Supporting Information for

Designing Long and Highly Conducting Molecular Wires with Multiple Nontrivial Topological States

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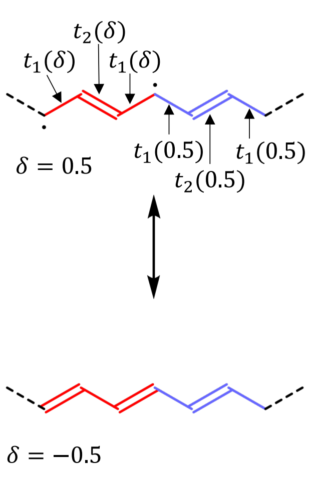
I. Tight-binding method

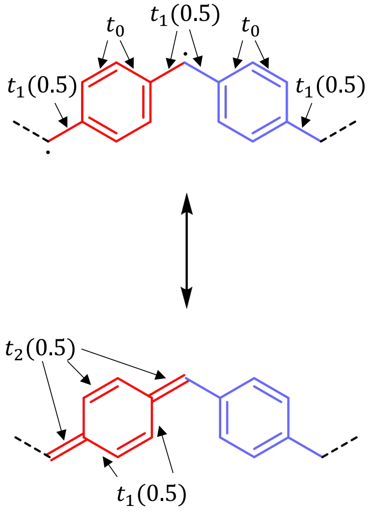
In the tight binding method, the general form of the single-particle Hamiltonian, with the on-site energy of carbon set to zero, can be written as:

$$\mathbf{H}_0 = -\sum_{i,j} t_{i,j} |i\rangle\langle j| + H.c. \tag{1}$$

where $t_{i,j}$ is the coupling between the *i*-th site and its neighboring *j*-th site. The Hamiltonian $\mathbf{H}_0$ is generated by including all the nearest neighbor couplings between all atoms in the molecule as illustrated below for **L1**[m], **C1**[m], **L2**[m], and **C2**[m].



L1[m] or **C1**[m]



L2[m] or **C2**[m]

Here, $t_1(\delta) = t_0 \exp(-\delta)$, and $t_2(\delta) = t_0 \exp(\delta)$. $\delta = 0.5$ represents the topological structural limit and $\delta = -0.5$ represents the trivial structural limit. As an example, we show the Hamiltonian for **L1**[1] and **C1**[1] at the topological limit below:

$$\mathbf{H}_0(\mathbf{L1}[1]) = \begin{pmatrix} 0 & -t_1(0.5) & 0 & 0 \\ -t_1(0.5) & 0 & -t_2(0.5) & 0 \\ 0 & -t_2(0.5) & 0 & -t_1(0.5) \\ 0 & 0 & -t_1(0.5) & 0 \end{pmatrix} \tag{2}$$

and

$$\mathbf{H}_0(\mathbf{C1}[1]) = \begin{pmatrix} 0 & -t_1(0.5) & 0 & 0 & 0 & -t_1(0.5) \\ -t_1(0.5) & 0 & -t_2(0.5) & 0 & 0 & 0 \\ 0 & -t_2(0.5) & 0 & -t_1(0.5) & 0 & 0 \\ 0 & 0 & -t_1(0.5) & 0 & -t_1(0.5) & 0 \\ 0 & 0 & 0 & -t_1(0.5) & 0 & -t_2(0.5) \\ -t_1(0.5) & 0 & 0 & 0 & -t_2(0.5) & 0 \end{pmatrix} \tag{3}$$

The coupling between the left and right electrodes, $\mathbf{\Gamma}_\mathrm{L}$ and $\mathbf{\Gamma}_\mathrm{R}$, are defined as:

$$\mathbf{\Gamma}_\mathrm{L} = \mathit{\Gamma}_\mathrm{L}|L\rangle\langle L| \tag{4}$$

and

$$\mathbf{\Gamma}_\mathrm{R} = \mathit{\Gamma}_\mathrm{R}|R\rangle\langle R| \tag{5}$$

where L and R are the atomic sites directly connecting to the left and right electrode, respectively. In this work, we set $\mathit{\Gamma}_\mathrm{L} = \mathit{\Gamma}_\mathrm{R} \equiv \mathit{\Gamma} = 0.1t_0$ for symmetric electrode-molecule couplings. The total Hamiltonian is:

$$\widetilde{\mathbf{H}} = -\frac{i}{2}(\mathbf{\Gamma}_\mathrm{L} + \mathbf{\Gamma}_\mathrm{R}) + \mathbf{H}_0 \tag{6}$$

