

Topology-Dependent Channel Formation Governs Electron Transport from One-Dimensional to Two-Dimensional C₆₀ Networks

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Abstract

Understanding electron transport from single molecules to extended molecular networks is essential for molecular electronics. In this study, electron transport properties of a one-dimensional C_{60} chain and a two-dimensional tetragonal C_{60} (t- C_{60}) network were investigated, using the Au- C_{60} -Au junction as a reference system. Non-equilibrium Green's function calculations combined with density functional theory were performed to analyze transmission characteristics and current-voltage behavior.

The C_{60} chain shows suppressed transmission near the Fermi level, leading to low conductance, whereas the tetragonal C_{60} network maintains effective transport channels and exhibits enhanced low-bias current. Transmission pathway analysis reveals that these differences originate from topology-dependent channel formation caused by orbital connectivity and coherence. These results demonstrate that electron transport in C_{60} -based materials is governed by effective channel formation rather than simple dimensionality, providing insight into the design of molecular electronic systems.

Introduction

Fullerene C_{60} has been extensively studied as a prototypical system in both molecular electronics and condensed matter physics due to its unique electronic structure and structural versatility [1]. In single-molecule junctions, electron transport is governed by discrete molecular orbitals and their hybridization with metallic electrodes, where conduction is often dominated by a small number of transmission eigenchannels that can be directly related to molecular orbital symmetries [2]. In contrast, when C_{60} molecules are polymerized or arranged in crystalline networks, intermolecular bonding leads to the formation of extended electronic states and significantly modifies the transport characteristics.

Polymerization of C_{60} is known to induce substantial changes in the electronic structure through the formation of covalent intermolecular bonds, which enhance π -conjugation and alter band dispersion [3]. Depending on the bonding geometry (e.g., 6-6 vs 5-6 connections), the resulting systems may exhibit semiconducting, metallic, or even semimetallic behavior. Moreover, polymerized fullerene systems such as alkali-doped AC_{60} have been shown to possess complex electronic properties with strong three-dimensional character, despite their apparent one-dimensional structural motifs [4]. Experimentally, polymeric fullerene chains have been realized in systems such as RbC_{60} and KC_{60} , where covalent bonding between neighboring molecules leads to chain-like structures with distinct electronic properties [5]. In addition to these quasi-one-dimensional systems, two-dimensional polymerized phases of C_{60} , including tetragonal networks formed via intermolecular cycloaddition reactions, have also been reported under high-pressure and high-temperature conditions [6]. Such t- C_{60} structures provide an intermediate regime between isolated chains and fully three-dimensional networks, offering a unique platform to investigate the evolution of electronic properties with increasing connectivity. These studies collectively demonstrate that intermolecular connectivity alone does not uniquely determine electronic transport, but rather modifies the underlying electronic structure in a nontrivial manner.

A central question that remains insufficiently understood is how electron transport evolves when transitioning from an isolated molecule to extended molecular networks. It is often intuitively assumed that increasing intermolecular connectivity enhances conductance by providing continuous pathways for electron propagation. However, first-principles studies have shown that even simple C_{60} dimers or chains can exhibit suppressed conductance due to scattering at intermolecular junctions and unfavorable orbital alignment [7]. Furthermore, transport properties in molecular systems are highly sensitive to symmetry, orbital hybridization, and quantum interference effects [8], indicating that the relationship between structural connectivity and electrical conductance is not necessarily monotonic.

In addition, nonequilibrium effects under finite bias play a crucial role in determining transport properties at the nanoscale. For C_{60} -based junctions, bias-induced changes in electronic structure and coupling can significantly influence conductance and even lead to nonlinear or fluctuating transport behavior [9]. Despite these advances, a systematic and unified comparison of transport across different connectivity regimes—ranging from single molecules to polymer chains and crystalline networks—remains lacking, particularly under finite-bias conditions.

Related all-carbon C_{60} junction studies have already demonstrated that transmission is strongly affected by the topology of the molecule-electrode interface, gate voltage, disorder, and contact geometry [23,24]. These studies, together with first-principles work on C_{60} bridges [7], show that connectivity alone is not sufficient to predict conductance. The present work differs in comparing an extended 1D polymerized chain and a 2D tetragonal network within the same finite-bias NEGF-DFT framework, while using Au- C_{60} -Au only as a molecular-junction reference.

