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Preview

Molecular Engineering: A Key Route to Improve the Performance of Molecular Devices

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Charged parallel conductance pathways were integrated into a molecular nanocircuit through rational molecular engineering to reveal a synergistic effect of chemical gating and constructive quantum interference, thus leading to a giant enhancement of conductance.

With tremendous advances in both experiments and theory, the molecular electronics system has matured into a platform that has started to develop beyond the basic understanding of charge transport mechanisms and to expand in different research directions, proving its interdisciplinarity.[1,2] In combination with other disciplines, this platform has shown remarkable flexibility originating from the abundant diversity in the molecular structures (achieved via flexible molecular design and synthesis), whose properties can be fine-tuned by external gating, such as biological, chemical, optical, magnetic, electric and thermal stimuli (Figure 1).[3] This flexibility offers endless opportunities to discover and understand fundamental physical phenomena and novel effects of materials at the atomic or molecular level that are not accessible using traditional approaches. This tunability allows researchers to install various desirable functions, such as wiring, switching, thermoelectricity, rectification, quantum interference (QI), spintronics and sensing with single-molecule sensitivity.

Toward practical molecular electronic devices, a prerequisite for molecular wires is high conductance, which can be regulated by quantum interference, a phenomenon describing the interference between the different molecular orbitals in the molecule. However, a maximum four-fold conductance enhancement is predicted by theory in neutral intramolecular circuits with two constitutionally identical channels. This limitation has been recently broken in this issue of *Matter* by Hongliang Chen et al.,[4] who designed and constructed a charged intramolecular circuit featuring a tetracationic cyclophane with parallel channels, showing a surprising 50-fold conductance enhancement.

For the first time, they chose 1–DS·4PF_6, a tetracationic cyclophane consisting of two identical extended viologen units connected to common phenylene sulphide anchors at each end, to afford charged intramolecular circuits (Figure 2). By using a scanning tunneling microscopic break junction (STM–BJ) technique, they reproducibly measured their conductance and found that the conductance of the double-channel symmetrical cyclophane differed significantly by one order of magnitude higher than that of the single-channel control (as proved by both one-dimensional and two-dimensional conductance-displacement histograms). Based on the observed fact and considering the nature of the dicationic backbone, they hypothesized that in addition to constructive QI, strong chemical gating effects might occur between the parallel tunneling channels. This was further demonstrated by the quantitative flicker noise analysis showing that charge transport in 1–DS-based nanocircuits is through-space dominated.

To prove the reliability of this observation, through smart molecular engineering they further synthesized three additional charged derivatives with various backbones, that is, with bipyridinium units (2–DS), with dipyridylethane units (3–DS), and with dipyridylethene units (4–DS). Compared to single-channel conductance, the enhancement factors of all the two-channel conductance are ~6.4 (2–DS), ~22.4 (3–DS) and ~53.7 (4–DS), respectively. All the enhancement factors of charged intramolecular circuits are beyond the single-molecule superposition limit and demonstrate that the conductance enhancement factor is sensitive to the interplay between the Fermi energy of Au and the orbital energy levels of the molecules.

To understand the origin of the conductance enhancement in charged double-channel cyclophanes, they performed systematic first-principle calculations of the quantum transport properties of molecular junctions, formed by the single-channel control and double-channel target molecules. The theoretical calculations indicated the LUMO energy level shifts from –4.52 eV (single-channel) to –5.12 eV (double-channel). It is the intrinsic chemical gating effect

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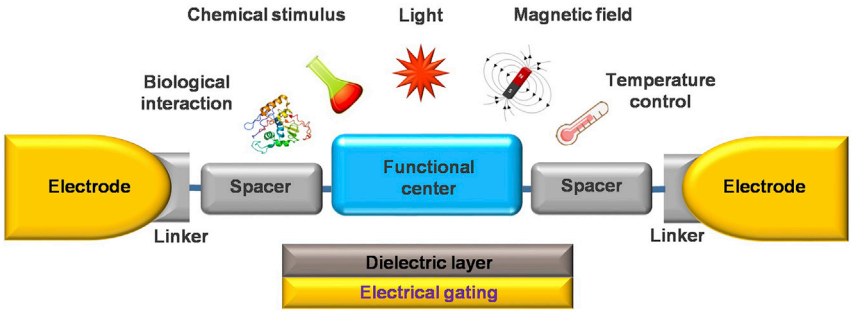

Figure 1. Schematic Strategy of Creating Functional Single-Molecule Junctions
Various molecular junctions with expected or even unpredictable functions can be constructed by designing functional molecular bridges whose conductance can be tuned by external gating, such as biological, chemical, optical, magnetic, electric, and thermal stimuli.

(electrostatic interactions) between two charged backbones (i.e., one backbone gates the other one and vice versa) that leads to this energy shifting. As a result, the gating effect in double-channel cyclophanes can shift the LUMO level-dominant conducting states closer to the electrode Fermi level, leading to a larger conductance.

To summarize, a synergistical effect of chemical gating originating from mutual electrostatic interactions and constructive QI in parallel two-channel intramolecular circuits enhances the total conductance, a giant conductance that is 50-fold more than that of a control molecule. One problem remaining is a detailed interpretation that explains the differences in conductance enhancements: whether it relies on the gating efficiencies, molecular lengths, torsion angles, aromaticity, or other mechanisms.

The finding of the synergistic effect is meaningful because this strategy could be a powerful tool to modulate the molecular conductance as demonstrated by previous works,[5,6] where light and electrical field were used to control the side-group chemical potential to produce a single-molecule, two-mode switch. The next step would be the utilization of this finding to build multifunctional molecular devices, such as molecular transistors, molecular computers, and quantum logic gates, which will invite intense research. As proved by this work, strong collaboration among materials scientists, engineers, physicists, electronic engineers, chemists, and biologists will foster its rapid development of the booming field of single-molecule electronics and solve the key issues in physical, chemical, and life sciences.[7,8] Molecular engineering aimed to construct new molecular devices has been the key to the success in improving the device performance toward practical applications.

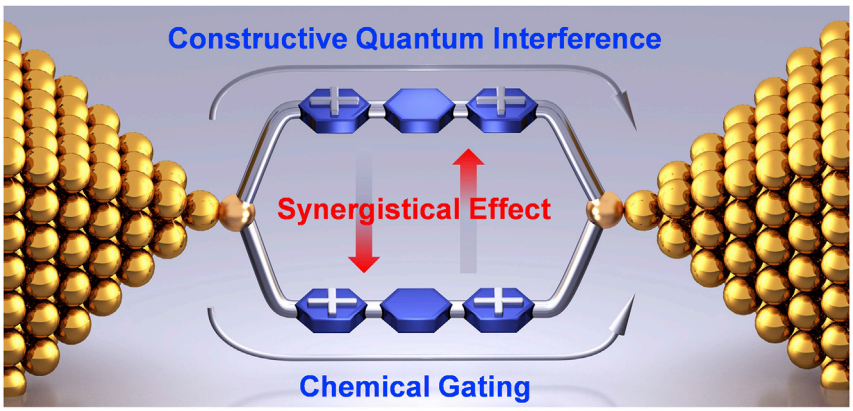

Figure 2. Schematic of an Intramolecular Circuit across a Tetracationic Double-Channel Cyclophane
A synergistic effect of chemical gating and constructive quantum interference is shown.

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