SUPPORTING INFORMATION

Visualizing Quantum Interference in Molecular Junctions

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1. Calculating T(E)

For the molecular junction model, the isolated molecule is described by a Hamiltonian *H*. When the molecule is connected to the electrodes, it is no longer an isolated system. The Hamiltonian for the open system which considers the interaction with the electrodes (H') can be expressed as,

$$H' = H + \Sigma \tag{S1}$$

$$\text{and} \quad \Sigma = \Sigma_L + \Sigma_R$$

where Σ_L and Σ_R are the self-energies of the left and right lead, respectively. Technically, H' is not a proper Hamiltonian since the self-energy is not Hermitian. The anti-Hermitian part of the self-energy is described by Γ,

$$\Gamma_L = i\left(\Sigma_L - \Sigma_L^{\dagger}\right) = -2\mathrm{Im}[\Sigma_L] \tag{S2}$$

$$\Gamma_R = i\left(\Sigma_R - \Sigma_R^{\dagger}\right) = -2\mathrm{Im}[\Sigma_R] \tag{S3}$$

Transport through the single-molecule junction is described by a Green's function,

$$G(E) = [EI - H']^{-1} = [EI - (H + \Sigma)]^{-1} \tag{S4}$$

where *I* is the identity matrix and *E* is the energy of the electron. With the Green's function, one can calculate the transmission function using the formula,

$$T(E) = \mathrm{Tr}[\Gamma_L G \Gamma_R G^{\dagger}] \tag{S5}$$

A more in-depth discussion of these equations can be found in these texts.[1, 2]

2. Calculating Q(E)

To elucidate QI, we must consider the eigenbasis of H'. Since H' is not Hermitian, there are two sets of eigenvectors, $|\psi_i\rangle$ and $|\bar{\psi}_i\rangle$ for H' and $H'^{\dagger}$, respectively:

$$H'|\psi_i\rangle = z_i|\psi_i\rangle \tag{S6}$$

$$H'^{\dagger}|\bar{\psi}_i\rangle = z_i^*|\bar{\psi}_i\rangle \tag{S7}$$

$$and \quad \langle\bar{\psi}_i|\psi_j\rangle = \delta_{ij} \tag{S8}$$

In the third line, we have additionally normalized the eigenvectors. Importantly, the eigenvectors of H' are also the eigenvectors of the Green's function,

$$G(E)|\psi_i\rangle = \frac{1}{E - z_i}|\psi_i\rangle \tag{S9}$$

$$G^{\dagger}(E)|\bar{\psi}_i\rangle = \frac{1}{E - z_i^*}|\bar{\psi}_i\rangle \tag{S10}$$

This eigenbasis is distinct from the MO basis, which is the eigenbasis of the isolated Hamiltonian (H). Previous works have referred to these eigenvectors as molecular conductance orbitals (MCO).[3] However, since the coupling to the electrodes is typically small, the MCOs will be very similar to the MOs, so we do not make a distinction between these bases in the main text.

Since H' is not Hermitian, the eigenvalues z_i will be complex and take the form,

$$z_i = \varepsilon_i - i\gamma_i \tag{S11}$$

where ε_i is the energy of the MCO and γ_i is the coupling of the MCO to the electrodes. Therefore, an energy-coupling diagram can be produced by plotting $-Im[z_i]$ vs $Re[z_i]$ for all eigenvalues of H' (Figure 5g).

To obtain the Q matrix, we can expand the transmission function formula in the eigenbasis of G (and H') yielding,

$$\begin{aligned} T(E) &= \mathrm{Tr}[\Gamma_L G \Gamma_R G^\dagger] \\ &= \sum_i \langle \psi_i | \Gamma_L G \Gamma_R G^\dagger | \bar{\psi}_i \rangle \\ &= \sum_{ij} \langle \psi_i | \Gamma_L G | \psi_j \rangle \langle \bar{\psi}_j | \Gamma_R G^\dagger | \bar{\psi}_i \rangle \\ &= \sum_{ij} \frac{\langle \psi_i | \Gamma_L | \psi_j \rangle \langle \bar{\psi}_j | \Gamma_R | \bar{\psi}_i \rangle}{(E - z_j)(E - z_i^*)} \end{aligned} \tag{S12}$$

where we have made use of the completeness relation,

$$I = \sum_j |\psi_j\rangle\langle\bar{\psi}_j| \tag{$S13$}$$

We see that we have deconstructed the transmission function into terms comprising single MCOs (for $i = j$) and pairs of MCOs (for $i \neq j$), which represent the noninterfering and interfering contributions to transmission, respectively.[4]