C_{60} -based systems provide an ideal platform to address this issue, as they enable controlled variation of connectivity and dimensionality while preserving a common molecular building block. In this work, I present a comparative study focusing on electron transport in two representative C_{60} -based systems: (i) a one-dimensional C_{60} chain modeled as an effectively isolated system and (ii) a transport pathway along a crystallographic direction in t- C_{60} . As a reference, results for a single-molecule junction (Au- C_{60} -Au) are also provided. Using the nonequilibrium Green's function (NEGF) formalism combined with density functional theory (DFT) [10], I analyze transmission spectra, bias-dependent transport, and current-voltage characteristics within a unified theoretical framework.

I demonstrate that electron transport in these systems exhibits strongly non-monotonic and bias-dependent behavior. While the t- C_{60} network supports efficient low-bias transport due to finite transmission near the Fermi level, the one-dimensional C_{60} chain shows suppressed transmission in this region, resulting in reduced conductance. In contrast, the Au- C_{60} -Au junction exhibits resonant transport at higher bias, governed by molecule-electrode hybrid states. These results indicate that electron transport is not determined solely by connectivity or dimensionality, but rather by the formation of effective transport channels near the Fermi level.

Our findings provide a unified perspective on electron transport in C_{60} -based systems, highlighting that topology-dependent channel formation provides a useful qualitative descriptor of nanoscale conduction across molecular and extended regimes.

Calculation method

2.1 Theoretical Framework

Electronic transport properties were investigated using the non-equilibrium Green's function (NEGF) formalism combined with density functional theory (DFT), as implemented in the QuantumATK software package (Synopsys Inc.) [11]. This approach allows for the self-consistent calculation of the electronic structure under an applied bias voltage.

2.2 Device Construction and Geometry

Three representative C_{60} -based configurations were constructed to evaluate the impact of topology and dimensionality on transport (Fig. 1):

1. C_{60} chain (1D): A linear chain consisting of C_{60} molecules periodically connected via [2 + 2] cycloaddition bonds. A vacuum spacing of approximately 15 Å was maintained in the transverse directions to eliminate inter-chain interactions.
2. Tetragonal C_{60} (t- C_{60} , 2D): A two-dimensional network where C_{60} molecules are bonded in a tetragonal lattice. Electron transport was evaluated along one of the lattice directions to probe the intrinsic transport properties of the network.
3. Au- C_{60} -Au junction (Reference): A single C_{60} molecule sandwiched between two semi-infinite Au(100) electrodes. This serves as a standard reference to compare network-based transport with conventional single-molecule junctions.

For the C_{60} chain and t- C_{60} systems, I employed semi-infinite C_{60} units as the electrodes themselves. This "all-carbon" modeling approach allows for the direct evaluation of intrinsic transport properties governed by intermolecular connectivity, free from the influence of metal–molecule contact resistance. The atomic coordinates of the C_{60} molecules were based on experimentally established geometries. For the polymerized phases (chain and t- C_{60}), the intermolecular C–C bond length formed by [2 + 2] cycloaddition was set to 1.61 Å, consistent with previously reported values [6].

2.3 Computational Details

Electronic structures were calculated using DFT with norm-conserving Troullier–Martin pseudopotentials [12]. The exchange–correlation potential was described by the generalized gradient approximation

(GGA) in the Perdew–Burke–Ernzerhof (PBE) form. A double-z plus polarization (DZP) basis set was employed for carbon atoms [13]. The real-space mesh cutoff energy was set to 75 Ry.

For the Brillouin-zone integration, dense k-point sampling was used along the transport direction, with at least 100 points in the calculations. In the transverse directions, a single Γ point was used for the isolated 1D chain because of the large vacuum gap, whereas transverse k-point sampling was included for the periodic t-C₆₀ network. The present study focuses on a comparative analysis performed with the same computational framework. The numerical settings used here (DZP basis and 75 Ry mesh cutoff) are reported explicitly to define the level of approximation; systematic basis-set and geometry-convergence studies were not performed and are therefore recognized as limitations of the calculated absolute conductance values.

2.4 Transport Analysis

The transmission function $T(E, V)$ was calculated using the Landauer formalism. The transmission function is given by:

$$T(E, V) = \text{Tr} \left[\Gamma_L G^R \Gamma_R G^A \right]$$

1

where Γ_L and Γ_R represent the coupling matrices between the central scattering region and the left and right electrodes, respectively, and G^R and G^A are the retarded and advanced Green's functions of the central region. The trace is taken over the basis functions describing the system.

The zero-bias conductance is given by:

$$G = \frac{2e^2}{h} T(E_F, V = 0)$$

2

where E_F is the Fermi level.

The current–voltage (I–V) characteristics were calculated using the formula [14]:

$$I(V) = \frac{2e}{h} \int T(E, V) [f_L(E) - f_R(E)] dE$$

3

where f_L and f_R are the Fermi–Dirac distribution functions for the left and right electrodes, respectively. Bias-dependent calculations were performed from 0 to 2.0 V. The bias range was chosen to capture both low-bias coherent transport and high-bias resonance effects.

