} This behavior is attributed to a so-called ' σ -delocalization', arising from interactions between the localized Si-Si σ-bonds along the molecular backbone depending on its conformation.¹⁷ We note, however, that physical organic chemists conventionally use the term ' σ delocalization' to describe a very different type of σ -orbital interactions¹⁸ in cyclic and caged saturated hydrocarbons and/or their cations (related to the concept of σ -aromaticity), boron clusters, etc.^{19,20,21} To avoid confusion, throughout this work we will refer to the enhanced overlap between the localized σ -bonds as an 'oligosilane-like' behavior. In alkanes, which lack π -conjugation and conventional σ -delocalization, conductance superposition was tested only for rather short (under 7Å) molecular bridges, which are likely subject to 'noise' from direct electrode-electrode tunneling in such a narrow nanogap.²²

In this work, we aim to boost the transport in fully saturated hydrocarbon molecular wires by means of their topology. Investigated systems feature diverse molecular topologies, including one-, two- and three-dimensional²³ linear, cyclic and caged alkane wires, as well as π -conjugated linear acenes²⁴⁻²⁵²⁶ for comparison purposes (Chart 1). Among selected 3D nanocarbons, there are several representative tetrahedral carbon (degree 6) nanothreads: zipper polymer, tube(3,0), polytwistane and polymer I,^{27,28} – as well as linear polymantane nanothreads.²⁹ These systems are generally

This document is the Accepted Manuscript version of a Published Work that appeared in final form in the Journal of Physical Chemistry Letters, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see https://pubs.acs.org/doi/10.1021/acs.jpclett.8b03556. accessible synthetically³⁰³¹³²³³ and feature multiple chains of tetrahedral carbon atoms that, in the context of this work, serve as individual conducting blocks, connected in parallel. Geometries of all investigated nanowires were optimized at the PBE0-D3BJ/def2-SVP level of theory. Junction geometries were obtained by optimizing the wires, anchored on two opposite ends to the model Au(111) electrodes with methylthio linkers, at the same level of theory. Transmission properties of these junctions were computed using the non-equilibrium Green's function formalism combined with density functional theory (NEGF-DFT) at the PBE/DZP level.³⁴ Detailed description of all computations is given in the Supporting Information. Topological features of the studied hydrocarbons were analyzed as follows. In this work, we adopt the term ' σ -conductance channel' for pathways through single C-C bonds along the molecular backbone connecting the -SCH₃ linkage sites. Yen's ranking loopless paths algorithm³⁵ was used to count the number of such channels n_l of length l in each wire (see Figures S3 and S7 in the Supporting Information). An individual C–C bond can be shared by several pathways; two pathways are considered non-identical if they are different by at least two C–C bonds. Length *l* corresponds to the number of C–C bonds connecting the –SCH₃ linkage sites; we adopt a symbolic notation *l* for the shortest conduction path and l + i (where i = 2, 4, 6, ...) for longer ones. Taking into account the exponential decay of conductance with length ($G \sim e^{-\beta L}$, where L is the nanogap size, Eq. 5), conductance through a longer channel, G_{l+i} , surpasses that of the shortest path, G_l , when $\frac{n_{l+i}}{n_l} > e^{-\beta i}$ (Eq. 6).



Chart 1. Studied hydrocarbon wires. Columns from left to right: notations, adopted throughout this work, *e.g.*, 'zipper' for zipper polymer, 'tube' for tube(3,0), twistane for polytwistane and 'polymer' for polymer I; structures of the longest representatives (single 'building' units are shown in red, Arabic numbers denote the homologue numbers, positions of the –SCH₃ linkers are indicated with the wavy lines); PBE0-D3BJ/def2-SVP optimized geometries of the isolated molecular wires – views from the side and along the wire.

Junction conductance. Computed zero-bias transmission probabilities at Fermi level (*i.e.*, $T(E_F) = G(E_F)/G_0$, where G_0 is the quantum of conductance) in all studied junctions are shown in Figure 2A. In the linear acenes, $G(E_F)/G_0$ remains roughly the same despite the increasing nanogap *L* (from 10Å in benzene to 15Å in the tetracene junction) due to the accompanying lowering of their LUMO level (from *ca.* 0 eV in benzene to under -2 eV in tetracene) and correspondingly strengthening coupling with the gold's Fermi level.³⁶ In the alkane wires, energy levels of the frontier molecular orbitals (FMOs) are nearly identical in systems of different dimensionality and length (see Figure S5 in the Supporting Information). The observed systematic decrease in their zero-bias transmission probabilities down to very small magnitudes (below $10^{-6} G_0$) with increasing molecular length can

This document is the Accepted Manuscript version of a Published Work that appeared in final form in the Journal of Physical Chemistry Letters, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <u>https://pubs.acs.org/doi/10.1021/acs.jpclett.8b03556</u>. thus be attributed to the exponential decay law (Eq. 5). However, once these $G(E_F)/G_0$ values are plotted against the corresponding nanogaps L (Figure 2B), it becomes clear that the studied carbon nanothreads possess noticeably different transport properties despite their nearly identical MO characteristics.