We define a matrix, Q (for quantum interference), whose elements (i, j) correspond to a term in the summation,

$$Q_{ij} \equiv \frac{\langle \psi_i | \Gamma_L | \psi_j \rangle \langle \bar{\psi}_j | \Gamma_R | \bar{\psi}_i \rangle}{(E - z_j)(E - z_i^*)} \tag{S14}$$

Note that Q is Hermitian because Γ_L and Γ_R are Hermitian,

$$Q_{ij}^* = \frac{\langle \psi_j | \Gamma_L^\dagger | \psi_i \rangle \langle \bar{\psi}_i | \Gamma_R^\dagger | \bar{\psi}_j \rangle}{(E - z_j^*)(E - z_i)} = \frac{\langle \psi_j | \Gamma_L | \psi_i \rangle \langle \bar{\psi}_i | \Gamma_R | \bar{\psi}_j \rangle}{(E - z_i)(E - z_j^*)} = Q_{ji} \tag{S15}$$

To obtain a matrix formula for Q, we can define a matrices P whose columns are the eigenvectors of H' and P^{-1} whose rows are the eigenvectors of $H'^{\dagger}$:

$$P = (\cdots \quad \psi_i \quad \cdots) \ and \ P^{-1} = \begin{pmatrix} \vdots \\ \bar{\psi}_i \\ \vdots \end{pmatrix} \tag{S16}$$

Using P and P^{-1}, we can construct matrices A and B,

$$\begin{aligned} A &= P^{\dagger}\Gamma^{L}GP \qquad and \quad A_{ij} = \langle \psi_i | \Gamma_L G | \psi_j \rangle \\ B &= P^{-1}\Gamma^{R}G^{\dagger}P^{-1\dagger} \quad and \quad B_{ij} = \langle \bar{\psi}_i | \Gamma_R G^{\dagger} | \bar{\psi}_j \rangle \end{aligned} \tag{S17}$$

From the definition of Q, we see that Q is simply an entrywise product of A and B^{T},

$$Q = A \circ B^{\mathrm{T}} \quad and \quad Q_{ij} = A_{ij}B_{ji} \tag{S18}$$

This leads to the matrix formula for Q presented in the main text,

$$Q = (P^{\dagger}\Gamma^{L}GP) \circ (P^{-1}\Gamma^{R}G^{\dagger}P^{-1\dagger})^{\mathrm{T}} \tag{S19}$$

The equivalence of $Q(E)$ and $T(E)$ can be quickly seen using the identity,

$$\sum_{ij} A_{ij}B_{ji} = \mathrm{Tr}[AB] \tag{S20}$$

From this identity we have that,[5]

$$\begin{aligned} \sum_{ij} Q_{ij} &= \mathrm{Tr}[(P^{\dagger}\Gamma^{L}GP)(P^{-1}\Gamma^{R}G^{\dagger}P^{-1\dagger})] \\ &= \mathrm{Tr}[\Gamma_L G \Gamma_R G^{\dagger}] = T(E) \end{aligned} \tag{S21}$$

Therefore, the Q matrix is mathematically equivalent to the transmission function.

3. Transmission Coefficients

The transmission coefficients can be obtained by additional expansion of equation S12. Since Γ_L and Γ_R are Hermitian they can be expressed in terms of their respective eigenvalues, γ_ℓ and γ_r, and eigenvectors, $|\ell\rangle$ and $|r\rangle$,

$$\Gamma_L = \sum_\ell \gamma_\ell |\ell\rangle\langle\ell| \qquad and \qquad \Gamma_R = \sum_r \gamma_r |r\rangle\langle r| \tag{S22}$$