Analysis of transport mechanisms is as follows: To elucidate the origin of electron transport, the following analyses were performed:

- Transmission spectra near the Fermi level
- Bias-dependent transmission evolution
- Current–voltage (I–V) characteristics
- Molecular projected self-consistent Hamiltonian (MPSH) states
- Transmission pathways.

MPSH states were calculated using Green's functions and visualized as isosurfaces with an isovalue of 0.1. Particular attention was paid to states near the Fermi level, which correspond to HOMO- and LUMO-derived transport channels [2,15]. Transmission pathway analysis was employed to visualize spatial current flow and to identify continuous or suppressed conduction channels within each system [10,16].

This "all-carbon" modeling approach allows for the direct evaluation of intrinsic transport properties governed by intermolecular connectivity, free from the influence of metal–molecule contact resistance. While this idealized setup differs from experimental metal-contacted junctions, it provides a clear framework for isolating topology-driven transport mechanisms.

Results and discussion

3.1 Electronic Transmission at Zero Bias

I focus on electron transport in two representative C_{60} -based network systems: a C_{60} chain and a two-dimensional t- C_{60} network (Fig. 1). These systems allow us to examine how transport evolves with increasing intermolecular connectivity while preserving the same molecular building block. For reference, a single-molecule Au- C_{60} -Au junction is also considered as a benchmark system representing resonant transport in isolated molecular devices.

Figure 2 shows the zero-bias transmission spectra for the two network systems. The C_{60} chain exhibits a pronounced suppression of transmission around the Fermi level, with $T(E_F) = 0.018$, indicating inefficient low-energy transport despite intermolecular bonding. The present data establish a transmission minimum near E_F , but do not by themselves constitute a transmission-eigenchannel analysis of quantum interference. The suppression is therefore attributed more conservatively to inefficient orbital coupling and nodal structure at the intermolecular junctions, as supported by the MPSH states and transmission pathways discussed below. In contrast, the t- C_{60} system has $T(E_F) = 1.4$ and hence finite, substantially larger transmission at the Fermi level. The comparison shows that increased geometric connectivity does not automatically determine conductance; the spatial organization of the available transport pathways is also important.

The zero-bias conductance values obtained in this study are $1.8 \times 10^{-2} G_0$ for the C₆₀ chain, $1.4 G_0$ for the t-C₆₀ system, and $3.0 \times 10^{-1} G_0$ for the Au-C₆₀-Au junction. Within the Landauer picture, $G/G_0 = T(E_F)$; thus the value $1.4 G_0$ for t-C₆₀ is physically allowed because the total transmission is the sum of contributions from more than one propagating mode and is not restricted to unity. The present calculation, however, does not resolve the individual transmission eigenvalues, so the number and weights of these modes are not assigned here. For Au-C₆₀-Au, experimental conductances of approximately $0.01-0.1 G_0$ have been reported [19,20], whereas the present idealized geometry gives approximately $0.3 G_0$. This factor-of-3-30 difference is significant and should not be regarded as quantitative agreement. It can plausibly reflect the strong sensitivity of C₆₀ junction conductance to adsorption site, electrode surface structure, molecule-electrode separation, structural relaxation, and finite-temperature effects. Accordingly, the Au-C₆₀-Au result is used here primarily as a qualitative reference for bias-dependent resonant transport rather than as a parameter-free reproduction of a particular experiment.

3.2 Bias-Dependent Transport and I–V Characteristics

The bias dependence of the transmission spectra (Fig. 3) further highlights the contrasting transport mechanisms. In the C₆₀ chain, the suppression of transmission near the Fermi level persists under low bias, limiting the contribution of low-energy states to transport. Even as the bias increases, the transmission enhancement remains moderate, reflecting the absence of strongly coupled states within the bias window. In contrast, the t-C₆₀ system maintains finite transmission over a wide energy range and exhibits relatively weak bias dependence. The presence of multiple conduction pathways reduces sensitivity to local orbital mismatch and enables more robust transport under nonequilibrium conditions.

These differences are directly reflected in the current-voltage (I-V) characteristics shown in Fig. 4. In the low-bias regime, the t-C₆₀ junction exhibits significantly higher current than the C₆₀ chain, consistent with its finite transmission at the Fermi level. The C₆₀ chain remains weakly conductive across the investigated bias range because of the persistent suppression of low-energy transmission. The Au-C₆₀-Au junction shows qualitatively different behavior: its current rises more rapidly as bias increases and becomes comparable to, then exceeds, that of t-C₆₀ at approximately 1.5 V in the present calculation. This crossover coincides with the increasing contribution of transmission features away from E_F as the bias window broadens. Because bias-dependent orbital tracking and charge analysis were not performed, this behavior is described here as resonance-assisted transport rather than being assigned to a specific Stark-shifted or charged molecular state.

