Cumulene Wires Display Increasing Conductance with Increasing Length

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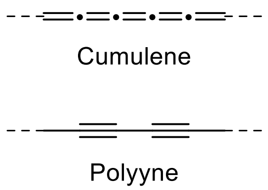
ABSTRACT

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, Polyenes, Conductance Decay, Molecular Wires

TEXT

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 doubles bonds are the 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[11-14] are lagging far behind due to synthetic challenges and the low stability of long *sp*-carbon wires, especially the cumulene forms.[15-19] Here, we synthesize a series of stable cumulene and polyyne molecular wires and characterize their electronic properties using scanning tunneling microscope-break junction (STM-BJ) technique.[20-21]



Scheme 1. Structure of cumulene and polyyne.

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 4 carbons in the chain. Both ends of those molecules are substituted with phenyl groups, which increase the stability.[16-18] Thiomethyl linker groups are introduced enable forming molecular junctions using gold electrodes due to their aurophilic nature. The detailed synthetic procedures for all compounds are in the Section 2 of the Supporting Information (SI). To examine the electronic properties of these molecules, we perform the single-molecular conductance measurement by STM-BJ technique.[20-21] Briefly, we repeatedly construct molecular-junctions in ambient condition by driving a gold STM tip in and out of contact with a gold-coated substrate in the presence of a solution of the target molecule. During this process, an Au-Au contact is ruptured to create a gap that can 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 find average conductance of the molecular junctions.

Figure 1b shows the one-dimensional conductance histograms of the cumulene **C4**, **C6** and **C8** measured from solutions in 1,2,4-trichlorobenzene (TCB) at a bias of 100 mV. Each histogram is compiled from more than 3000 individual measurements without data selection. From these histograms we can see that, **C6** shows a higher conductance than the shorter molecule **C4**, whereas the longest cumulene **C8** shows the highest conductance. Figure 1c shows the 1D histograms of the polyyne series **Y4**, **Y6** and **Y8**, also measured in TCB at a 100 mV bias. 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 the SI.

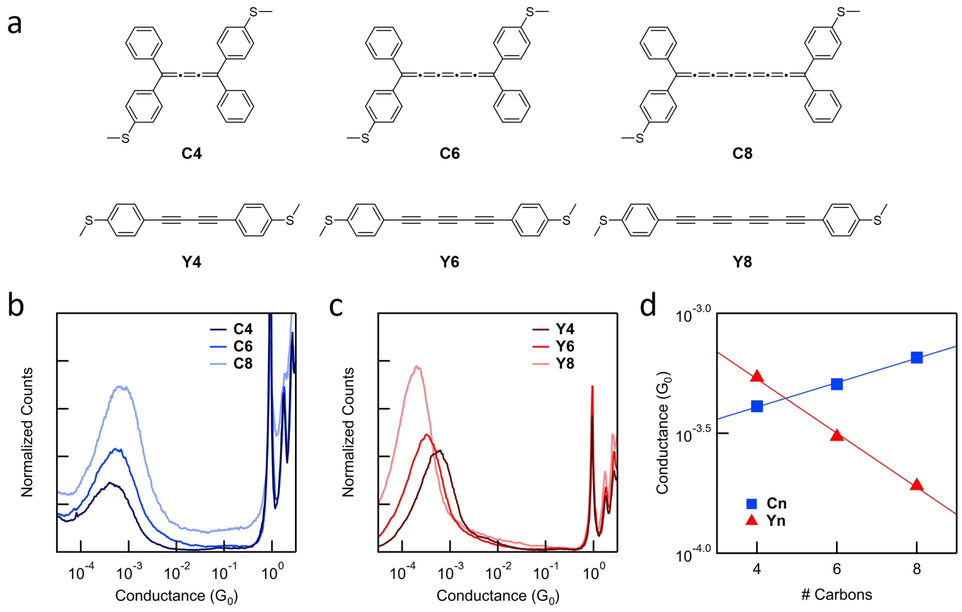


Figure 1. (a) Structure of all molecules investigated here. (b) Logarithmically binned one-dimensional (1D) histograms of conductance traces measured with cumulenes with different length measured at 100 mV from TCB solutions. (c) 1D histograms of polyynes measured with the same conditions. (d) Conductance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

In Figure 1d, we plot the peak conductance values of the 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.[22] 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 semi-logarithm plot indicating that conductance depends exponentially on length as $G = Ae^{-\beta N}$, where G is the conductance and N is the number of carbons in the backbone. For the polyynes, we obtain a positive β of 0.26 per carbon, which is consistent with previous reports.[11, 13-14] By contrast, the conductance of cumulenes increases exponentially with increasing molecular length. We obtain a negative β 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 package[23-24] with a B3LYP exchange-correlation functional.[25-28] We show, in Figure 2a and 2b, energy optimized structures of **C8** and **Y8** junctions, respectively. Since 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 7 carbon-carbon bonds bridging their 8 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 when compared to polyynes. The smaller magnitude of BLA in cumulene is related to a lowering of their HOMO-LUMO gap (Figure S3 in the SI).[8,29-30] Importantly, BLA is reversed in cumulenes (when compared to polyynes and polyenes), which explains their unique negative decay constant as has been found using a tight binding model.[8,31] To better understand this, we calculate the transmission functions of these molecules by modeling the junction with Au_{18} clusters representing the electrodes and calculate the transmission with AITRANSS package using a non-equilibrium Green's function formalism albeit at zero bias.[32-