The eigenvectors describe the nature of the coupling with the electrodes and the eigenvalues describe the strength of the coupling. Inserting these expressions into equation S12, we have,[3]

$$\begin{aligned} T(E) &= \sum_{\ell r}\sum_{ij} \gamma_\ell \gamma_r \frac{\langle\psi_i|\ell\rangle\langle\ell|\psi_j\rangle\langle\bar{\psi}_j|r\rangle\langle r|\bar{\psi}_i\rangle}{(E - z_j)(E - z_i^*)} \\ &= \sum_{\ell r}\sum_{ij} \gamma_\ell \gamma_r \frac{\langle\bar{\psi}_j|r\rangle\langle\ell|\psi_j\rangle}{E - z_j} \cdot \frac{\langle\psi_i|\ell\rangle\langle r|\bar{\psi}_i\rangle}{E - z_i^*} \\ &= \sum_{\ell r}\sum_{ij} t_{\ell r,j} t_{\ell r,i}^* = \sum_{\ell r}\left|\sum_i t_{\ell r,i}\right|^2 \end{aligned} \tag{S23}$$

where $t_{\ell r,i}$ is the transmission coefficient for the *i*th MCO for transmission between $|\ell\rangle$ and $|r\rangle$, and is given as,

$$t_{\ell r,i} = \sqrt{\gamma_L \gamma_R}\,\frac{\langle\bar{\psi}_i|r\rangle\langle\ell|\psi_i\rangle}{E - z_i} \tag{S24}$$

Note that since Γ_L and Γ_R are positive semi-definite,[1] γ_L and γ_R are nonegative, and $\sqrt{\gamma_L \gamma_R}$ is well-defined. Additionally, Q_{ij} can be expressed in terms of the transmission coefficients as,

$$Q_{ij} = \sum_{\ell r} t_{\ell r,j} t_{\ell r,i}^* \tag{S25}$$

4. Hückel Models

For the Hückel models presented in the paper, we assumed the *wide-band limit* (energy independent coupling between the molecule and the electrodes). In this limit, the self-energies become,

$$\Sigma_L = -\frac{i}{2}\Gamma_L \quad and \quad \Sigma_R = -\frac{i}{2}\Gamma_R$$

Furthermore, we assume the molecule is coupled to the left and right electrode via a single *p* orbital on either end of the molecule with coupling strength γ. Note that the results presented in the manuscript will not be significantly different if these restrictions are relaxed.

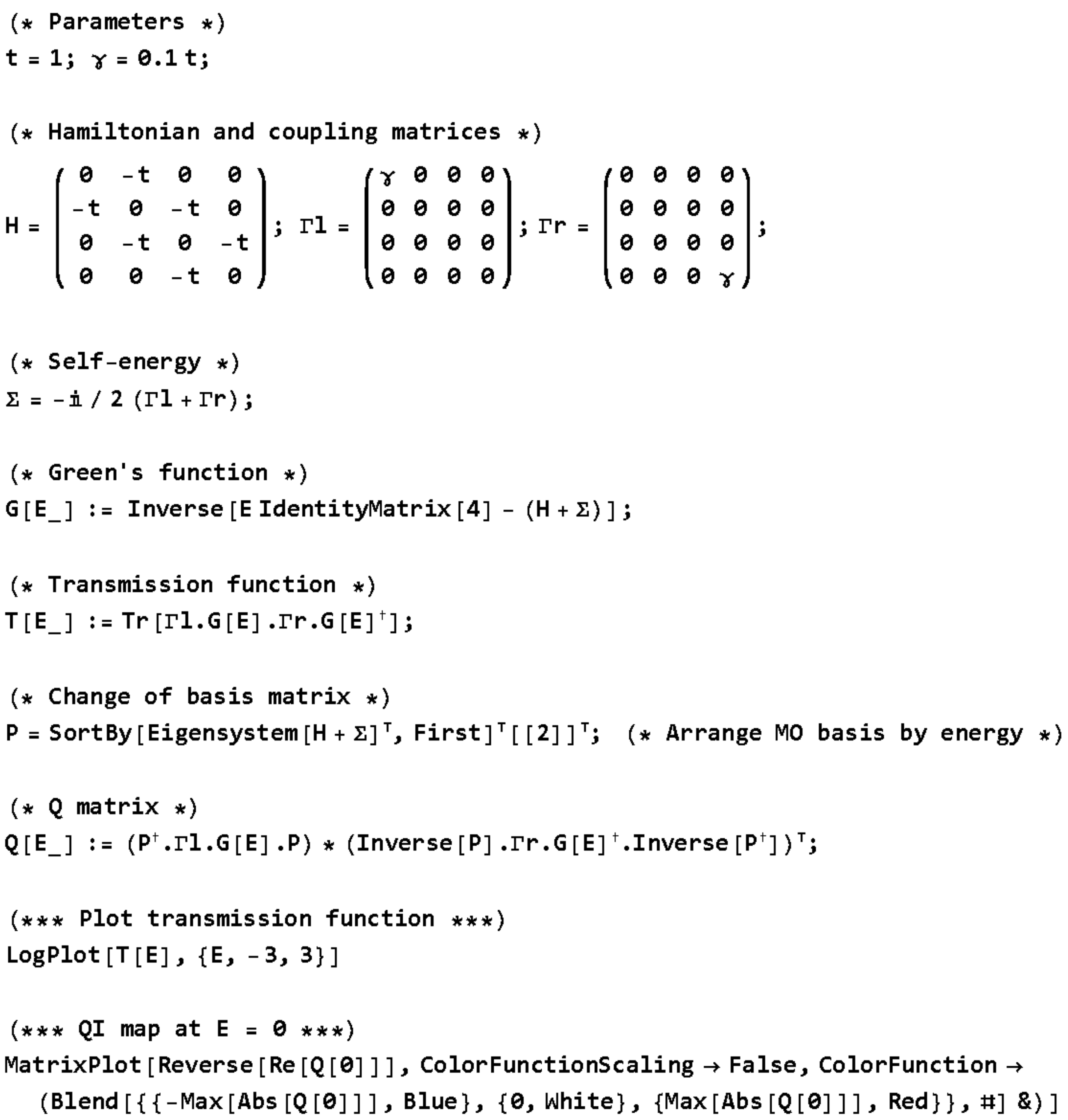
With these assumptions, the molecular junction of 1-4 butadiene is described by the following matrices,