3.3 Microscopic Origin: MPSH and Transmission Pathways

To elucidate the microscopic origin of these differences, the spatial distribution of electronic states and transport pathways was examined. The MPSH states shown in Fig. 5 provide a qualitative view of states near the Fermi level. The plotted HOMO/LUMO energies are $-0.29/0.14$ eV for the C₆₀ chain, $-0.22/0.01$ eV for t-C₆₀, and $-1.17/0.14$ eV for Au-C₆₀-Au, corresponding to separations of approximately 0.43, 0.23,

and 1.31 eV, respectively. These MPSH states should not be identified directly with transmission eigenchannels; rather, they are used here to examine the spatial continuity and nodal character of frontier-state amplitudes. In the C_{60} chain (Fig. 5(a)), the frontier-state amplitudes extend over neighboring C_{60} units but show nodal/low-amplitude regions at intermolecular junctions. The corresponding transmission pathways (Fig. 6(a)) are fragmented at several intermolecular bonds. Within the resolution of the present analysis, these observations support an intermolecular bottleneck picture based on inefficient orbital continuity, without requiring assignment to a specific quantum-interference eigenchannel.

In contrast, the $t\text{-}C_{60}$ system exhibits qualitatively different behavior. The MPSH states (Fig. 5(b)) are more delocalized and symmetrically distributed over multiple neighboring molecules, indicating improved orbital overlap in multiple directions. This leads to a more uniform spatial distribution of the wavefunction amplitude near the Fermi level. It should be noted, however, that the orbital contribution at the $[2 + 2]$ intermolecular junctions remains relatively weak, similar to that in the C_{60} chain, likely due to nodal characteristics of the wavefunction at these bonding sites. This suggests that the enhanced transport does not originate from individual junctions but from the collective network connectivity.

Consistently, the transmission pathway analysis of $t\text{-}C_{60}$ (Fig. 6(b)) shows continuous and well-connected current flow along the transport direction, with multiple parallel pathways contributing to conduction. The presence of these alternative pathways reduces the impact of local orbital mismatch and enables robust electron propagation across the system. For comparison, the transmission pathway of the C_{60} chain (Fig. 6(a)) shows partially interrupted current flow at intermolecular junctions, reflecting the limited effectiveness of individual connections in sustaining continuous transport. In the $\text{Au}\text{-}C_{60}\text{-}\text{Au}$ junction (Fig. 6(c)), the current is primarily localized through the central molecule and strongly influenced by molecule-electrode coupling, resulting in a more confined transport pathway characteristic of resonant tunneling.

Overall, these results demonstrate that electron transport in C_{60} -based systems is governed not simply by connectivity or dimensionality, but by the formation of continuous and delocalized transport channels near the Fermi level. The tetragonal network benefits from multiple conduction pathways that enhance robustness against interference effects, whereas the one-dimensional chain is more susceptible to orbital mismatch and quantum interference, leading to suppressed conductance.

The interpretation should be considered within the limitations of the present model. In particular, the polymerized structures were not re-optimized, individual transmission eigenchannels and LDOS/IPR(inverse participation ratio) measures were not calculated, and the all-carbon network devices are not directly equivalent to metal-contacted experimental junctions. The conclusions therefore concern qualitative differences among the modeled topologies and the calculated transmission pathways, rather than a unique quantitative decomposition of the conductance into individual channels.

Conclusion

In summary, I have performed a comparative NEGF-DFT study of electron transport in C₆₀-based systems spanning a 1D polymerized C₆₀ chain, a 2D tetragonal C₆₀ network, and an Au-C₆₀-Au single-molecule reference junction. The calculations reveal strongly topology- and bias-dependent transport behavior.

Specifically, the 1D C₆₀ chain exhibits strongly suppressed transmission near the Fermi level and remains weakly conductive over the investigated bias range. In contrast, t-C₆₀ retains finite Fermi-level transmission and substantially larger low-bias current. The Au-C₆₀-Au junction shows a more rapid current increase at higher bias and crosses the t-C₆₀ current at approximately 1.5 V in the present model.

