

Supporting Information for:

Designing Principles of Molecular Quantum Interference Effect Transistors

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S1. Methodology

The systems investigated are molecular devices composed of a π -conjugated ring connected to two semi-infinite electrodes. The Hückel type Hamiltonian of the total system can be written in the second quantized form as,

$$H = \sum_{\mu} \varepsilon d_{\mu}^{\dagger} d_{\mu} + \sum_{\mu} t \left(d_{\mu}^{\dagger} d_{\mu+1} + d_{\mu+1}^{\dagger} d_{\mu} \right) + \sum_{k_{\alpha}} \varepsilon_{k_{\alpha}} c_{k_{\alpha}}^{\dagger} c_{k_{\alpha}} + \sum_{\alpha, k_{\alpha}, \mu} (V_{k_{\alpha} \mu} c_{k_{\alpha}}^{\dagger} d_{\mu} + H.c.)$$

Where ε is the onsite energy of the system; t is the hopping between nearest neighboring sites; $\varepsilon_{k\alpha}$ is the energy of the k -th eigen state of electrode α ; $V_{k\alpha\mu}$ is the coupling matrix element between site μ of the molecule and the k -th eigen state of electrode α ; d_μ^\dagger , d_μ , $c_{k\alpha}^\dagger$, $c_{k\alpha}$ are the creation and annihilation operators for the molecular sites and electrodes, respectively.

The time-dependent current is obtained via the time-dependent density functional theory for open system (TDDFT-OS) method.¹⁻⁴ The equations of motion of reduced single electron density (RSDM) and the dissipation matrices reads,

$$i\dot{\sigma}_D(t) = [h_D(t), \sigma_D(t)] - \sum_{\alpha} [\varphi_{\alpha}(t) - \varphi_{\alpha}^{\dagger}(t)] \quad (1)$$

$$i\dot{\varphi}_{\alpha}(\varepsilon, t) = [h_D(t) - \varepsilon - \Delta_{\alpha}(t)]\varphi_{\alpha}(\varepsilon, t) + [f_{\alpha}(\varepsilon) - \sigma_D]\Gamma_{\alpha}(\varepsilon) + \sum_{\alpha'} \int d\varepsilon' \varphi_{\alpha, \alpha'}(\varepsilon, \varepsilon', t) \quad (2)$$

$$i\dot{\varphi}_{\alpha, \alpha'}(\varepsilon, \varepsilon', t) = -[\varepsilon + \Delta_{\alpha}(t) - \varepsilon' - \Delta_{\alpha'}(t)]\varphi_{\alpha, \alpha'} + \Gamma_{\alpha'}(\varepsilon')\varphi_{\alpha}(\varepsilon, t) - \varphi_{\alpha'}^{\dagger}(\varepsilon', t)\Gamma_{\alpha}(\varepsilon) \quad (3)$$

Where $h_D(t)$ and $\sigma_D(t)$ are the Fock operator and RSDM of the device at time t , respectively; $\varphi_{\alpha}(\varepsilon, t)$ is the energy resolved first-tier dissipation matrix of electrode α with $\varphi_{\alpha}(t) = \int d\varepsilon \varphi_{\alpha}(\varepsilon, t)$; $f_{\alpha}(\varepsilon) = 1/[e^{\beta(\varepsilon - \mu_{\alpha})} + 1]$ is the Fermi-Dirac distribution function for electrode α , where β is the inverse temperature and μ_{α} is the equilibrium Fermi energy; $\Delta_{\alpha}(t) = -V_{\alpha}(t)$ is the energy shift caused by applied voltage for all single-electron levels in electrode α ; $\Gamma_{\alpha}(\varepsilon)$ is the line-width matrix due to

electrode α ; $\varphi_{\alpha,\alpha'}(\varepsilon, \varepsilon', t)$ is the second-tier dissipation matrix. The time-dependent electric current through electrode α can be obtained by taking the trace of the dissipative term,

$$I_{\alpha}(t) = iTr\{\varphi_{\alpha}(t) - \varphi_{\alpha}^{\dagger}(t)\} \quad (4)$$

The steady state currents through the electrodes are evaluated through the Landauer-Büttiker formula, i.e.,

$$I = \frac{2e}{h} \int d\varepsilon (f_L(\varepsilon) - f_R(\varepsilon)) T(\varepsilon) \quad (5)$$

The time-dependent local current from site m to site n can be expressed in terms of lesser Green's function,

$$I_{mn}(t) = \frac{2e}{\hbar} \sum_{i \in m} \sum_{j \in n, n \neq m} (V_{ij} G_{ji}^{<}(t, t) - V_{ji} G_{ij}^{<}(t, t)) \quad (6)$$

Where V_{ij} is the hopping element (i, j) in Fock matrix; $G_{ij}^{<}(t, t') = i \langle c_j^{\dagger}(t') c_i(t) \rangle$ is the lesser Green's function in time domain.