Figure 2. Computed zero-bias transmission probabilities (NEGF-DFT at PBE/DZP+ZORA level, logarithmic scale) at Fermi level of the studied hydrocarbon wires of different families, attached to Au(111) electrodes (A, see labels in Chart 1); (B) plotted against the nanogap length for L > 10Å to exclude very compact junctions with direct interactions between the molecular core and the electrodes bypassing the linker. Dashed line denotes the average $G(E_F)/G_0 = 10^{-2}$ in acene wires. In the legend, numbers in brackets are computed exponential decay constants β for each family (Eq. 5).

For a given nanogap, one-dimensional linear alkane wires have the lowest transmission, followed by two-dimensional cycloalkane wires. Three-dimensional saturated hydrocarbon wires generally afford higher conductance (by over 3 orders of magnitude), particularly polymantanes and polytwistanes and at larger nanogaps. The quickest decay of conductance with nanogap length is observed in the cycloalkane series ($\beta = 1.49$), the slowest – in polytwistanes ($\beta = 0.55$). A possible explanation for this behavior lies in the pronounced oligosilane-like nature of the latter: among the studied nanowires they have the smallest C–C–C bond angles and the highest contributions of carbon's atomic *p*-orbitals (*sp*^{2.82}) to the C–C bond orbitals. Taken together, these factors point to an enhanced overlap between the σ -electron densities of the adjacent C–C bonds along the conductance channels, associated in the studied systems, particularly the polytwistanes, with higher zero-bias transmission.

Conductance superposition. Despite the existence of multiple σ -conductance pathways of different lengths, for the vast majority of investigated wires (Chart 1), conductance through the shortest channel is significantly higher than through the longer ones (see Figure S7 and Table S2 in the Supporting Information). Qualitatively, both the number of the shortest transport channels, n_i , and the zero-bias transmission increase with the dimensionality²³ of the wires, from 1D alkanes to 2D cyclohexanes to various 3D nanothreads. According to the conductance superposition law, amplification of the transport properties due to numerous transport channels in the investigated 'multiwire' hydrocarbons with respect to a reference single-wire alkane of the same length, *i.e.* $G_{multiwire}/G_{alkane}$, should be proportional to n_l . Computed zero-bias transmissions, however, greatly (by orders of magnitude) surpass the linear (Eq. 2) and, in most systems, even the quadratic (Eq. 4) superposition laws (Figure 3). Instead, as n_l increases, the wire transmission first rapidly grows (by ~2-3 orders of magnitude for shorter l and as much as 5 orders for l = 17), reaching a maximum around 5-50 transport pathways depending on the wire type, and then slowly subsides. Thus, there appears to be a saturation point for the amplification of conductance in the multichannel carbon nanothreads, beyond which weaving more carbon chains into the wire becomes ineffective. This 'sweet spot' is particularly well matched in polytwistanes ($n_l = 3.45$ for l = 4.18). While conductance saturation has been reported for linear acenes of increasing length due to molecular orbital factors,³⁷ behavior observed here for the fully saturated systems of identical length but different topology is yet to be rationalized.



Figure 3. Computed zero-bias transmissions (circles, on a logarithmic scale) of various saturated hydrocarbon wires featuring the same-length shortest conductance pathways (l), plotted against the number of these conductance channels n_l . Line series correspond to the quadratic superposition law (Eq. 4), based on the extrapolated zero-bias conductance of the corresponding alkane. See also Table S3 in the Supporting Information.

Design of more conductive carbon nanothreads. While the conductance of 3D carbon nanothreads surpasses that of their 1D and 2D counterparts by orders of magnitude, it is nonetheless minute in absolute terms, falling below 10⁻⁵ already at a 15Å nanogap. Thus, while the observed conductance superposition beyond the Kirchhoff's law is interesting, it is hardly useful at such low transmissions. To achieve more palpable G values, we turn to our observation that polytwistanes are the most conductive among the studied nanothreads due to their oligosilane-like behavior, reflected in an increased contribution of the atomic *p*-orbitals to C–C bonds. This notion is further verified by comparing bonding and transmission properties of a linear *n*-alkane C₁₂H₂₆ to its permethylated analogue: the former features secondary C-atoms (Csec; notations Ctert and Cquat are adopted for tertiary and quaternary carbon atoms throughout this work) along its conductance path with, on average, $sp^{2.5}$ hybridization and affords $G(E_F) \sim 1 \times 10^{-9}G_0$, while the latter involves $sp^{3.1}$ hybridization of quaternary carbon atoms along its backbone and forms a junction with $2 \times 10^{-8} G_{\theta}$ conductance at the Fermi level (see Table S4 and Figure S14 in the Supporting Information). Both systems obviously offer only a single conductance channel, thus we can speculate that a 20-fold increase in the zero-bias transmission from C_{sec}-C_{sec} to C_{quat}-C_{quat} path is due to an increasingly oligosilane-like behavior of the latter. Armed with this principle, we have constructed and investigated a series of nanothreads based on a polytwistane motif featuring both the multiple σ conductance channels and the quaternary carbon chains (Chart 2).