Taken together, the MPSH distributions and transmission pathways indicate that the spatial continuity of available transport pathways is an important qualitative descriptor beyond simple dimensionality or bond count. Because the present structures were not re-optimized and individual transmission eigenchannels were not resolved, this conclusion is intentionally limited to the comparative behavior of the modeled structures rather than a quantitative channel decomposition. The results provide a basis for further studies in which structural relaxation and eigenchannel analysis can be treated explicitly.

Declarations

CRedit authorship contribution statement

YM: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization.

Declaration of competing interest

The author declares that there are no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Figures

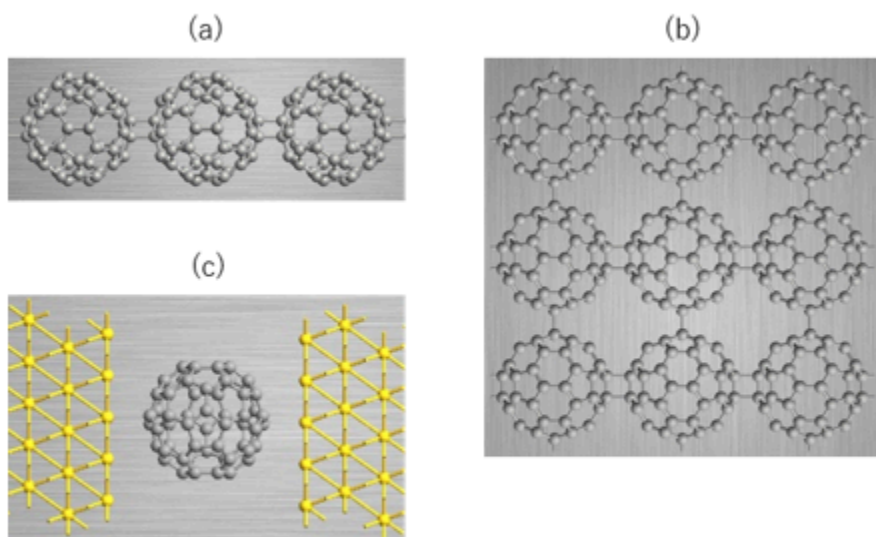


Figure 1. Device structures of (a) C₆₀ chain, (b) tetragonal C₆₀ (t-C₆₀), and (c) C₆₀ between Au(100) electrodes (Au-C₆₀-Au).

Figure 1

See image above for figure legend.

