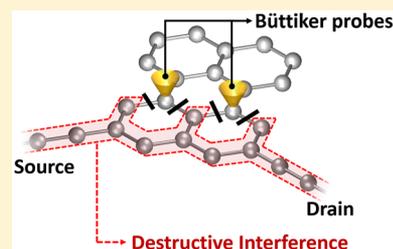


Designing Principles of Molecular Quantum Interference Effect Transistors

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ABSTRACT: To explore the designing principles for the quantum interference effect transistors, a series of simulations are carried out on a 2,5-linked perylene molecular junction composed of two subsystems connected via destructive quantum interference. Simulation results suggest that the overall conductance of a large π -conjugated system is determined by its subsystem connected directly to the electrodes. A Büttiker probe can be treated as a resistor, and to first-order approximation, its effect is found equivalent to severing its surrounding bonds. These findings greatly simplify the design of molecular quantum interference effect transistors.



The idea of utilizing quantum interference (QI) to control the conductance of molecular electronic devices has been explored since 1988,¹ both theoretically and experimentally.^{2–9} As a typical structure with QI, the meta-linked benzene molecule has been studied thoroughly due to its simple structure and physical picture.^{1,2,10–15} The low conductivity under small bias voltage is attributed to the destructive QI of its electron transport pathways. Previous study suggests that the destructive QI in meta-linked benzene is strong enough to survive nuclear vibrations at room temperature and therefore implies the practicality of molecular quantum interference effect transistors (QuIETs).¹⁶ One way to manipulate QuIETs is by altering the electronic structure of the molecular devices through chemical modifications, chemical reaction, or an electric field.^{3,4,17–19} Another way is to control the phase of the coherent current through either the Aharonov–Bohm effect^{20,21} or, more straightforwardly, introducing Büttiker probes. A Büttiker probe is an extra electrode used to eliminate the phase information on the electrons, the net current through which is confined to zero by tuning its chemical potential.^{22–24} The function of a Büttiker probe may be realized by scanning tunneling microscope (STM) techniques where the coupling strength is related to the tip–molecule distance and can be adjusted by the piezovoltage.¹⁷ We demonstrated how Büttiker probes could be used as a tool to fine-tune the coherence/decoherence effect in QuIETs.²⁵ In the same work, by employing time-dependent density functional theory for open system (TDDFT-OS),^{26–29} we showed that QI in a meta-linked benzene system requires finite time to establish.

Thanks to its structural simplicity, studies on the meta-linked benzene molecule provide a good understanding of QI. On the other hand, due to its small size, manipulating a benzene among electrodes is difficult. Chemical modifications or the use of more complex structures are necessary in realizing QuIETs in practice as well as in expanding their applications. Molecules containing multiple π -conjugated rings have more charge

transport pathways and more sites for manipulation, therefore providing a potential opportunity to design future QI-based molecular electronic devices. In fact, structures such as anthraquinone-based molecular devices have been investigated widely.^{30–33} A simple graphical scheme to predict the existence of QI-induced transmission antiresonance for a complex conjugated system has also been formulated.³⁴ However, all of those works were focused on the conductance of certain chemical structures rather than the mechanisms to switch on/off the QuIETs. Coherence and decoherence of the system have not been addressed. Moreover, those studies are all done at steady state, therefore lacking the transient dynamics of how QI originates and develops. In this Letter, following the same line of investigation as our previous work on a meta-linked benzene system,²⁵ we devise a large π -conjugated system with the presence of Büttiker probes and perform time-dependent simulations, aiming at extracting design principles for the development of future QuIETs. Because this work focuses primarily on general rules that can be applied to simplify the procedure of selecting potential candidates for QuIETs, electrical characteristics of specific devices will not be discussed. Details about the concept of QuIET and how it works can be found in the 2006 paper by Cardamone et al.,¹⁷ where the I – V characteristics and the transconductance of a sulfonated vinylbenzene-based device were investigated.

A perylene molecule attached to two semi-infinite carbon chain electrodes through its 2,5-positions is selected for investigation. Compared to the most representative case of a meta-linked benzene molecule for studying QI, more electron transport pathways are involved in the perylene structure, and therefore, the patterns of QI are expected to be more complex. For simplicity, a Hückel-type Hamiltonian is used to describe

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the system, where the nearest-neighbor hopping elements are set as 2.0 eV and the onsite energies are set as 0 without loss of generality. The coupling strengths between the electrodes and the system of interest are set as 2.0 eV too. A bias voltage of 2 mV is applied instantaneously after $t = 0$ and is assumed to create a linear potential drop across the simulation box. Time-dependent currents are solved employing the TDDFT-OS method.^{26–28} Because the bias voltage applied is much smaller than the coupling strengths and the hopping values, the wide-band-limit (WBL) approximation is adopted to describe the line width function of the electrodes. The equations for evaluating the currents through the electrodes as well as the local currents are listed in the [Supporting Information](#). Influence from nuclear vibration is neglected because our previous works indicate that QI in molecular devices is robust against electron–phonon interaction in both steady-state and transient dynamics.¹⁶