The Green's function is then obtained as:

$$\mathbf{G}(E) = \left[E\mathbf{I} - \widetilde{\mathbf{H}}\right]^{-1} \tag{7}$$

The transmission function can then be calculated as:

$$T(E) = \mathrm{Tr}[\mathbf{\Gamma}_\mathrm{L}\mathbf{G}(E)\mathbf{\Gamma}_\mathrm{R}\mathbf{G}^\dagger(E)] \tag{8}$$

We use Mathematica to compute all transmission data presented in the manuscript. A sample code for **L1**[1] is shown below:

```
(* Taking Diradical Polyacetylene (m = 2) as example *)
(* Parameters *)
t0 = 1; γ = 0.1; δ = 0.5;
t1 = t0 * Exp[ - δ];t2 = t0 * Exp[δ];

(* Hamiltonian and Gamma matrices *)
H = {{0, - t1, 0, 0}c, { - t1, 0, - t2, 0}, {0, - t2, 0, - t1}, {0, 0, - t1, 0}};
Γl = SparseArray[{1, 1}-> γ, {4, 4}];
Γr = SparseArray[{4, 4}-> γ, {4, 4}];
(* Self - energy *)
```

```
Σ = - I / 2(Γl + Γr);

(* Green's Function *)
G[E_]:=Inverse[E IdentityMatrix[4] - (H + Σ)];

(* Transmission function *)
T[E_]:=Tr[Γl.G[E].Γr.G[E]\[ConjugateTranspose]];

(* Plot transmission function *)
LogPlot[{T[E]}, {E, - 1, 1}]
```

II. Quantum interference

Quantum interference (QI) between molecular orbital channels is determined by the phase of the orbitals, which is the phase difference between the two binding sites of the molecule to the electrodes. With $E_F = 0$, Eq. 8 can be simplified to[1-2]:

$$T(E_F) = \Gamma^2 \left| \frac{\Delta_{L,R}}{\det(\widetilde{\mathbf{H}})} \right|^2 \tag{9}$$

where $\Delta_{L,R}$ is the minor determinant of $\widetilde{\mathbf{H}}$ with respect to its (*L*,*R*) element. By Eq. 9 and the Hamiltonian of **L1**[*m*], the calculated analytical result of $T(E_F)$ for **L1**[*m*] can be written as[2]:

$$\begin{aligned} T_{\mathbf{L1}[m]}(E_F) &= \left| \frac{-t_1^{4m-2} t_2^{2m-1}}{(-1)^{m-1}\left(t_1^{4m} t_2^{2(m-1)} + \frac{\Gamma^2}{4} t_1^{4(m-1)} t_2^{2m}\right)} \right|^2 \\ &= \left| \frac{(-1)^m \frac{\Gamma}{2}}{t_0 e^{-3\delta} + \frac{i\Gamma}{2}} + \frac{(-1)^{m-1} \frac{\Gamma}{2}}{-t_0 e^{-3\delta} + \frac{i\Gamma}{2}} \right|^2 \end{aligned} \tag{10}$$

where $t_1 \equiv t_1(0.5)$, and $t_2 \equiv t_2(0.5)$. Eq. 10 is equivalent to having an occupied and an unoccupied orbital resonance-based transmission t_{Occupied} and $t_{\text{Unoccupied}}$ at energies:

$$\varepsilon_{\text{Occupied}} = -t_0 e^{-3\delta} \tag{11}$$

and

$$\varepsilon_{\text{Unoccupied}} = t_0 e^{-3\delta} \tag{12}$$

These effective resonances have a coupling:

$$\gamma_{\text{Occupied}} = \gamma_{\text{Unoccupied}} = \frac{\Gamma}{2} \tag{13}$$