[33] We use smaller (Au_{18}) electrodes as these calculations are made using the B3LYP functional, which is more accurate but computationally expensing. The trends obtained here are in good agreement with calculations made with Au_{60} electrodes using PBE. Calculation results are presented in Figure 2d. We see the HOMO and LUMO resonances of the cumulenes are closer to the Fermi energy (E_F) of the junction in cumulenes compared to polyynes. Furthermore, the gap between the HOMO and LUMO resonances shrinks faster with increasing molecular length in 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 and thus a weakening in the electrode-molecule coupling. This narrowing 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 β value for polyynes and the unusual negative β value for cumulenes, analogous to the results observed in the experiments. Note that the calculated conductance values are higher than the experimental ones likely due to established errors in the formalism.[34]

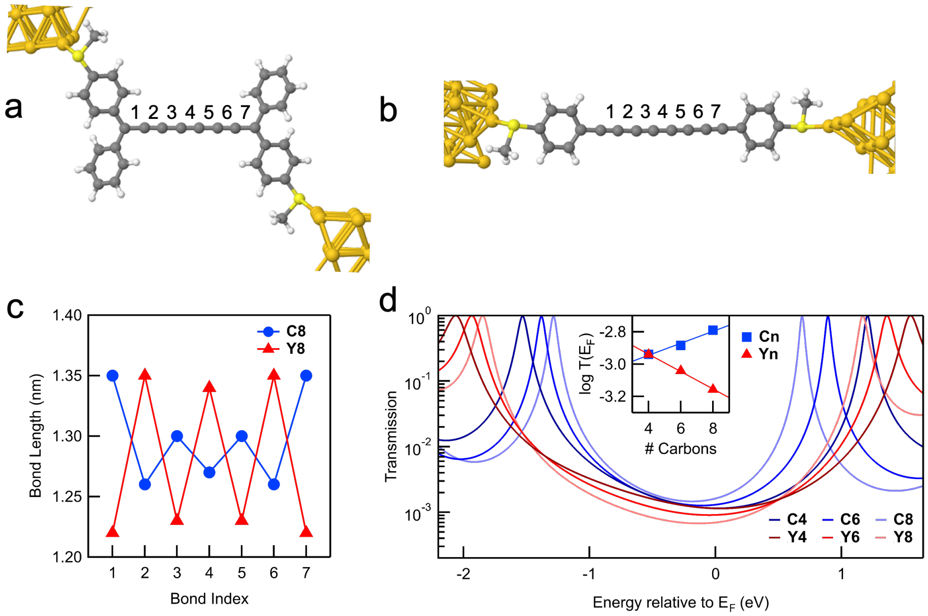


Figure 2. (a) DFT calculated junction structures composed of **C8** and (b) **Y8**, along with the bond indices on the backbones. Visualization is fulfilled by VESTA 3 program[35]. (c) Bond length alternations (BLA) of **C8** and **Y8**. (d) Calculated transmission functions for cumulenes and polyynes as a function of energy. The Fermi energy is determined from the average of the HOMO and LUMO energy of the Au_{18}-molecule-Au_{18} cluster.

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 non-polar solvent and propylene carbonate (PC), a polar solvent. The measurements conducted in PC are done with 100 mM of tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. As shown in Figure 3, although the conductance values are slightly different in different solvents,[31, 36] the conductance increases with increasing molecular length in each case. We obtain a negative β of -0.12 per carbon and -0.18 per carbon in TD and PC, respectively. These measurements confirm that the unusual negative β 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 explored the electronic properties of these two series by single-molecular conductance measurements and theoretical calculations. The two series of compounds show different conducting behaviors due to their distinct BLA. For polyenes, the conductance drops with increasing chain length, while 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.

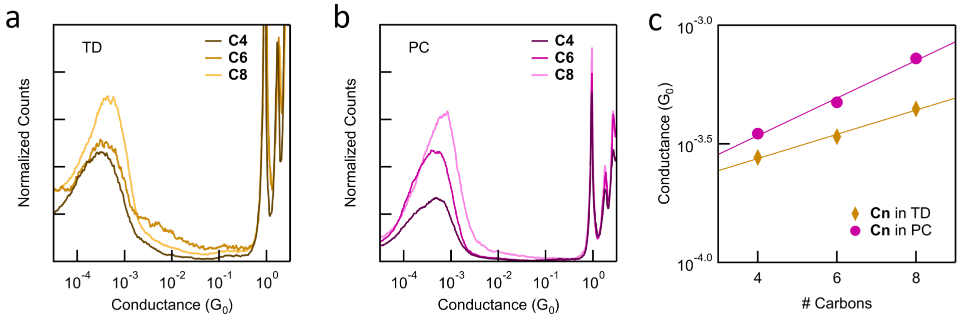


Figure 3. 1D histograms of cumulenes of different lengths measured at 100 mV in (a) TD and (b) PC. (c) Conductance determined from Gaussian fits to histogram peaks from (a) and (b) as a function of the number of carbons in the backbone along with a linear fit on a semi-log scale.

ASSOCIATED CONTENT

Supporting Information.

Synthetic details and additional data. The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interest.

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