The Büttiker probe approach is used to control the state of the molecular device through dephasing effect,⁵⁻⁶ which is described by a self-energy term $\Sigma_p^r = -i\Gamma_p$ and an associated chemical potential μ_p , where $p = 1, 2, \dots, N$ with N being the total number of Büttiker probes. As a result, another set of dissipation matrices $\varphi_p(t)$ are generated, which can be solved in the same way as $\varphi_{\alpha}(t)$ for source and drain electrodes. Usually, there will be net currents passing through the Büttiker probes. However, by carefully adjusting the chemical potential μ_p , the current conservation law can be conserved and

the net currents through the Büttiker probes will be zero. Such values of chemical potentials can be easily obtained by solving a set of linear equations when bias voltage is small and temperature is low.⁷

S2. The effect of varying the coupling strength between the molecular junction and the Büttiker probe on current.

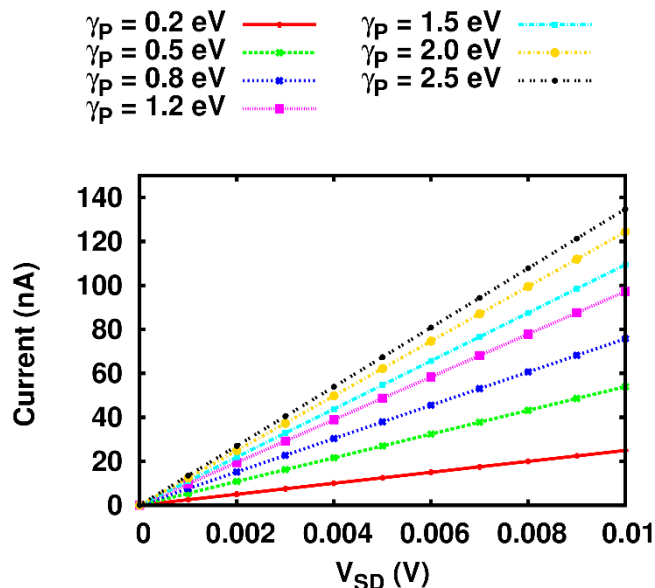


Figure S1. Steady state current versus the source-drain voltage with büttiker probes of different coupling strengths on position 3 and 4 for 2, 5-linked perylene junction.

The decoherence effect of Büttiker probe can be achieved by scanning tunneling microscope (STM) techniques, where the coupling strength γ_P between the molecular junction and Büttiker probe is a function of the distance between the STM tip and the substrate where molecular junction is located.

We investigate the effect of varying the coupling strength of the Büttiker probe on current. Fig. S1 shows the steady state current through the electrode of the 2, 5-linked perylene junction with two Büttiker probes placed at position 3 and 4. Since the wide-band-limit approximation is adopted on the electronic structure of the electrode, the largest bias voltage is confined to 0.01 V and the I-V curves are expected to be in the linear response region. The coupling strength is tuned from 0.2 eV to 2.5 eV, which mimics the situation of different separations between the STM tip and the molecule junction on substrate. It can be found from Fig. S1 that the enhancement on the coupling strength indeed induces a larger source-drain current. The results are consistent with our theoretical analysis. When the coupling strength is enhanced, more electrons will go into the Büttiker probes and lose their phases when exit. As a result, the destructive interference is suppressed and the source-drain current increases.

S3. The response of the transient current to switching on/off the Büttiker probes for a 2, 5-linked perylene based molecular junction.

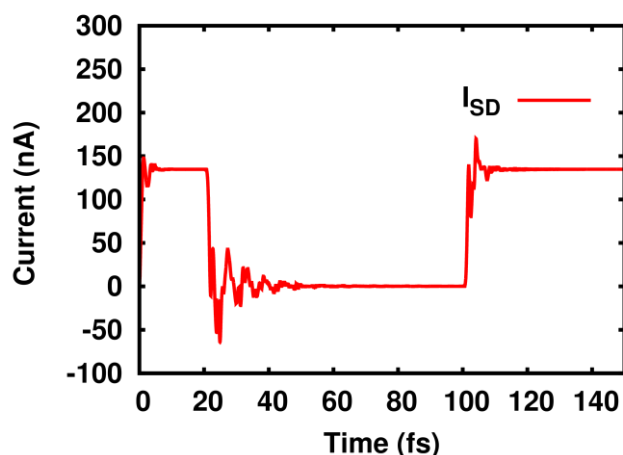


Figure S2. Time-dependent source/drain current of the 2, 5-linked perylene molecule with two Büttiker probes at position 3 and 4 being switched off at $t=20$ fs then switched on again at $t=100$ fs.

The response of the transient current to switching on/off the Büttiker probes placed at position 3 and 4 for a 2, 5-linked perylene based molecular junction is shown in Fig. S2. At the initial time, the Büttiker probes are switched on and the source/drain current increases after bias voltage is applied. It takes about 10 fs for the current to reach its steady state. At $t=20$ fs, the Büttiker probes are suddenly switched off and the current begins to drop due the recovery of the destructive interference. The oscillations of the current followed take about 30 fs before a very small residue current (~ 0.36 nA) is reached. At $t=100$ fs, the Büttiker probes are switched on again, and the current recovers to its original steady state value in about 20 fs. The on/off ratio for this setup is between 10^3 and 10^4 .

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