Electronics, Organic electronics, Nanotechnology

Realization of high-efficiency hopping conduction in several-nanometer-scale molecular wires

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Abstract

When the molecular length exceeds several nanometers, charge carriers such as holes become localized within the molecule and migrate by hopping between molecular electronic states (hopping sites), which becomes the dominant charge - transport mechanism. Establishing design strategies to enhance this hopping transport is essential for achieving long-distance charge conduction. The activation energy (E_a) for hopping conduction is determined by the sum of the energy difference between adjacent hopping sites (ΔE_{hs}) and the reorganization energy (λ). In this study, we reduced λ by introducing rigid fused-ring structures into the π-conjugated hopping sites. Furthermore, ΔE_{hs} was minimized by periodically introducing twisted structures, and extending the molecular length to several nanometers enabled highly efficient hopping conduction.

Background & Results

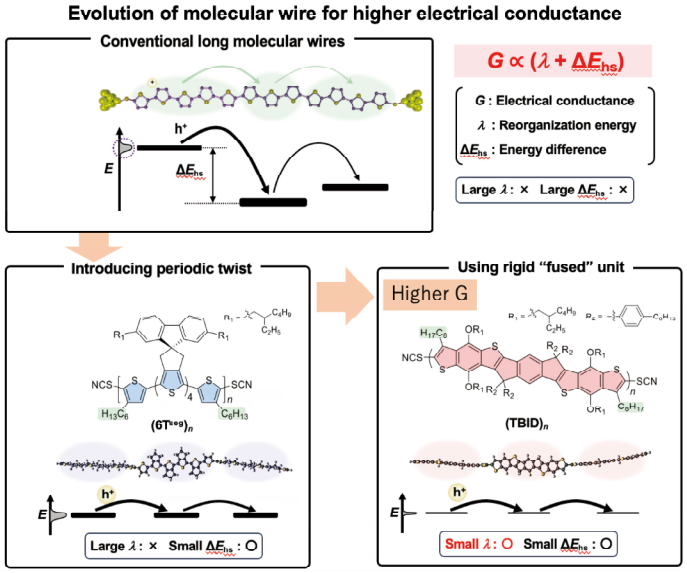
Since the 1970s, when theoretical proposals demonstrated the feasibility of single-molecule diodes, research on the electronic properties of individual molecules has primarily advanced through theoretical approaches. To conduct electricity through a molecule, it is necessary to create a single-molecule junction by bridging the molecule between electrodes. Measurement techniques for the electrical conductance of single-molecule junctions have developed rapidly over the past 20 years. These developments have deepened our understanding of charge-transport mechanisms at the nanoscale.

In single-molecule junctions, two main types of electrical conduction are typically observed: tunneling conduction, where electrons pass directly through the molecule as quantum waves, and hopping conduction, where injected charges move step by step, activated by thermal energy. It has been thought that tunneling dominates in short molecules, while hopping becomes predominant as the molecule lengthens; however, the exact transition point between these mechanisms had not been clearly identified. Because it has been extremely challenging to prepare, via organic synthesis, molecular systems that simultaneously fulfill the following requirements necessary for validating hopping conduction experimentally: (i) a molecular length on the nanometer scale, (ii) fully encapsulated structures that eliminate intermolecular interactions, and (iii) precise control over molecular length.

Under these circumstances, the present study represents a pioneering effort that elucidates how the molecular structure of organic molecules influences intramolecular hopping conduction. Furthermore, it demonstrates that enhancing hopping conduction is a promising strategy for realizing novel electronic functions. Based on these findings, further advancements in hopping efficiency are expected to enable the development of new operating principles and device architectures, the rational design of molecular wires for single-molecule electronics, and the performance enhancement of organic semiconductor materials for organic electronics.

Significance of the research and Future perspective

Molecules are the smallest units of matter that humans can design and synthesize. Understanding how a single molecule conducts electricity and exhibits electronic functionality is fundamental to developing faster and more energy-efficient computing technologies. Such research requires the integration of synthetic chemistry, precision measurement, and theoretical modeling. Our findings provide a new design guideline for realizing long-distance charge transport within organic molecules. These insights are also expected to contribute to improving the performance of conductive polymers, which play a vital role in flexible electronics and other next-generation materials.



Patent	
Treatise	Yamada, Ryo; Ohto,Tatsuhiko; Ie, Yutaka et al. Periodically twisted molecular wires based on a fused unit for efficient intramolecular hopping transport. J. Am. Chem. Soc. 2024, 146, 23529. doi: 10.1021/jacs.4c07548 Ie, Yutaka; Yamada, Ryo; Tada, Hirokazu et al. Improving intramolecular hopping charge transport via periodical segmentation of π-conjugation in a molecule. J. Am. Chem. Soc. 2021, 143, 599. doi: 10.1021/jacs.0c10560 Ie, Yutaka; Yamada, Ryo, Tada, Hirokazu et al. Highly planar and completely insulated oligothiophenes: Effects of π-conjugation on hopping charge transport. J. Phys. Chem. Lett. 2019, 10, 3197. doi: 10.1021/acs.jpclett.9b00747
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