For single 1D TI molecules with two topological radical states, such as **L1**[1], the effective Occupied and Unoccupied states from the two-level model (Eqs. 10-13) are the actual HOMO and LUMO channels. While for molecules with more than two topological states, such as **L1**[*m* > 1], the effective Occupied and Unoccupied levels are just mathematical entities and not the actual molecular resonances. However, it is clear from this expression, that the energies of the effective

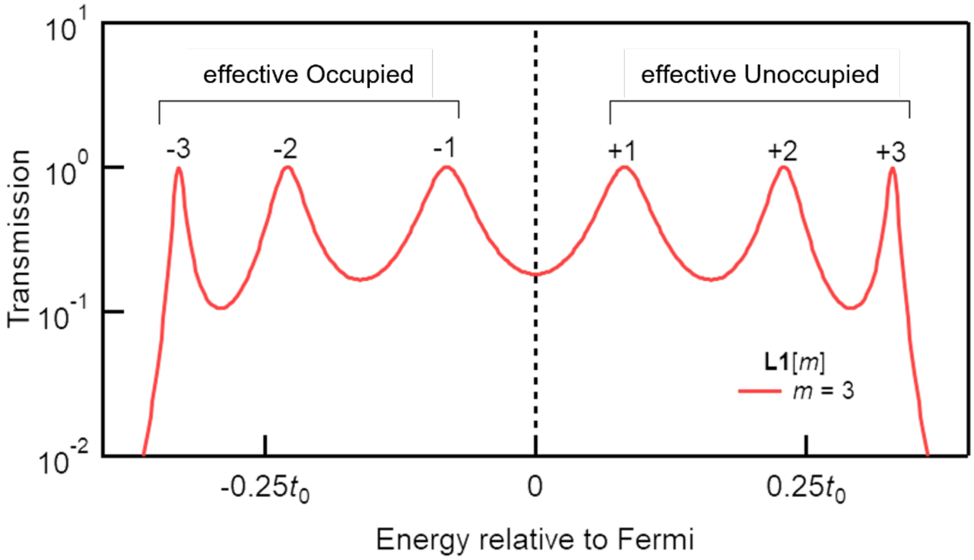
Occupied and Unoccupied channels are independent of the length m (Eqs. 11-12), but the actual HOMO and LUMO states of the **L1**[m] system get closer when m increases (Figure 2A-2B in the main text). The energies of the effective Occupied and Unoccupied states in the two-level model (Eqs. 11-12) are the geometric average of the eigen energies of the topological states:

$$\varepsilon_{\text{Occupied}} = -\sqrt[m]{\prod_{j=1}^{m} \left|\varepsilon_{-j}\right|} \tag{14}$$

and

$$\varepsilon_{\text{Unoccupied}} = \sqrt[m]{\prod_{j=1}^{m} \left|\varepsilon_{+j}\right|} \tag{15}$$

where the subscripts -1, -2, … , -m are indices of the topological states below E_F, and +1, +2, … , +m are indices of the topological states above E_F, as shown below for $m = 3$:



Eqs. 14-15 can be derived by solving the reduced molecular Hamiltonian where only the topological states are included. For $m = 1$, the energies of the effective Occupied and Unoccupied states are the same as the real HOMO and LUMO states, which are the eigenvalues for the reduced Hamiltonian:

$$\boldsymbol{\mathcal{H}}_1 = \begin{pmatrix} 0 & b \\ b & 0 \end{pmatrix} \tag{16}$$

where b is the coupling between the two radicals. The eigenvalues for $\boldsymbol{\mathcal{H}}_1$ is $(\lambda^1_{-1}, \lambda^1_{+1}) = (-b, b)$, where in the notation $\lambda^m_{\pm j}$, the subscript $\pm j$ is the orbital index, and the superscript m is the number of TI units. Similarly, for $m = 2$, which has four radical states, the reduced Hamiltonian becomes:

