Anti-ohmic Nanoconductors: Myth, Reality and Promise

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Abstract: The recent accomplishments in the design of molecular nanowires characterized by an increasing conductance with length has embarked the origin of extraordinary new family of molecular junctions referred to as "anti-ohmic" wires. Herein, this highly desirable, non-classical behavior, has been examined for the longer enough molecules exhibiting pronounced diradical character in their ground state within the unrestricted DFT formalism with spin and spatial symmetry breaking. We demonstrate that highly conjugated acenes signals higher resistance in open-shell singlet (OSS) configuration as compared to their closed-shell counterparts. This anomaly has been further put to proof for experimentally certified cumulene wires, which reveals phenomenal modulation in the transport characteristics such that an increasing conductance is observed in closed-shell limit, while higher cumulenes in OSS ground state yields a regular decay of conductance.

Molecular nanowires mediating long range charge transport are desirable for their potential applications in future molecular scale circuitry.¹⁻³ Most of the conventional molecular wires suffer from an exponential decay of conductance (G) with wire length (L) as $G = Ae^{-\beta L}$, wherein positive β value signifies a decay of conductance. However, in recent years, molecular wires with unusual attenuation factors, such as $\beta=0$ (i.e., G independent of L) or even negative β values (i.e., G increasing with L) have become sparkle in the eyes of research community.⁴⁻⁶ Such extraordinary wires exhibiting negative β values in phenomenological violation of the classical Ohm's law are called as anti-ohmic nanoconductors. This reversed exponential decay of conductance with length was first reported by Tada and Yoshizawa for nanographenes with zigzag edges.⁷ Subsequently, the molecular wires based on porphyrin derivatives were presented with low attenuation factors^{8,9} which was later endorsed by an experimental achievement by Leary et al.¹⁰ Afterwards, several guiding principles were chronicled to explicate the non-trivial reversed conductance/length trends. Tsuji et al. suggested that if the bond length alternation of molecule is reversed, β will be negative.¹¹ Mandado and coworkers proposed an example of quinoid wires with exceptional anti-ohmic behavior.^{12,13} Alongside, Stuyver et al. connected this behavior to diradical character.^{14,15} Other correlated factors including captodative substitution and effect of aromaticity have also been employed to obtain anti-ohmic nanoconductors.^{13,16} Contrastingly, in the framework of multi-reference calculations, regular decay of conductance was observed.¹⁷ Followed by this, broken symmetry DFT calculations taking into account the spin-symmetry breaking effects also revealed a decrease in conductance with length for the alleged anti-ohmic wires.¹⁸

With these ongoing trial and error debates on the feasibility of anti-ohmic wires, we undertook a theoretical inves-

tigation of length-dependence of the conductance in molecular wires exhibiting pronounced diradical character in their ground state. In the context of diradical character, the highly conjugated polyacenes, consisting of linearly fused benzene rings, have been widely debated in literature.^{19,20} While after the pioneering study by Bendikov et al., it is generally accepted that short acenes (up to hexacene) have a closed-shell singlet (CSS) ground state, while higher acenes are predicted to be in open-shell singlet (OSS) ground state.²¹ The transport characteristics of acenes have been examined by numerous theoretical reports,²²⁻²⁵ while the effect of spin polarized nature of higher acenes on the electron transport has been rarely considered.²⁶ Assuming the non-magnetic ground state, Visontai et al. found that conductance of the acene series is an oscillatory function of length.²⁷ In an experimental study, Kaliginedi et al. observed positive β value for the series of lower acenes.²⁸ While a recent computational study claimed that acenes with meta connection to electrodes exhibit an increase in conductance with length.²⁹ Thus, the length dependence of conductance for acenes has remained a persistent puzzle. On the other hand, poles apart from polyacenes, there had been many speculations about 1-D linear chain of sp-hybridized carbon atoms, which potentially exist in two forms: the polyyenic type with alternate single and triple bonds and the cumulenic type with consecutive double bonds.^{30,31} Among the two series, cumulenes have seen the light of the day with an experimental observation of negative β values.^{32,33} Notwithstanding, the synthesis of polyynes has been extensively reported, culminating with the isolation of [22]polyyne, however, due to dramatic increase in reactivity, [9]cumulene is the longest derivative studied to date.³⁴ This increased reactivity of $[n]$ cumulenes itself points towards the open-shell character in longer cumulenes. However, the open-shell nature of cumulenes has not been reported hitherto.