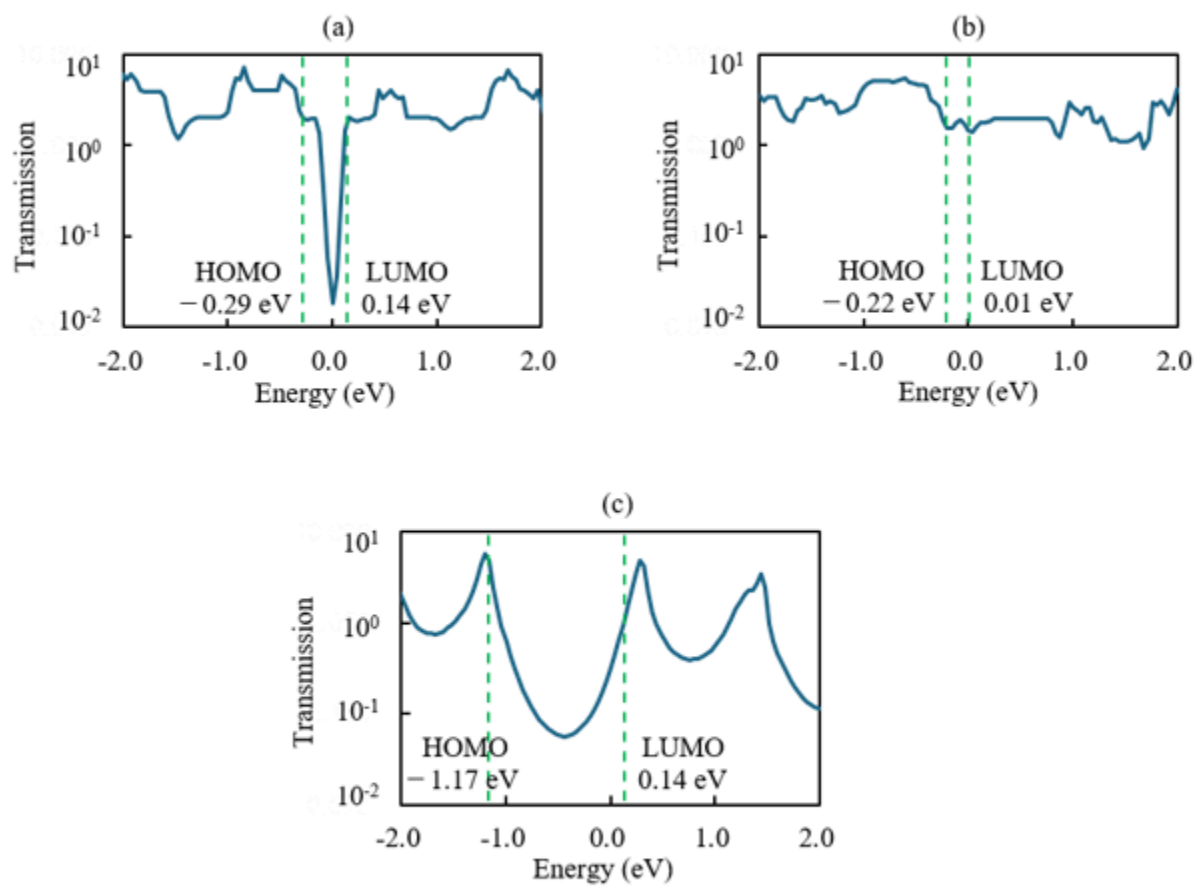


Figure 2. Transmission spectra of (a) C_{60} chain, (b) $t-C_{60}$, and (c) $Au-C_{60}-Au$.

Figure 2

See image above for figure legend.