$$\boldsymbol{\mathcal{H}}_2 = \begin{pmatrix} 0 & b & 0 & 0 \\ b & 0 & b & 0 \\ 0 & b & 0 & b \\ 0 & 0 & b & 0 \end{pmatrix} \tag{17}$$

with eigenvalues $(\lambda^2_{-2}, \lambda^2_{-1}, \lambda^2_{+1}, \lambda^2_{+2}) = \left(\frac{-\sqrt{5}-1}{2}b, \frac{-\sqrt{5}+1}{2}b, \frac{\sqrt{5}-1}{2}b, \frac{\sqrt{5}+1}{2}b\right)$. We note that the eigenvalues of $\boldsymbol{\mathcal{H}}_1$ can be expressed in terms of those of $\boldsymbol{\mathcal{H}}_2$ as:

$$\lambda^1_{-1} = -\sqrt{|\lambda^2_{-1}\lambda^2_{-2}|} \quad \text{and} \quad \lambda^1_{+1} = \sqrt{|\lambda^2_{+1}\lambda^2_{+2}|} \tag{18}$$

Extending this to larger m, we can write the eigenvalues of $\boldsymbol{\mathcal{H}}_1$ in terms of those of $\boldsymbol{\mathcal{H}}_m$ following the same expression:

$$\lambda^1_{-1} = -\sqrt[m]{|\lambda^m_{-1}\lambda^m_{-2} \dots \lambda^m_{-m}|} \quad \text{and} \quad \lambda^1_{+1} = \sqrt[m]{|\lambda^m_{+1}\lambda^m_{+2} \dots \lambda^m_{+m}|} \tag{19}$$

Eqs. 19 are equivalent to Eqs. 14-15 under the relations $\varepsilon_{\text{Unoccupied/Occupied}} = \lambda^1_{\pm 1}$, and $\varepsilon_{\pm j} = \lambda^m_{\pm j}$.

The couplings between the effective Occupied and Unoccupied states and the electrodes (Eq. 13) are the sum of the individual states:

$$\gamma_{Occupied} = \gamma_{\text{Unoccupied}} = \sum_{j=1}^{m} \gamma_{-j} \text{ or } \sum_{j=1}^{m} \gamma_{+j} \tag{20}$$

Eqs. 20 can be derived from Fermi's golden rule[3-4], where the transition rate (coupling) from initial molecular states $|j\rangle$ (j = 1, 2, … , m) and final electrode states $|f\rangle$ is:

$$\gamma_{\text{total},j\to f}(E_F) = \frac{2\pi}{\hbar^2} \sum_{\substack{\text{all molecular} \\ \text{states } j}} \sum_{\substack{\text{all electrode} \\ \text{states } f}} |\langle f|V|j\rangle|^2 \mathcal{D}(E_F)$$

$$= \frac{2\pi}{\hbar^2}\left(\sum_{\substack{\text{all electrode}\\ \text{states } f}} |\langle f|V|1\rangle|^2 \mathcal{D}(E_F) + \sum_{\substack{\text{all electrode}\\ \text{states } f}} |\langle f|V|2\rangle|^2 \mathcal{D}(E_F) + \cdots \right.$$

$$\left. + \sum_{\substack{\text{all electrode}\\ \text{states } f}} |\langle f|V|m\rangle|^2 \mathcal{D}(E_F)\right)$$

$$= \gamma_1 + \gamma_2 + \cdots + \gamma_m \tag{21}$$

where V is the coupling for the transition $j \to f$ to first order in perturbation theory, and $\mathcal{D}(E_F)$ is the density of state of the electrode at E_F.

Lastly, according to Eq. (10), the Occupied and Unoccupied channels are out-of-phase (different by a factor of -1). Therefore, there is constructive quantum interference (QI) between the two effective channels. Similarly in a linear π-system, such as **L1**[m], the actual HOMO and LUMO are out-of-phase since LUMO has one more nodal plane than HOMO (Figure S1), which renders the effective model a good analog to the actual model.

We have demonstrated the relations between the effective model and the actual model in terms of the three main factors of transmissions: molecular orbital energy levels, molecule-electrode couplings, and QI. In conclusion, mathematically, the transmission for **L1**[m] has the same form as that of a 1D TI system with two radical states within the topological band.