$$H + \Sigma = \begin{pmatrix} -\frac{i\gamma}{2} & -t & 0 & 0 \\ -t & 0 & -t & 0 \\ 0 & -t & 0 & -t \\ 0 & 0 & -t & -\frac{i\gamma}{2} \end{pmatrix} \quad \Gamma_L = \begin{pmatrix} \gamma & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad \Gamma_R = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma \end{pmatrix}$$

where $H + \Sigma$ is the Hamiltian for the open system, and Γ_L and Γ_R describe the coupling to the electrodes. The parameter *t* is the hopping integral that describes the coupling between *p* orbitals of carbon atoms within the molecule. Note that conventionally *t* is defined as negative; however, we have defined *t* to be positive. Without loss of generality we set the on-site energy for carbon atoms to zero ($E_C = 0$). Furthermore, we assume that the Fermi energy is approximately equal to this on-site energy ($E_F \approx E_C$). The other molecular junctions presented in the paper are modeled similarly.

5. Mathematica Code

Code used to obtain the QI map for 1-4 butadiene (Figure 2c):



```
(* Parameters *)
t = 1; γ = 0.1 t;

(* Hamiltonian and coupling matrices *)
    ( 0  -t   0   0 )         ( γ 0 0 0 )         ( 0 0 0 0 )
H = (-t   0  -t   0 ); Γl =  ( 0 0 0 0 ); Γr =  ( 0 0 0 0 );
    ( 0  -t   0  -t )         ( 0 0 0 0 )         ( 0 0 0 0 )
    ( 0   0  -t   0 )         ( 0 0 0 0 )         ( 0 0 0 γ )

(* 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]†];

(* Change of basis matrix *)
P = SortBy[Eigensystem[H + Σ]ᵀ, First]ᵀ[[2]]ᵀ;  (* Arrange MO basis by energy *)

(* Q matrix *)
Q[E_] := (P†.Γl.G[E].P) * (Inverse[P].Γr.G[E]†.Inverse[P†])ᵀ;

(*** Plot transmission function ***)
LogPlot[T[E], {E, -3, 3}]

(*** QI map at E = 0 ***)
MatrixPlot[Reverse[Re[Q[0]]], ColorFunctionScaling → False, ColorFunction →
  (Blend[{{-Max[Abs[Q[0]]], Blue}, {0, White}, {Max[Abs[Q[0]]], Red}}, #] &)]
```