Chart 2. Designed hydrocarbon wires with multiple conductance channels involving quaternary carbon atoms. Columns from left to right: notations, adopted throughout this work (mono-, di- and tri-OT stands for the number of 'conjoined' oligotwistane chains); structures of the longest representatives (single 'building' units are shown in red, quaternary carbon atoms are marked with blue circles, Arabic numbers denote the

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Interestingly, due to the chosen linkage sites (slightly different from the oligotwistane series in Chart 1), these wires have only one shortest but numerous longer conductance pathways satisfying the $\frac{n_{l+i}}{n_l} > e^{-\beta i}$ condition (Eq. 6, see Table S2 in the Supporting Information). In addition to multiple transport channels, they are also characterized with higher contributions of the *p*-orbitals to the hybridized carbon orbitals in C_{quat}-C_{quat} bonds, symptomatic of the oligosilane-like behavior $(sp^{3.1})$. Computed zero-bias transmissions of these systems (Figure 4) indicate that the mono-OT wires predictably resemble closely twistanes in Chart 1, affording exponentially decaying conductance 2-3 orders of magnitude above that of the alkane series. On the other hand, di- and tri-OT series display remarkable retention of conductance ($\beta < 0.2$) that is also significantly higher – ~10⁻⁵ G_0 in tri-OT and ~10⁻⁴ G_0 in di-OT at up to 20Å nanogap – compared to all other tetrahedral carbon systems. Notably, new peaks corresponding to the highest occupied molecular orbitals close (~0.4 eV) to the Fermi level appear in the transmission spectra of the wires with two and three conjoined oligotwistane chains (see Figure S14 in the Supporting Information). This could potentially suggest that their higher conductance is due to molecular orbital-related factors – as is the case in conventional π -conjugated systems – rather than their topology. However, no such peaks are observed in the spectra of a permethylated alkane, which nonetheless affords conductance 20 times higher than the analogous *n*-alkane. Furthermore, a very similar system to di-OT-6 but with a different linkage site and consequently different topology of the σ -conductance channels has an identical high-energy transmission peak near E_F yet displays conductance 5 times lower than di-OT-6 (see Figure S9 in the Supporting Information). Finally, these transmission peaks are rather narrow and correspond to molecular orbitals, considerably localized on the central core and thus not significantly coupling in transport (see Figure S10 in the Supporting Information).^{34a}



This document is the Accepted Manuscript version of a Published Work that appeared in final form in the Journal of Physical Chemistry Letters, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <u>https://pubs.acs.org/doi/10.1021/acs.jpclett.8b03556</u>. **Figure 4.** Computed zero-bias transmission probabilities (NEGF-DFT at PBE/DZP+ZORA level, logarithmic scale) at Fermi level of acene, alkane and designed hydrocarbon wires, attached to Au(111) electrodes (see labels in Chart 1 and Chart 2). In the legend, numbers in brackets are computed exponential decay constants β for each family (Eq. 5).

Crucially, persistently substantial conductance in di- and tri-OT is due not only to multiple σ conductance channels of different lengths, but also to the fact that they occur through adjacent C_{quat}-C_{quat} bonds. This is additionally illustrated by our results for extended diamondoid wires (with conjoined polymantane chains), which lack neighboring quaternary carbon atoms and hence offer conductance pathways following the C_{tert}-C_{quat} bonds instead. Transmission spectra of these wires also involve peaks closer to E_F by ~0.6 eV than in the analogous diamondoid series, however in the vicinity of the Fermi level the spectra of extended systems essentially overlap with those of the corresponding prototypical polymantanes (see Figure S11 in the Supporting Information). This further supports the notion that it is the multiple channels involving chains of adjacent C_{quat}-C_{quat} bonds, associated with the oligosilane-like behavior, that cause the outstanding conductance in the fully saturated conjoined oligotwistane series di- and tri-OT.

In the present work, we elucidate the conductance superposition patterns in the single-molecule junctions featuring multichannel tetrahedral carbon nanowires. Our results reveal that in the threedimensional nanothreads, conductance increases with the growing number of σ -conductance channels only until a certain threshold, corresponding to *ca*. 5-50 such pathways, thus violating conventional superposition laws. Higher transmission can nonetheless be achieved in fully saturated hydrocarbons if their conductance channels consist of chains of adjacent quaternary carbon atoms, which possess an oligosilane-like electronic structure. Guided by these principles, we have designed conjoined oligotwistane threads, which, based on NEGF-DFT computations, afford zero-bias conductance of *ca*. $10^{-4}G_{\theta}$, (~6 orders of magnitude above that of a corresponding linear alkane at ~20Å nanogap) and display much slower conductance decay with distance ($\beta < 0.2$, compared to $\beta > 1.0$ in linear alkanes). Conventional approaches to highly conductive single-molecule junctions involve π -conjugated systems with appropriately tuned energy levels of the frontier molecular orbitals. Our findings put forward an alternative strategy for modulating the transport in unimolecular electronics that is based on molecular topology and succeeds even in systems completely lacking π -conjugation, *e.g.*, carbon nanothreads, diamondoids and graphane derivatives.

Supporting Information

Details of computational procedures, full set of results, computed transmission spectra, geometries of all species.

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