In the relentless quest for the anti-ohmic nanowires in this work, we sought to re-examine the length dependence of molecular conductance for both acene and experimentally validated³² cumulene series suspended between two gold electrodes. The electrical conductance has been explicitly determined within the Landauer formalism using restricted closed-shell wavefunction for lower members in the series. While, broken symmetry (BS) wavefunction in an unrestricted formalism with spin and spatial symmetry breaking is used for higher members with OSS ground state. To the best of our knowledge, this is the first study of transport characteristics with increasing length, explicitly taking into account the spin polarized nature of the molecular species.

While the CSS ground state for lower acenes and cumulenes is well recognized in literature, but there is no clear consensus on the higher members of the series, yet. Thus, to unravel the size-dependent onset of open-shell nature, ground state electronic properties are first examined for the isolated acenes and cumulenes, shown in insets of Figure 1.

Figure 1. (a,c) Relative energy difference ($\Delta E_{OSS-CSS}$) in meV calculated from UDFT and RDFT optimized geometries at B3LYP/def2-TZVP level for (a) $n = 1$ to 12 acenes, (c) $n = 4$ to 25 cumulenes. (b,d) Computed $\langle S^2 \rangle$ values in BS state at UB3LYP/def2-TZVP level and radicaloid character (y) for (b) acenes, blue curve denotes variation in $\langle S^2 \rangle_{BS}$ values and orange curve represent y values, (d) cumulenes, $\langle S^2 \rangle_{BS}$ (blue/pink colors for even/odd members) and y values (orange/brown colors for even/odd members). The negative $\Delta E_{OSS-CSS}$, increasing $\langle S^2 \rangle$ and $y > 0.5$ indicates that OSS state is favoured as a ground state from $n = 7$ acene and $n = 16$ cumulene onwards. The oscillatory behavior of $\Delta E_{OSS-CSS}$, $\langle S^2 \rangle$ and y curves signifies even-odd effects in cumulene series.

The relative energy difference between the OSS and CSS states, reveals that upto $n=6$ acene (Figure 1a) and $n=14$ cumulene (Figure 1c), both CSS and OSS solutions converge to same CSS state and yields $\Delta E_{OSS-CSS} = 0$, indicating that CSS state is ground state for the lower members of heterologous series. For $n=7$ acene, $\Delta E_{OSS-CSS} = -65$ meV marks the transition in ground state from the CSS to OSS state. The increasing ΔE upto -650 meV for $n=12$, ultimately outstrips the CSS behavior of the system for higher acenes. The emergence of OSS ground state, for $n \geq 7$, is in complete agreement with previous DFT calculations on higher acenes.^{21,35,36} Interestingly, the similar kind of build-up of OSS character is also observed for cumulene series from $n=16$ onwards (Figure 1c). Although, $\Delta E_{OSS-CSS}$ for cumulenes is significantly lower than acenes, however a maxima of $\Delta E_{OSS-CSS} = -138$ meV for $n=24$ cumulene clearly reveals an OSS ground state for the higher cumulenes as well.

To further authenticate the essence of OSS character, spin-squared value $\langle S^2 \rangle$ in BS state and radicaloid character (y), which are used as the descriptors of diradical character of a molecule^{37,38} are presented in Figure 1b and Figure 1d for acenes and cumulenes respectively. The diagnostic value of $\langle S^2 \rangle$ in BS determinant should be 1.0 for a singlet diradical state. Any deviation from the expected $\langle S^2 \rangle_{BS} = 1$ indicates spin contamination due to contributions from other low lying excited spin states. Here, $\langle S^2 \rangle = 0$ upto $n=5$ acene and $n=13$ cumulene indicates CSS ground state. Afterwards, the $\langle S^2 \rangle$ value shows a regular increase with the increasing n for both the series. For intermediate members, i.e., $n=6$ acene and $n=14, 15$ cumulenes, $\langle S^2 \rangle_{BS} \sim 0.17$ indicates the preferential existence of molecule in CSS

ground state with small spin contamination. Thereafter, $\langle S^2 \rangle_{BS}$ starts approaching towards 1.0 indicating diradical ground state for $n \geq 7$ for acenes and $n \geq 16$ for cumulenes. However, for the higher members, the spin contamination in OSS becomes large with $\langle S^2 \rangle = 1.69$ for $n=12$ acene and 1.40 for $n=25$ cumulene pointing towards the mixing of low-lying triplets. Qualitatively, similar trends are also found in radicaloid character (y), which classify singlet molecular systems into three categories: (i) closed-shell ($y = 0$), (ii) intermediate diradical ($0 < y < 1$), (iii) pure open-shell ($y = 1$) systems.³⁹ The increasing radicaloid character with increasing length, i.e., $y > 0.5$ from $n=7$ acene and $n=16$ cumulene onwards unambiguously confirms that OSS spin polarized state supersedes the CSS state as the ground state. Notably, for cumulenes, all the aforementioned indices, i.e., $\langle S^2 \rangle_{BS}$, y and $\Delta E_{OSS-CSS}$, displays an oscillatory behaviour associated with even-odd effects along the series attributed to the different helical orbital structure of the odd-cumulene series. This eventually reflects in the form of marginally lower diradical character for the odd-cumulenes than their even counterparts.