6. Additional Figures

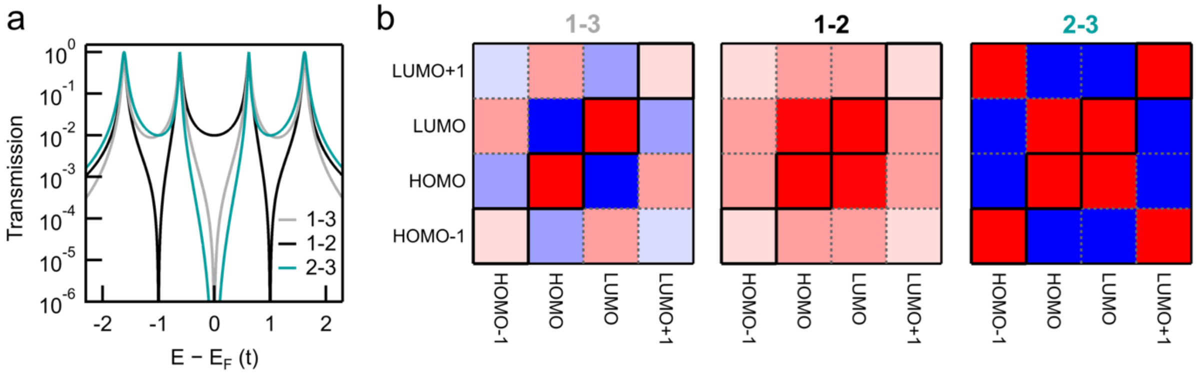


Figure S1. *a) Transmission functions for molecular junctions of 1-3 butadiene, 1-2 butadiene, and 2-3 butadiene. Numbers indicate contact point between the molecule and the electrodes. b) Corresponding QI maps at* E_F*. Figures obtained from a Hückel model with hopping integral t and coupling* $\gamma = 0.1\ t$*.*

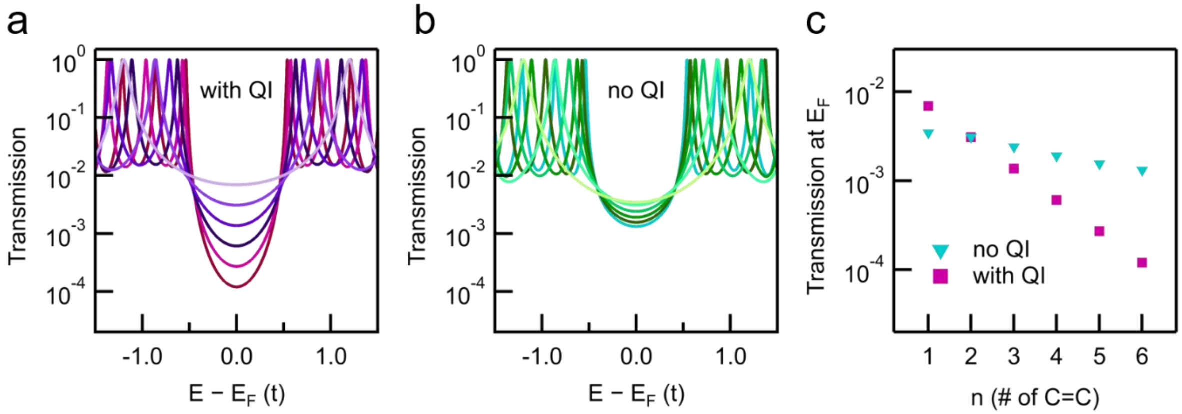


Figure S2. *a,b) Transmission function for polyene of increasing length (a) with and (b) without QI. c) Transmission at* E_F *versus number of monomer units for polyene. Figures obtained from a Hückel model with alternating coupling* $t_1 = 0.8\ t$*, and* $t_2 = 1.2\ t$*, and* $\gamma = 0.1\ t$*.*