Using the effective model, the QI between Occupied and Unoccupied, T_{QI}, as defined in the main text can be calculated from the cross term in Eq. 10: [2]

$$T_{\mathrm{QI}} = 2\mathrm{Re}\left[t_{\mathrm{Occupied}} t^{*}_{\mathrm{Unoccupied}}\right] \tag{22}$$

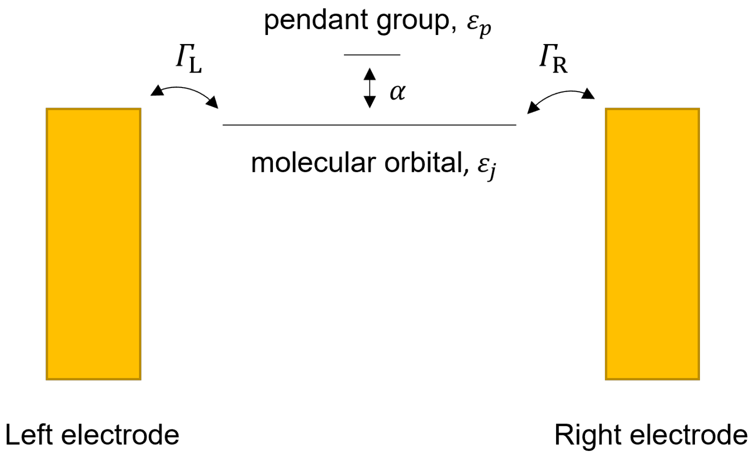
By substituting Eq. 10 into Eq. 22 and solving the Hamiltonian of **L1**[m], we obtain T_{QI} for **L1**[m]:

$$T_{\mathrm{QI}}(\mathbf{L1}[m]) = \frac{\frac{\Gamma^2}{2}\left(\left(t_0 e^{-3\delta}\right)^2 - \frac{\Gamma^2}{4}\right)}{\left((t_0 e^{-3\delta})^2 - \frac{\Gamma^2}{4}\right)^2 + (t_0 e^{-3\delta})^2 \Gamma^2} \tag{23}$$

Figure 2D in the main text is a plot of Eq. 23.

III. Fano resonance

Fano resonance often results from having a pendant group on the main molecular wire. Such a pendant group affects the transmission function as detailed below.



Consider a pendant group attached to a molecular wire such that it is coupled to the wire molecular orbital j through a parameter α and has an on-site energy ε_p. The transmission across this single-level can be calculated through a tight-binding approach as[5]:

$$T(E) = \frac{\Gamma_{\mathrm{L}}\Gamma_{\mathrm{R}}}{\left(E - \varepsilon_j - \dfrac{\alpha^2}{E - \varepsilon_p}\right)^2 + \dfrac{(\Gamma_{\mathrm{L}} + \Gamma_{\mathrm{R}})^2}{4}} \tag{24}$$

From Eq. 24, the Fano resonance occurs at $E = \varepsilon_p$ and this destructive QI leads to a decrease in the conductance of the topological wires. However, in the effective Occupied and Unoccupied model (Eq. 10), $\varepsilon_{\mathrm{Occupied}}$ and $\varepsilon_{\mathrm{Unoccupied}}$ are not dependent on the wire length m (Eqs. 11-12). Hence, the conductance-length relation is not affected by Fano resonance however the magnitude of the conductance at E_F does change depending on α and ε_p as shown in Figure S3.