With such an understanding for the ground state electronic properties, an intriguing quest arises to determine the fate of molecules with OSS ground state in molecular devices. To do so, acenes and cumulenes are placed between two gold electrodes consisting of two Au₉ clusters via thiol anchoring groups, as shown in Figure 2a and Figure 3a. The electron transport calculations are performed using Non-Equilibrium Green's Function combined with DFT (NEGF-DFT) as implemented in *Artaios*⁴⁰ (Details in Section 1 of SI). The transmission spectra is computed in both CSS and OSS limit to take into account the

Figure 2. (a) Junction schematics showing para (*p*) and meta (*m*) connected acenes suspended between two Au₉ clusters via thiol anchoring groups. (b) Calculated transmission spectra for $n = 1$ to 6 *p*-acenes and *m*-acenes in CSS ground state. (c) Transmission spectra for $n = 7$ to 12 *p*-acenes and *m*-acenes in CSS state (top panel) and OSS ground state (bottom panel). The vertical dotted line denotes the position of Fermi level.

spin-polarization effects. As for polyacenes, we have previously reported that acenes with meta connection to electrodes leads to suppression of conductance as compared to their para connected analogs due to destructive quantum interference (DQI), which further intensify with increasing molecular length.⁴¹ Thus, taking into consideration the fundamental role played by QI effects, we have examined acenes with both para and meta connections to Au electrodes (Figure 2a). On the other hand, due to different helical orbital structure of odd-cumulene series, even and odd cumulene series are treated separately (Figure 3a).

Before proceeding, let us make the discussion more concrete by focusing on the elemental factors enumerated in literature that influence the conductance.⁷ The argument embarks on the familiar zeroth order Green's function⁴² written as

$$G_{lr}^{mol}(E) = \frac{C_{l,HOMO}C_{r,HOMO}^*}{E - \varepsilon_{HOMO}} + \frac{C_{l,LUMO}C_{r,LUMO}^*}{E - \varepsilon_{LUMO}} \quad (1)$$

where $C_{l/r,HOMO}$ and $C_{l/r,LUMO}$ are the MO coefficients of the HOMO and LUMO at the connecting sites l and r and $\varepsilon_{HOMO/LUMO}$ are the HOMO/LUMO orbital energies. According to Eq 1, the following two factors drive the conductance. First, is the alignment of frontier HOMO and LUMO orbitals w.r.t Fermi energy. The smaller HOMO-LUMO gap leads to smaller energy offset between the frontier MOs and Fermi level of the electrode, and results in higher conductance. Thus, a wire should possess a decreasing HOMO-LUMO gap with length. The second dominant factor is the numerator of Eq.1, i.e., orbital coefficients at the contact sites which control the electrode-molecule coupling strength and should remain substantial with increasing length. Thus, the strong orbital localization at the contact sites and narrowing of HOMO-LUMO gap with length can commute an efficient electron transport with a plausible anti-ohmic behavior.

The transmission spectra for $n = 1$ to 6 acenes in CSS ground state is shown in Figure 2b. The evolution of resonance peaks associated with the energy eigenvalues of molecule indicates several trends with competing effects on

conductance. The first is energy offset between resonance peaks originating from frontier HOMO and LUMO states and Fermi energy, which decreases with increasing number of benzene rings. Thereby, decreasing the HOMO-LUMO gap with increasing molecular length, which acts to increase the conductance. The second is the increase in number of resonant peaks appearing in conductance spectra with the increment of the length which also favours the increase in conductance. This is in line with the increase in density of MOs with increasing n , as illustrated in orbital energy diagram plot (Figure S12 in SI). The other competing factor is the broadening of the frontier resonant peaks, which results from the coupling of molecular states to the extended states of the electrode.⁴³ Here, the reduction in the width of frontier peaks along the series implies that the coupling of acenes with electrodes gets weakened upon increasing the length which plausibly decreases the conductance. This can be directly inferred from the spatial distribution of MOs (Figure S3 in SI) which reveals that orbital coefficients falls off quickly at the terminal connecting sites with increasing length which eventually results in weak coupling with electrodes. With these competing factors, the conductance, determined by the magnitude of transmission coefficient at the Fermi energy, reveals an evident decrease with the increasing molecular length for both para and meta configurations. However, the difference between the transmission values at Fermi energy is decreasing gradually with the increment of length, thus, implying that the conductance may saturate for longer enough acenes. All these trends including the decrease in conductance and evolution of frontier resonance peaks are robust for both *p*-acenes and *m*-acenes. However, as compared to *p*-acenes, *m*-acenes shows sharp dips near Fermi energy owing to DQI effects associated with the phase difference between electron waves traversing across the molecule.^{44,45}