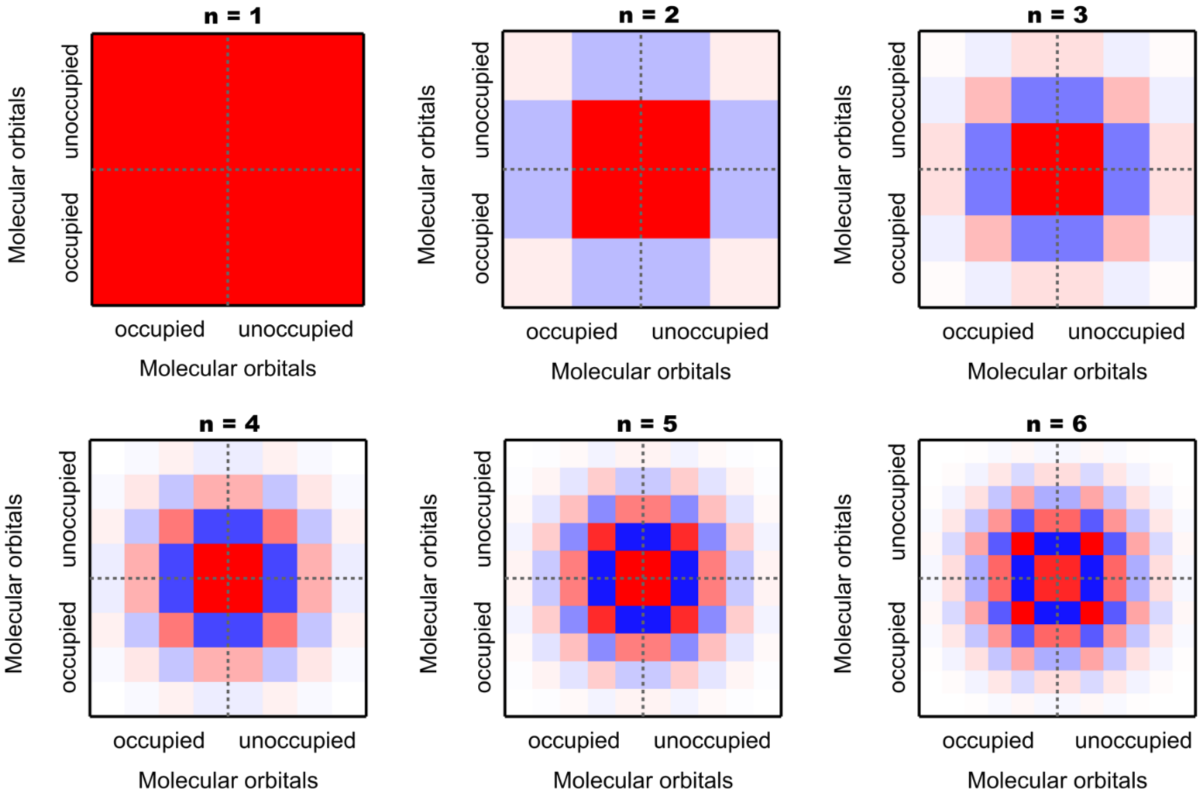


Figure S3. *QI maps for n = 1–6 polyene series. Dashed lines placed in between the HOMO and LUMO in each QI map. Note that the color scale is not the same for all QI maps. The color scale in each map is normalized to* Q_{max}.