IV. Additional figures

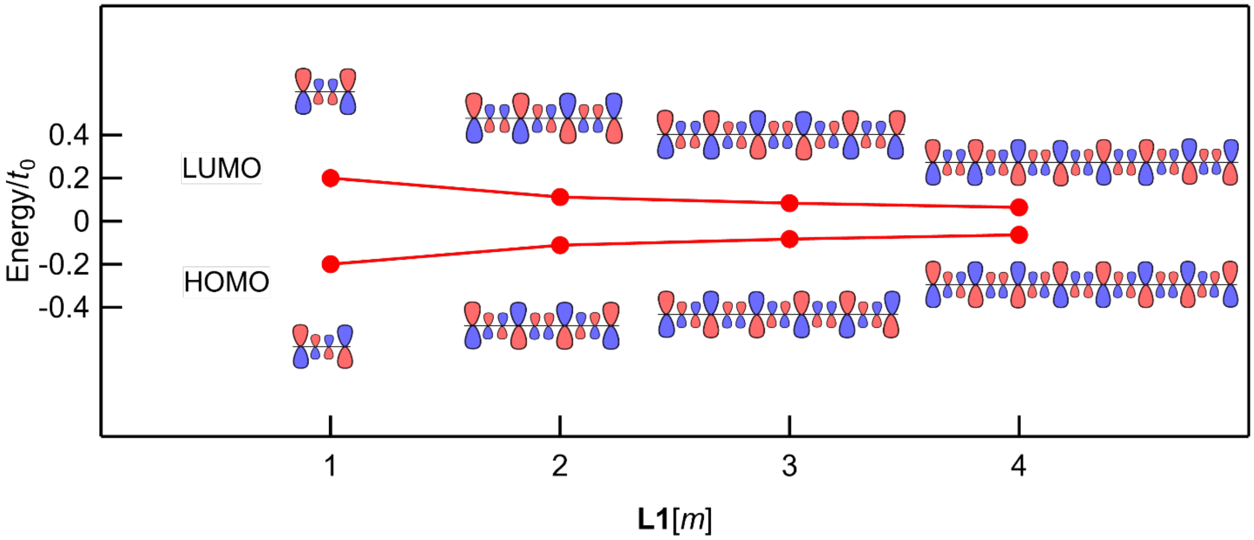


Figure S1. Eigenvalues of HOMO and LUMO against length for **L1**[1] to **L1**[4].