For higher acenes with OSS ground state, the transmission spectra for $n = 7$ to 12 in CSS and OSS ground state is shown in Figure 2c. In CSS state, the evolution of resonance peaks reveals similar trends as of $n = 1$ to 6, i.e., decreasing HOMO-LUMO gap approaching towards gap closure,

Figure 3. (a) Junction structures showing even (C4) and odd (C5) cumulenes suspended between two Au_9 clusters via thiol anchoring groups. (b) Calculated transmission spectra as a function of energy for even-cumulenes (C4 to C14) and odd-cumulenes (C5 to C15) in CSS ground state. (c) Transmission spectra for higher cumulenes, even-members (C16 to C24) and odd-members (C17 to C25) in CSS state (top panel) and OSS ground state (bottom panel). The vertical dotted line denotes the position of Fermi level.

increasing number of resonant peaks and simultaneous decreasing width of frontier resonant peaks. All these factors collectively resulted in a minor decay of conductance up to $n = 10$ and afterwards a notable increase is appeared for $n = 11$. On the other hand, in the more appropriate ground OSS state, the behavior of the molecular wire changes remarkably. The energy gap between frontier resonant peaks becomes independent of length and saturates to a constant value of ~ 1.60 eV. This gap saturation is consistent with HOMO-LUMO gap for isolated acenes, which saturates to a constant value of ~ 1.76 eV in OSS state, but shows a steady decrease in CSS state (Figure S1 in SI). Similar gap stabilization for higher acenes was also reported by Pilevarshahri et al.²⁶ Similarly, the other competing factors, i.e., number of resonant peaks and width of frontier resonant peaks also infuses to a constant value. These saturation factors are accompanied by sharp dips near Fermi level which now appeared irrespective of para/meta configuration. For meta configuration, conductance shows an evident decrease up to $n = 12$, while for para configuration it saturates at $n = 8$.

To bring the observed contrasting features of transmission spectra in CSS and OSS state on more solid ground, we calculated the transmission spectra for another genre of molecular wires, i.e., cumulenes, shown in Figure 3. Interestingly, corroborated with previous theoretical⁴⁶ and experimental measurements,³² cumulene wires provide us an example with desired anti-ohmic behavior. For the lower members exhibiting CSS ground state (Figure 3b), the transmission spectra shows an increase in the transmission coefficients at Fermi energy accompanied by narrowing of gap between the frontier HOMO-LUMO peaks for both even and odd-cumulene (C9 onwards) series. Although, the transmission trends are dependent on the energy level alignment relative to Fermi energy, still the trends of increasing conductance persists in a complete energy window between HOMO-LUMO resonant peaks, except where all the dips befalls at ~ -0.2 eV. We track down the origin of anti-ohmic behavior of cumulenes is rooted in frontier MOs (Figure S5 and S6 in SI) which are now completely delocalized over the complete molecule, in contrast to polyacenes where orbital coefficients

falls off quickly at the terminal benzene rings. The substantial weight of the conducting frontier MOs on the terminal contact sites together with decreasing HOMO-LUMO gap in cumulenes engender both the factors in Eq. 1 to favour an increase in conductance. On the other hand, for the higher members with OSS ground state (Figure 3c), a modest increase in conductance is observed in CSS state, while the more appropriate OSS state shows a clear decay of conductance. Overall, the conductance increases upto a maximum wherein the lower members of the series with CSS ground state persist in anti-ohmic regime, in contrast, the emergence of OSS ground state for the higher members, provokes a regular decay of conductance.

