Cumulene Wires Display Increasing Conductance with Increasing Length

Yaping Zang, Tianren Fu, Qi Zou, Fay Ng, Hexion Li, Michael L. Steigerwald, Colin Nuckolls, and Latha Venkataraman

ABSTRACT: One-dimensional sp-hybridized carbon wires, including cumulenes and polyynes, can be regarded as finite versions of carbynes. They are likely to be good candidates for molecular-scale conducting wires as they are predicted to have a high-conductance. In this study, we first characterize the single-molecule conductance of a series of cumulenes and polyynes with a backbone ranging in length from 4 to 8 carbon atoms, including [7]cumulene, the longest cumulenic carbon wire studied to date for molecular electronics. We observe different length dependence of conductance when comparing these two forms of carbon wires. Polyynes exhibit conductance decays with increasing molecular length, while cumulenes show a conductance increase with increasing molecular length. Their distinct conducting behaviors are attributed to their different bond length alternation, which is supported by theoretical calculations. This study confirms the long-standing theoretical predictions on sp-hybridized carbon wires and demonstrates that cumulenes can form highly conducting molecular wires.

KEYWORDS: Single-Molecule Transport, Cumulenes, Polyynes, Conductance Decay, Molecular Wires

Carbynes, or linear acetylenic carbon, are infinite linear chains of sp-hybridized carbons. They are predicted to be a mechanically strong and electrically insulating allotrope of carbon.\(^1\)\(^-\)\(^5\) By contrast, finite one-dimensional sp-carbon wires, or “oligocarbynes”, are predicted to have outstanding electronic characteristics and mechanical properties.\(^6\)\(^-\)\(^10\) Polyynes with alternating single and triple bonds and cumulenes with successive double bonds are two types of oligocarbynes (Scheme 1). These two systems, however, are predicted to have different electronic properties; in principle, long cumulenes are predicted to be metallic while polyynes are expected to be semiconducting.\(^8\) Although many theoretical studies have been devoted to understanding the electronic structure and properties of these two systems, experimental explorations\(^1\)\(^-\)\(^4\)\(^,\)\(^14\) are lagging behind due to synthetic challenges and the low stability of long sp-carbon wires, especially the cumulene forms.\(^5\)\(^-\)\(^9\) Here, we synthesize a series of stable cumulene and polyyne molecular wires and characterize their electronic properties using the scanning tunneling microscope based-break junction (STM-BJ) technique.\(^1\)\(^7\)

We first design and synthesize a series of cumulenes and polyynes with different length (Figure 1a) and denote these molecules by the number of carbons in their backbones; C4 is [3]cumulene while Y4 is [2]polyyne as they both have four carbons in the chain. Both ends of these molecules are substituted with phenyl groups, which increase their stability.\(^1\)\(^6\)\(^-\)\(^18\) Thiomethyl linker groups are introduced to form molecular junctions using gold electrodes due to their aurophilic nature. The detailed synthetic procedures for all compounds are in Section 2 of Supporting Information (SI).

To examine the electronic properties of these molecules, we perform the single-molecule conductance measurement using the STM-BJ technique.\(^2\)\(^0\),\(^2\)\(^1\) Briefly, we repeatedly construct molecular-junctions using gold electrodes due to their aurophilic nature. The detailed synthetic procedures for all compounds are in Section 2 of Supporting Information (SI). To examine the electronic properties of these molecules, we perform the single-molecule conductance measurement using the STM-BJ technique.\(^2\)\(^0\),\(^2\)\(^1\) Briefly, we repeatedly construct molecular-junctions in ambient condition by driving a Au STM tip in and out of contact with a Au-coated substrate in the presence of a solution of the target molecule. During this process, a Au–Au contact is ruptured to create a gap that can

Scheme 1. Structure of Cumulene and Polyyne

Cumulene

Polyyne

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be bridged by a molecule to form a single-molecular junction. We continuously record the conductance as a function of the electrode displacement during this process. Then, we construct histograms of these traces to analyze the conductance of these molecular junctions.

Figure 1. (a) Structure of all molecules investigated. (b) Logarithmically binned 1D histograms of conductance traces measured with cumulenes with different lengths measured at 100 mV from TCB solutions. (c) One-dimensional histograms of polynes measured under the same conditions. (d) Conductance determined from Gaussian fits to histogram peaks of cumulenes (blue) and polynes (red) as a function of the number of carbons in the chain.

Figure 2. (a) DFT calculated junction structures for C8 and (b) Y8 indicating the bond indices on the backbones. Visualization uses VESTA 3.5. (c) BLA of C8 and Y8. (d) Calculated transmission functions for cumulenes and polynes as a function of energy. The Fermi energy is determined from the average of the HOMO and LUMO energy of the Au19−molecule−Au19 cluster.
and polyenes), which explains their unique negative decay (Figure S3 in the Supporting Information). Importantly, structures of cumulene is related to a lowering of their HOMO when compared to polyynes. The smaller magnitude of BLA in (Figure 2c). The magnitude of BLA is smaller for cumulenes their bond length alternation (BLA), however, are distinct alternating bond lengths due to the alternating bond orders. The smaller magnitude of BLA in (Figure 2c). The magnitude of BLA is smaller for cumulenes than in polyynes. For polyynes, although the gaps decrease slightly, the resonances also get narrower with increasing length due to the reduction in weight of the conducting molecular orbitals on the terminal sulfurs. This weakens the electrode–molecule coupling and rapidly decreases the transmission at $E_F$. By contrast, in cumulenes, although the resonances do get narrower, this does not affect transmission at $E_F$ significantly as the resonances also get closer to $E_F$. These calculations therefore also yield a positive $\beta$ value for polyynes and the unusual negative $\beta$ value for cumulenes, in agreement with the experiments. Note that the calculated conductance values are higher than the experimental ones due to errors in the formalism.34