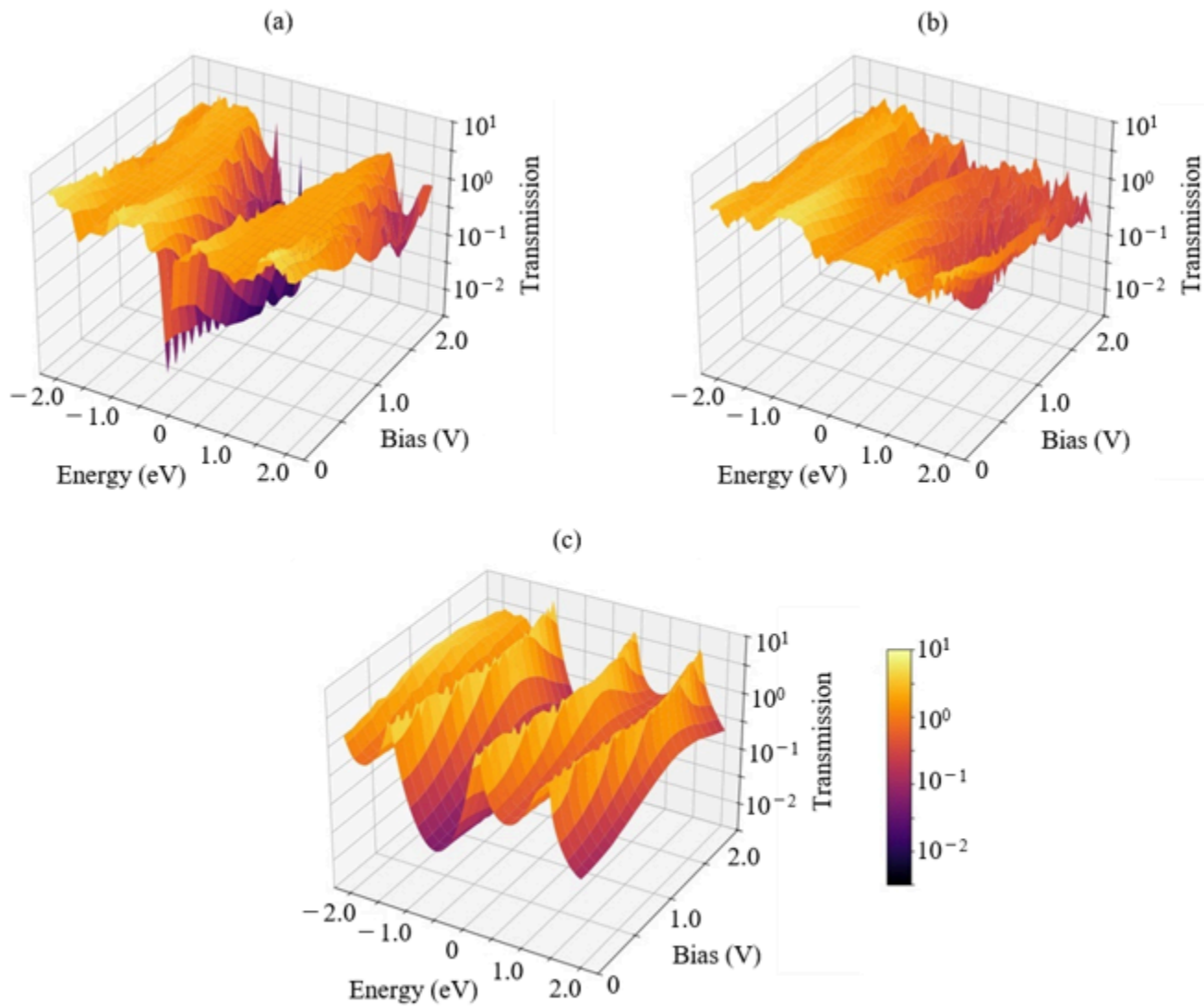


Figure 3. Transmission spectra depending on the bias of (a) C_{60} chain, (b) $t-C_{60}$, and (c) $Au-C_{60}-Au$.

Figure 3

See image above for figure legend.

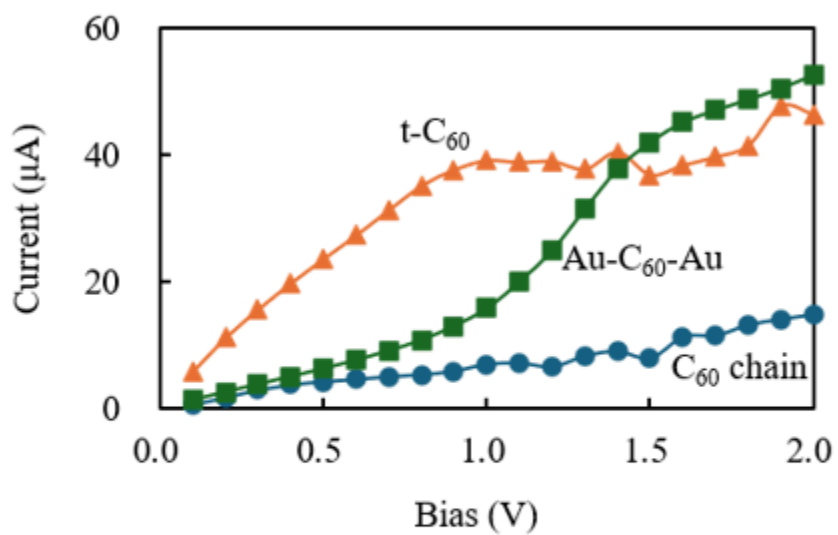


Figure 4. Current-bias characteristics of C₆₀ chain, t-C₆₀, and Au-C₆₀-Au.

Figure 4

See image above for figure legend.