It is now tempting to correlate the tunneling decay coefficients, β , in CSS and OSS state. Figure 4a shows the evolution of conductance as a function of n for p -acenes and m -acenes. It outlines that the overall trend of decreasing conductance with increasing molecular length is indeed unchanged in both CSS and OSS state. However, the decay is much shallower in OSS state than that in CSS state. As can be inferred from decay constant values, i.e. $\beta = 0.216$ in CSS state, whereas it decreases to 0.678 in OSS state for p -acenes. Similarly, m -acenes yields $\beta = 0.312$ in CSS state and 0.563 in OSS state. This implies that in OSS state, longer molecules leads to even higher resistance. On the other hand, for cumulenes (Figure 4b), inverted attenuation factors are observed. In CSS state, a steady increase in conductance is observed with negative β values, while OSS state, which is ground state for higher members, yields positive β values with regular decay of conductance. This indicates that anti-ohmic behavior do exists for lower cumulenes with CSS ground state, however if a restricted wavefunction is wrongly imposed to higher cumulenes with OSS ground state, it results in incorrect prediction of empirically negative β values. Thus the suggested positive correlation between diradical character and conductance^{15,47} is not as uni-equivocal.

To further understand the electronic structure governing the contrasting β values in CSS and OSS state, the spatial distribution of frontier HOMO and LUMO orbitals and their

Figure 4. (a) Molecular conductance (in units of G_0) v/s number of benzene rings (n) in CSS state (black curve) and OSS state (red curve) for *p*-acenes and *m*-acenes. Both CSS and OSS state shows a regular decay of conductance along the series with large positive β values in OSS state. (b) Conductance versus number of C-atoms (n) for even and odd-cumulenes. CSS state yields a negative β value with an increasing conductance, while OSS state reveals a decay of conductance for higher cumulene members. Spatial distribution of frontier HOMO and LUMO orbitals and HOMO-LUMO energy gaps are shown in insets.

energy gaps is shown in insets of Figure 4. In OSS state, longer molecules are subjected to spin-symmetry breaking which produces different spin-split orbitals for α and β electrons resulting from a mixing between HOMO and LUMO.⁴⁸ As illustrated by frontier MOs of $n = 10$ acene (inset of Figure 4a), in CSS state, HOMO and LUMO are more localized on zig-zag sites of the central benzene rings, while diminishing gradually to zero on reaching the terminal rings. On the other hand, the profiles of spin-split orbitals in OSS state reveals that among the two degenerate HOMOs, i.e., α -HOMO and β -HOMO, α -HOMO is localized on the hydrogenated C-atoms at one edge of the molecule, while β -HOMO is localized on the other edge with a disjoint character. The spin-split degenerate LUMOs also reveals the similar disjoint character. Contrarily, the inspection of frontier MOs for cumulenes (inset of Figure 4b) reveals completely delocalized orbitals over the whole molecular backbone in CSS state. For even cumulenes the π -system consists of parallel aligned p-orbitals, while in odd cumulenes the terminating motifs obtain an orthogonal configuration, which results in orbitals of helical shape.⁴⁹ Intriguingly, for even-cumulenes in OSS state, spin-symmetry breaking enforces the α -HOMO and β -HOMO to localize at opposite ends, thereby decreasing the delocalized character of frontier MOs in OSS state. Noteworthy, for odd cumulenes, the spin-symmetry breaks in a manner that the weight of two orthogonally oriented p-orbitals at the terminal C-atoms increases for one spin, while diminishes for the other spin configuration. This eventually leads to lifting of the degeneracy of spin-up and spin-down orbitals (as can be inferred from different HOMO-LUMO gap for spin-up and spin-down configurations in right panel

of Figure 4b). Apart from the symmetry breaking, OSS state witnesses a higher HOMO-LUMO gap as compared to CSS state for both acenes and cumulenes (Figure S1 and S2 in SI). Infact in CSS state, the HOMO-LUMO gap approaches towards gap closure with the increasing length, while in OSS state, the gap is an exchange gap between the spin-split molecular orbitals which is not strongly length dependent and saturates to a finite value. Thus, the decrease in delocalized nature of spin-split orbitals integrated with spontaneous increase of HOMO-LUMO gap in OSS state inhibits the efficient contact coupling in junction and results in an emphatic decrease in conductance.

In conclusion, the findings in this work add new prospective on the debate concerning the feasibility of anti-ohmic wires. The origin of anti-ohmic electron transport is rooted in to the intrinsic electronic structure of the molecule in junction wherein the decreasing gap between frontier electronic states and its localization at the terminal connecting sites of junction drives a nanowire into anti-ohmic regime. The current study put forth the preferential existence of the molecule in closed-shell state as another guiding rule to observe the desirable increase in conductance. We demonstrate that for acenes, orbital coefficients decay quickly at the terminal connecting sites. Thus, they exhibit a regular decay of conductance in both CSS and OSS state, accompanied by a larger resistance in OSS state. On the other hand, cumulenes display a priori all of the features required to be a true anti-ohmic wire. However, clouds over this horizon appear with the evolution from CSS to OSS state upon increasing length. For large enough molecules, the CSS state becomes unstable and undergoes spin-symmetry breaking which en-

forces α and β electrons to localize at the opposite ends of the molecule and dramatically reduces the delocalized nature of individual spin-up and spin-down channels. As a result, spin-split channels decouple from one of the contact and yields a consequent decay of conductance as compared to their CSS counterparts. Overall, the findings in this work puts a warning sign over the use of restricted wavefunction for the molecules with OSS ground state and emphasizes the existence of a molecular system in CSS state to observe the desired increase in conductance.