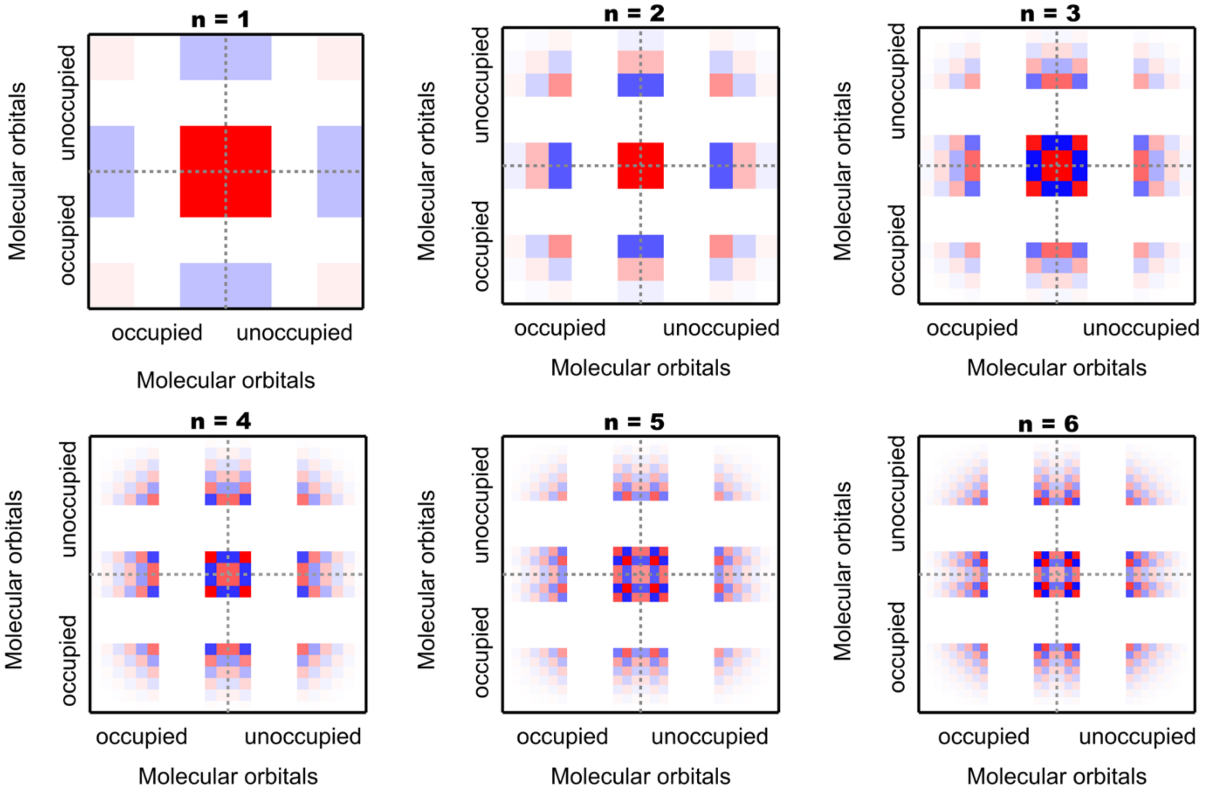


Figure S4. *QI maps for n = 1–6 oligophenyl series. Dashed lines placed in between the HOMO and LUMO in each QI map. Note that the color scale is not the same for all QI maps. The color scale in each map is normalized to* Q_{max}.

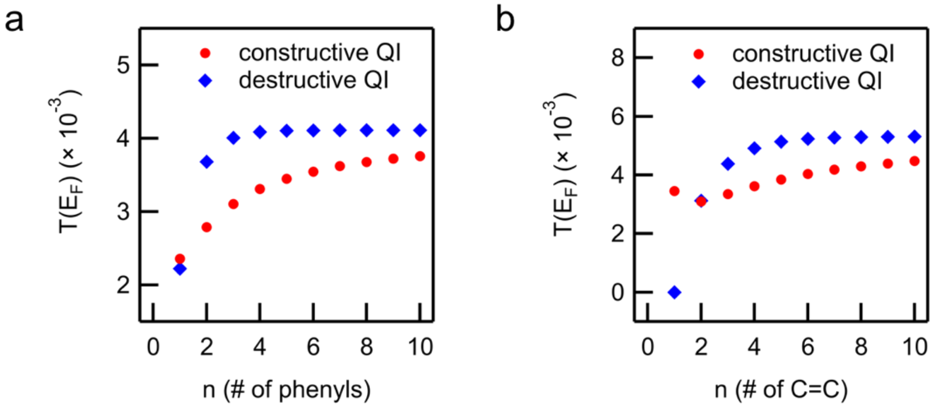


Figure S5. *Total constructive and destructive QI vs oligomer length for (a) oligophenyl and (b) polyene. Note linear scale.*

7. References

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4. Solomon, G. C.; Gagliardi, A.; Pecchia, A.; Frauenheim, T.; Di Carlo, A.; Reimers, J. R.; Hush, N. S., Molecular origins of conduction channels observed in shot-noise measurements. *Nano Letters* **2006,** *6* (11), 2431-2437.

5. Evers, F.; Korytár, R.; Tewari, S.; van Ruitenbeek, J. M., Advances and challenges in single-molecule electron transport. **2019,** *arXiv*, https://arxiv.org/abs/1906.10449 (accessed March 5, 2020).