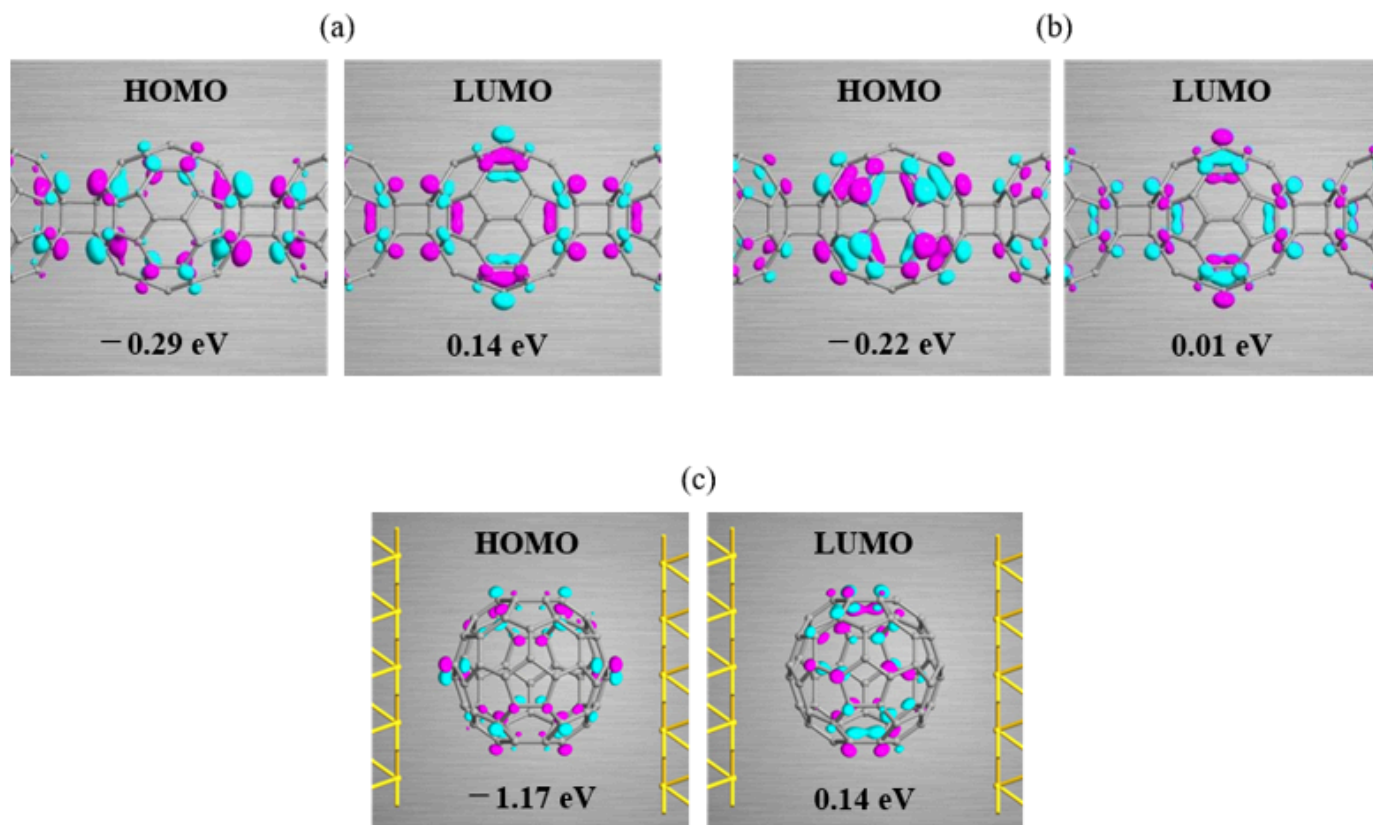


Figure 5. MPSH states of HOMO and LUMO of (a) C_{60} chain, (b) $t-C_{60}$, and (c) $Au-C_{60}-Au$.

Figure 5

See image above for figure legend.

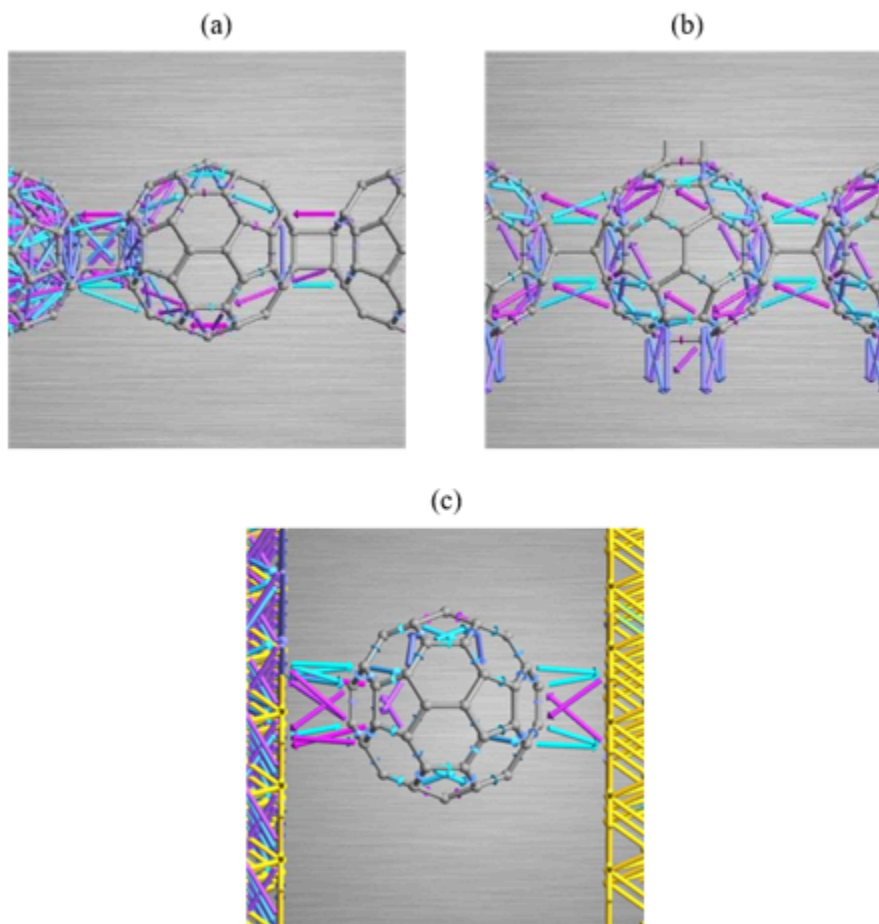


Figure 6. Transmission pathways of (a) C₆₀ chain, (b) t-C₆₀, and (c) Au-C₆₀-Au.

Figure 6

See image above for figure legend.