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Supporting Information Available: Computational details, computed total energies, $\langle S^2 \rangle$ values in gas phase and molecular junction, radicaloid character, HOMO-LUMO gap, spatial distribution and energetics of frontier MOs, spin density distribution, even-odd effects in cumulenes.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Datta, S. *Electronic transport in mesoscopic systems*; Cambridge university press, 1997.
- (2) Tao, N. J. Electron transport in molecular junctions. *Nanoscience And Technology: A Collection of Reviews from Nature Journals* **2010**, 185–193.
- (3) Weiss, E. A.; Ahrens, M. J.; Sinks, L. E.; Gusev, A. V.; Ratner, M. A.; Wasielewski, M. R. Making a molecular wire: charge and spin transport through p ara-phenylene oligomers. *J. Am. Chem. Soc.* **2004**, *126*, 5577–5584.
- (4) Lee, H. J.; Cho, S. J.; Kang, H.; He, X.; Yoon, H. J. Achieving Ultralow, Zero, and Inverted Tunneling Attenuation Coefficients in Molecular Wires with Extended Conjugation. *Small* **2021**, *17*, 2005711.
- (5) Gunasekaran, S.; Hernangómez-Pérez, D.; Davydenko, I.; Marder, S.; Evers, F.; Venkataraman, L. Near length-independent conductance in polymethine molecular wires. *Nano Lett.* **2018**, *18*, 6387–6391.
- (6) Kuang, G.; Chen, S.-Z.; Wang, W.; Lin, T.; Chen, K.; Shang, X.; Liu, P. N.; Lin, N. Resonant charge transport in conjugated molecular wires beyond 10 nm range. *J. Am. Chem. Soc.* **2016**, *138*, 11140–11143.
- (7) Tada, T.; Yoshizawa, K. Reverse exponential decay of electrical transmission in nanosized graphite sheets. *J. Phys. Chem. B* **2004**, *108*, 7565–7572.
- (8) Li, Z.; Park, T.-H.; Rawson, J.; Therien, M. J.; Borguet, E. Quasi-ohmic single molecule charge transport through highly conjugated meso-to-meso ethyne-bridged porphyrin wires. *Nano Lett.* **2012**, *12*, 2722–2727.
- (9) Sedghi, G.; García-Suárez, V. M.; Esdaile, L. J.; Anderson, H. L.; Lambert, C. J.; Martín, S.; Bethell, D.; Higgins, S. J.; Elliott, M.; Bennett, N., et al. Long-range electron tunnelling in oligo-porphyrin molecular wires. *Nat. Nanotechnol.* **2011**, *6*, 517–523.
- (10) Leary, E.; Limburg, B.; Alanazy, A.; Sangtarash, S.; Grace, I.; Swada, K.; Esdaile, L. J.; Noori, M.; González, M. T.; Rubio-Bollinger, G., et al. Bias-driven conductance increase with length in porphyrin tapes. *J. Am. Chem. Soc.* **2018**, *140*, 12877–12883.
- (11) Tsuji, Y.; Movassagh, R.; Datta, S.; Hoffmann, R. Exponential attenuation of through-bond transmission in a polyene: Theory and potential realizations. *ACS nano* **2015**, *9*, 11109–11120.
- (12) Ramos-Berdullas, N.; Mandado, M. Electronic Properties of p-Xylylene and p-Phenylene Chains Subjected to Finite Bias Voltages: A New Highly Conducting Oligophenyl Structure. *Chem. Eur. J.* **2013**, *19*, 3646–3654.
- (13) Gil-Guerrero, S.; Ramos-Berdullas, N.; Mandado, M. Can aromaticity enhance the electron transport in molecular wires? *Org. Electron.* **2018**, *61*, 177–184.
- (14) Stuyver, T.; Fias, S.; De Proft, F.; Geerlings, P.; Tsuji, Y.; Hoffmann, R. Enhancing the conductivity of molecular electronic devices. *J. Chem. Phys.* **2017**, *146*, 092310.
- (15) Stuyver, T.; Zeng, T.; Tsuji, Y.; Geerlings, P.; De Proft, F. Diradical character as a guiding principle for the insightful design of molecular nanowires with an increasing conductance with length. *Nano Lett.* **2018**, *18*, 7298–7304.
- (16) Stuyver, T.; Zeng, T.; Tsuji, Y.; Fias, S.; Geerlings, P.; De Proft, F. Captodative substitution: a strategy for enhancing the conductivity of molecular electronic devices. *J. Phys. Chem. C* **2018**, *122*, 3194–3200.
- (17) Gil-Guerrero, S.; Peña-Gallego, Á.; Ramos-Berdullas, N.; Martín Pendas, A.; Mandado, M. Assessing the reversed exponential decay of the electrical conductance in molecular wires: the undeniable effect of static electron correlation. *Nano Lett.* **2019**, *19*, 7394–7399.
- (18) Ramos-Berdullas, N.; Gil-Guerrero, S.; Peña-Gallego, Á.; Mandado, M. The effect of spin polarization on the electron transport of molecular wires with diradical character. *Phys. Chem. Chem. Phys.* **2021**, *23*, 4777–4783.