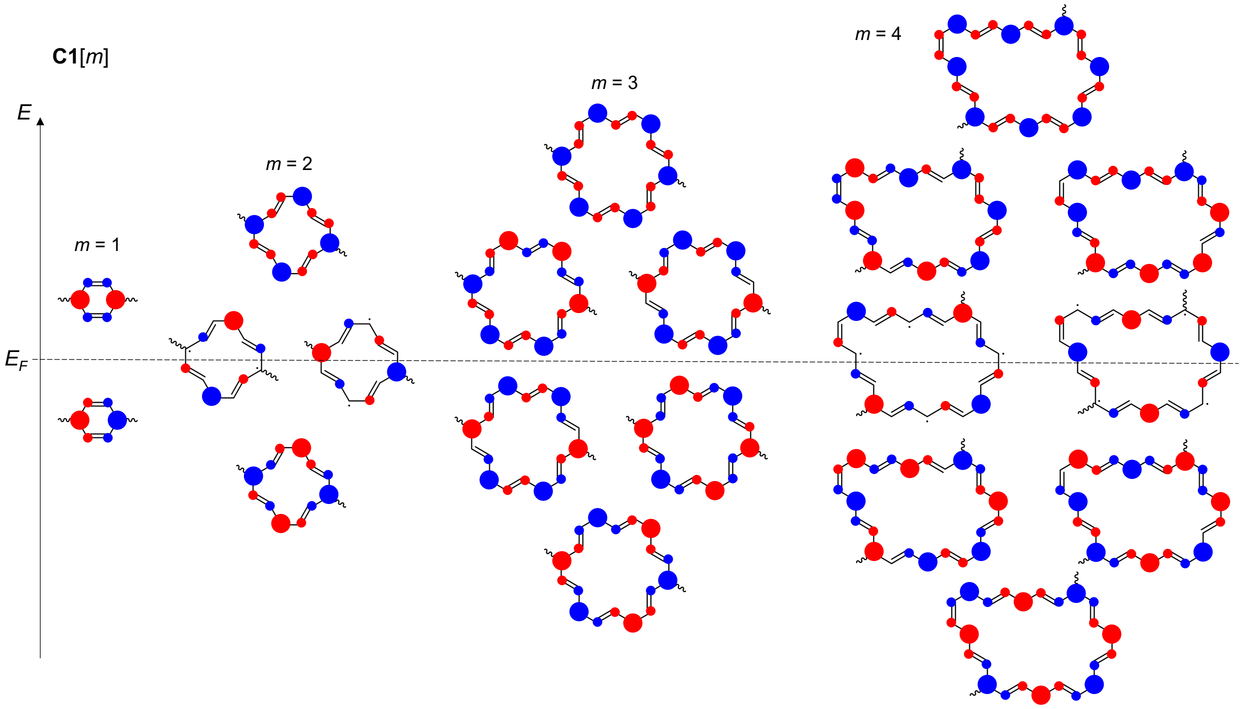


Figure S2. Calculated molecular orbitals of topological states for **C1**[1] to **C1**[4]. The wavy bonds indicate electrode-molecule coupling.

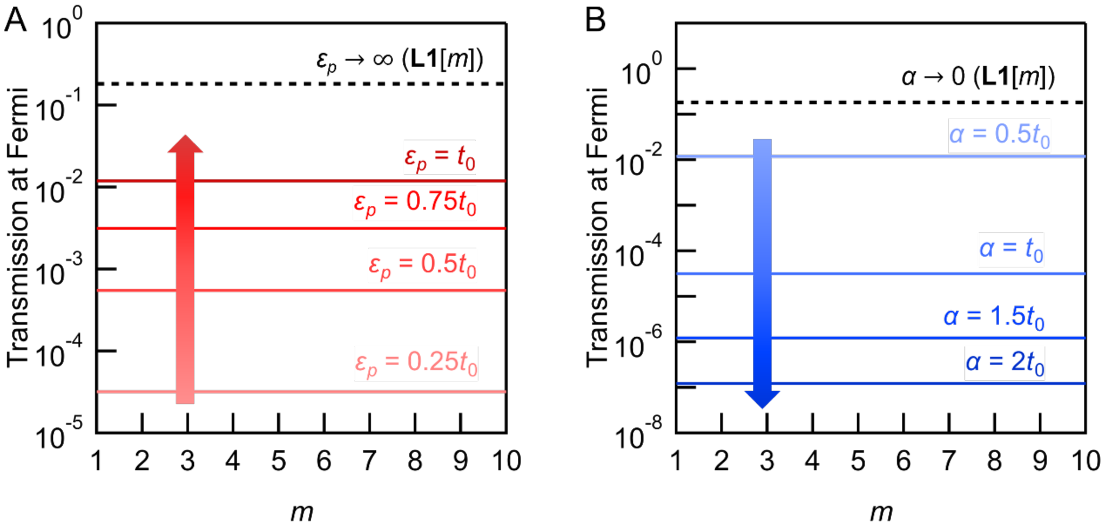


Figure S3. Conductance-length relationship for **L1**[*m*] for different (A) pendant onsite energy (ε_p) values and (B) coupling (α) values. The black dashed line indicates the transmission at Fermi for **L1**[*m*].

V. References

1. Gunasekaran, S.; Hernangomez-Perez, D.; Davydenko, I.; Marder, S.; Evers, F.; Venkataraman, L., Near Length-Independent Conductance in Polymethine Molecular Wires. *Nano Lett.* **2018,** *18* (10), 6387-6391.

2. Li, L.; Gunasekaran, S.; Wei, Y.; Nuckolls, C.; Venkataraman, L., Reversed Conductance Decay of 1D Topological Insulators by Tight-Binding Analysis. *J. Phys. Chem. Lett.* **2022,** *13* (41), 9703-9710.

3. Dirac, P. A. M., The Quantum Theory of the Emission and Absorption of Radiation. *Proc. R. Soc. London, Ser. A* **1927,** *114* (767), 243-265.

4. Fermi, E., Nuclear Physics. University of Chicago Press. **1950**.

5. Lambert, C. J., Basic Concepts of Quantum Interference and Electron Transport in Single-Molecule Electronics. *Chem. Soc. Rev.* **2015,** *44* (4), 875-888.