To further confirm that this unusual negative beta value is an inherent property of cumulenes, we repeat the single-molecule conductance measurements in two additional solvents, tetradecane (TD), a nonpolar solvent, and propylene carbonate (PC), a polar solvent. The measurements conducted in PC are done with 100 mM of tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. As shown in Figure 3, although the conductance values are slightly different in different solvents,35,36 the conductance increases with increasing molecular length in each case. We obtain a negative $\beta$ of $-0.12$ per carbon and $-0.18$ per carbon in TD and PC, respectively. These measurements confirm that the unusual negative $\beta$ value of cumulenes is an inherent characteristic associated with their unique electronic structures.

In conclusion, we have synthesized a set of cumulenes and polyynes as model compounds of long-chain sp-carbon structures and have explored the electronic properties of these two series by single-molecule conductance measurements and theoretical calculations. The two series of compounds show different conducting behaviors due to their distinct BLA. For polyynes, the conductance drops with increasing molecular length in each case. We obtain a negative $\beta$ of $-0.12$ per carbon and $-0.18$ per carbon in TD and PC, respectively. These measurements confirm that the unusual negative $\beta$ value of cumulenes due to the reduction in weight of the conducting molecular orbitals on the terminal sulfurs. This weakens the electrode–molecule coupling and rapidly decreases the transmission at $E_F$. By contrast, in cumulenes, although the resonances do get narrower, this does not affect transmission at $E_F$ significantly as the resonances also get closer to $E_F$. These calculations therefore also yield a positive $\beta$ value for polyynes and the unusual negative $\beta$ value for cumulenes, in agreement with the experiments. Note that the calculated conductance values are higher than the experimental ones due to errors in the formalism.34

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Figure 1c shows the one-dimensional (1D) histograms of the polyyne series Y4, Y6, and Y8. Unlike for the cumulenes, the conductance of Y8, the longest polyyne, is the lowest while that of Y4, the shortest polyyne, is the highest. The corresponding two-dimensional conductance-versus-displacement histograms are shown in Figure S1 in Supporting Information.

In Figure 1d, we plot the peak conductance values of both series against the number of carbon atoms in their backbones. Note that the width of the distributions is indicative of a range of junction geometries sampled in the experiments including variations in Au−S−C dihedral angles as has been observed before. Two different trends of conductance versus length can be clearly seen; increasing the number of carbons from 4 to 8, the polyyne series shows decreasing conductance while the cumulene series shows an increasing conductance. We also find that both conductance trends are nearly linear on the semilogarithm plot indicating that conductance depends exponentially on length as $G = G_0 e^{-\beta N}$, where $G$ is the conductance and $N$ is the number of carbons in the backbone. For the polyynes, we obtain a positive $\beta$ of 0.26 per carbon, which is consistent with previous reports. By contrast, the conductance of cumulenes increases exponentially with increasing molecular length. We obtain a negative $\beta$ of $-0.12$ per carbon. Such a negative decay suggests cumulene is an outstanding candidate of highly conducting molecular wires.

To understand the distinct properties of these two series, we turn to density functional theory (DFT) calculations, using the FHI-AIMS package23,24 with a B3LYP exchange-correlation functional.25 We show in Figure 2a,b energy optimized structures of C8 and Y8 junctions, respectively. Because we are primarily interested in the trends here, we focus on energy optimized geometries rather than sampling a range of geometries for each molecule. Both backbones have seven carbon–carbon bonds bridging their eight carbon atoms with alternating bond lengths due to the alternating bond orders. Their bond length alternation (BLA), however, are distinct (Figure 2c). The magnitude of BLA is smaller for cumulenes than in polyynes. For polyynes, although the gaps decrease slightly, the resonances also get narrower with increasing length due to the reduction in weight of the conducting molecular orbitals on the terminal sulfurs. This weakens the electrode–molecule coupling and rapidly decreases the transmission at $E_F$. By contrast, in cumulenes, although the resonances do get narrower, this does not affect transmission at $E_F$ significantly as the resonances also get closer to $E_F$. These calculations therefore also yield a positive $\beta$ value for polyynes and the unusual negative $\beta$ value for cumulenes, in agreement with the experiments. Note that the calculated conductance values are higher than the experimental ones due to errors in the formalism.34

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Figure 3. One-dimensional histograms of cumulenes of different lengths measured at 100 mV in (a) TD and (b) PC. (c) Conductance determined from Gaussian fits to histogram peaks from (a) and (b) as a function of the number of carbons in the backbone along with a linear fit on a semilog scale.

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increasing chain length, whereas for cumulenes we observe an increasing trend of conductance with increasing molecular length, as expected according to calculations. This discovery confirms the feasibility of creating molecular wires with sp-carbon chains.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.0c03794. Synthetic details and additional data (PDF)

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**Notes**

The authors declare no competing financial interest.

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