- (19) Houk, K.; Lee, P. S.; Nendel, M. Polyacene and cyclacene geometries and electronic structures: bond equalization, vanishing band gaps, and triplet ground states contrast with polyacetylene. *J. Org. Chem.* **2001**, *66*, 5517–5521.
- (20) Dos Santos, M. Electronic properties of acenes: Oligomer to polymer structure. *Phys. Rev. B* **2006**, *74*, 045426.
- (21) Bendikov, M.; Duong, H. M.; Starkey, K.; Houk, K.; Carter, E. A.; Wudl, F. Oligoacenes: theoretical prediction of open-shell singlet diradical ground states. *J. Am. Chem. Soc.* **2004**, *126*, 7416–7417.
- (22) Maiti, S. K. Quantum transport through polycyclic hydrocarbon molecules. *Phys. Lett. A* **2007**, *366*, 114–119.
- (23) Zhou, Y.; Jiang, F.; Chen, H.; Note, R.; Mizuseki, H.; Kawazoe, Y. Quantum length dependence of conductance in oligomers: First-principles calculations. *Phys. Rev. B* **2007**, *75*, 245407.
- (24) Liu, H.; Ni, W.; Zhao, J.; Wang, N.; Guo, Y.; Taketsugu, T.; Kiguchi, M.; Murakoshi, K. Nonequilibrium Green's function study on the electronic structure and transportation behavior of the conjugated molecular junction: Terminal connections and intramolecular connections. *J. Chem. Phys.* **2009**, *130*, 244501.
- (25) He, Y.; Cheng, N.; Zhao, J. First-principle study on the conductance of benzene-based molecules with various bonding characteristics. *Comput. Theor. Chem.* **2019**, *1154*, 1–10.
- (26) Pilevarshahi, R.; Rungger, I.; Archer, T.; Sanvito, S.; Shahatahmasebi, N. Spin transport in higher n-acene molecules. *Phys. Rev. B* **2011**, *84*, 174437.
- (27) Visontai, D.; Grace, I.; Lambert, C. Electron transport through ribbonlike molecular wires calculated using density-functional theory and Green's function formalism. *Phys. Rev. B* **2010**, *81*, 035409.
- (28) Kaliginedi, V.; Moreno-García, P.; Valkenier, H.; Hong, W.; García-Suárez, V. M.; Buiter, P.; Otten, J. L.; Hummelen, J. C.; Lambert, C. J.; Wandlowski, T. Correlations between molecular structure and single-junction conductance: a case study with oligo (phenylene-ethynylene)-type wires. *J. Am. Chem. Soc.* **2012**, *134*, 5262–5275.
- (29) Valdiviezo, J.; Rocha, P.; Polakovsky, A.; Palma, J. L. Non-exponential Length Dependence of Molecular Conductance in Acene-Based Molecular Wires. *ACS sensors* **2021**, *6*, 477–484.
- (30) Wang, C.; Batsanov, A. S.; Bryce, M. R.; Martin, S.; Nichols, R. J.; Higgins, S. J.; García-Suárez, V. M.; Lambert, C. J. Oligoynes single molecule wires. *J. Am. Chem. Soc.* **2009**, *131*, 15647–15654.
- (31) Jasper-Tönnies, T.; García-Lekue, A.; Frederiksen, T.; Ulrich, S.; Herges, R.; Berndt, R. Conductance of a freestanding conjugated molecular wire. *Phys. Rev. Lett.* **2017**, *119*, 066801.
- (32) Zang, Y.; Fu, T.; Zou, Q.; Ng, F.; Li, H.; Steigerwald, M. L.; Nuckolls, C.; Venkataraman, L. Cumulene wires display increasing conductance with increasing length. *Nano Lett.* **2020**, *20*, 8415–8419.
- (33) Xu, W.; Leary, E.; Hou, S.; Sangtarash, S.; González, M. T.; Rubio-Bollinger, G.; Wu, Q.; Sadeghi, H.; Tejerina, L.; Christensen, K. E., et al. Unusual Length Dependence of the Conductance in Cumulene Molecular Wires. *Angew. Chem. Int. Ed.* **2019**, *131*, 8466–8470.
- (34) Wendinger, D.; Tykwinski, R. R. Odd [n] cumulenes (n = 3, 5, 7, 9): synthesis, characterization, and reactivity. *Acc. Chem. Res.* **2017**, *50*, 1468–1479.
- (35) Jiang, D.-e.; Dai, S. Electronic ground state of higher acenes. *J. Phys. Chem. A* **2008**, *112*, 332–335.
- (36) Trinquier, G.; David, G.; Malrieu, J.-P. Qualitative views on the polyradical character of long acenes. *J. Phys. Chem. A* **2018**, *122*, 6926–6933.
- (37) Khurana, R.; Bajaj, A.; Ali, M. E. Tuning the Magnetic Properties of Diamagnetic Di-Blatter's Zwitterion to Antiferro- and Ferromagnetic Diradical. *ChemRxiv* **2021**, doi: <https://doi.org/10.26434/chemrxiv.14420255.v1>.
- (38) Kaur, P.; Ali, M. E. Influence of the Radicaloid Character of Polyaromatic Hydrocarbon Couplers on Magnetic Exchange Interactions. *ChemRxiv* **2021**, doi: <https://doi.org/10.26434/chemrxiv.14527185.v1>.
- (39) Yamaguchi, K. The electronic structures of biradicals in the unrestricted Hartree-Fock approximation. *Chem. Phys. Lett.* **1975**, *33*, 330–335.
- (40) Deffner, M.; Groß, L.; Steenbock, T.; Voigt, B.; Solomon, G.; Herrmann, C. Artaios—a code for postprocessing quantum chemical electronic structure calculations. 2010.

- (41) Bajaj, A.; Kaur, P.; Sud, A.; Berritta, M.; Ali, M. E. Anomalous Effect of Quantum Interference in Organic Spin Filters. *J. Phys. Chem. C* . **2020**, *124*, 24361–24371.
- (42) Yoshizawa, K.; Tada, T.; Staykov, A. Orbital views of the electron transport in molecular devices. *J. Am. Chem. Soc.* **2008**, *130*, 9406–9413.
- (43) Moth-Poulsen, K.; Bjørnholm, T. Molecular electronics with single molecules in solid-state devices. *Nat. Nanotechnol.* **2009**, *4*, 551–556.
- (44) Bajaj, A.; Khurana, R.; Ali, M. E. Quantum interference and spin filtering effects in photo-responsive single molecule devices. *J. Mater. Chem. C* **2021**, *9*, 11242 – 11251.
- (45) Aggarwal, A.; Kaliginedi, V.; Maiti, P. K. Quantum Circuit Rules for Molecular Electronic Systems: Where Are We Headed Based on the Current Understanding of Quantum Interference, Thermoelectric, and Molecular Spintronics Phenomena? *Nano Lett.* **2021**,
- (46) Garner, M. H.; Bro-Jørgensen, W.; Pedersen, P. D.; Solomon, G. C. Reverse bond-length alternation in cumulenes: Candidates for increasing electronic transmission with length. *J. Phys. Chem. C* **2018**, *122*, 26777–26789.
- (47) Tsuji, Y.; Okazawa, K.; Chen, B.; Yoshizawa, K. Mechanical Control of Molecular Conductance and Diradical Character in Bond Stretching and π -Stack Compression. *J. Phys. Chem. C* . **2020**, *124*, 22941–22958.
- (48) Malrieu, J.-P.; Trinquier, G. Can a topological approach predict spin-symmetry breaking in conjugated hydrocarbons? *J. Phys. Chem. A* **2016**, *120*, 9564–9578.
- (49) Hendon, C. H.; Tiana, D.; Murray, A. T.; Carbery, D. R.; Walsh, A. Helical frontier orbitals of conjugated linear molecules. *Chem. Sci.* **2013**, *4*, 4278–4284.