The simulated time-dependent current through the left/right electrode is plotted in [Figure 1b](#), from which a big surge of

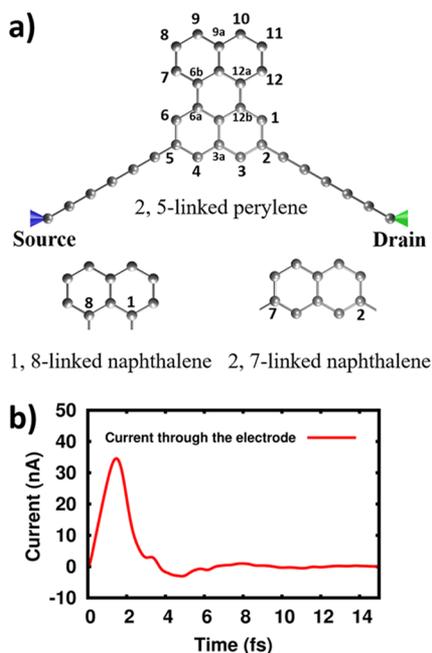


Figure 1. (a) Structure of the 2,5-linked perylene junction. The whole structure can be divided into two parts: the upper 1,8-linked and the lower 2,7-linked naphthalene subsystems, both of which exhibit destructive interference with a 3π or π phase difference between their two electron transport pathways. (b) Time-dependent current through the electrodes of the 2,5-linked perylene junction.

current in the first few femtoseconds is observed before a very small steady-state value is reached, indicating the formation of destructive interference. To understand the result, we divide the structure into two subsystems and study their conductance separately. As shown in [Figure 1a](#), the lower subsystem (from site 1 to 6) is composed of a naphthalene molecule attached to two electrodes through 2,5-positions. Similar to the meta-linked benzene case, a length difference of two bonds between the two branches of the ring induces destructive interference and forbids the current from passing through. The upper subsystem (from site 7 to 12) is another naphthalene molecule connected to the lower one through a 6b,12a-connection, which, when treated alone, induces destructive interference again thanks to

the 3π phase difference between its pathways. Because electrons are incapable of going through the 6b,12a-connection between the upper and lower naphthalene rings, we could think of them as two independent systems and infer that the overall effect is still destructive interference, as confirmed by [Figure 1b](#).

The simulation above reveals that the 2,5-linked perylene molecular junction is at the off state when no further manipulation is made. The next question follows naturally: How to switch on the device. We know that the occurrence of QI relies on the coherence of the system. In the meantime, the Büttiker probe introduces decoherence to a system. To begin with, two Büttiker probes are placed at positions 9 and 10 of the perylene molecule with a coupling strength of 2.0 eV. By tuning their chemical potentials, net currents through the probes are controlled to 0 at steady state. The simulation results are shown in [Figure 2a](#). It is found that the molecular

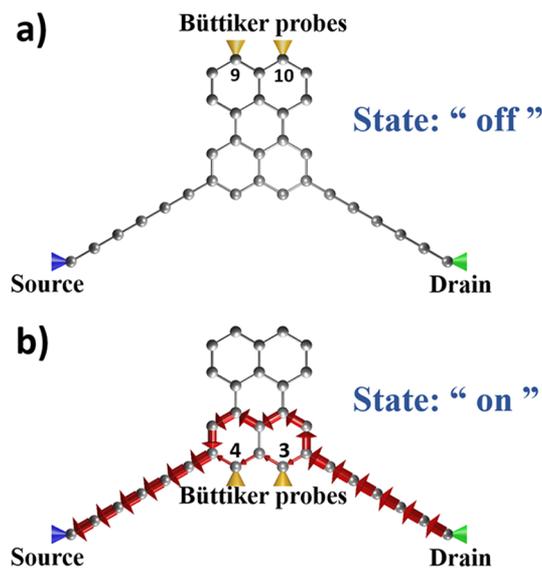


Figure 2. Steady-state local currents of the 2,5-linked perylene junction with two Büttiker probes placed at different locations. The sizes of the red arrows are proportional to the current strengths. (a) When the probes are placed at positions 9 and 10, the molecular junction is at the off state. (b) When the probes are placed at positions 3 and 4, the molecular junction is turned on.

junction is kept at the “off” state at steady state. This is understood as there is lack of communication between the two subsystems. Because Büttiker probes are acting on the upper naphthalene ring, the destructive QI in the lower structure is unaffected and the molecular junction is at the off state. The results reveal that the overall conductance of the system depends on the subsystem connected directly to the electrodes.

Then we place the two Büttiker probes at positions 3 and 4 in the shorter branch of the lower naphthalene ring, as shown in [Figure 2b](#). Unsurprisingly, we observe switching on of the device with strong current through the electrode at steady state, verifying the dephasing effect of the Büttiker probes. It is also noticed that the main current is along the longer branch of the lower naphthalene ring. We also tried different coupling strengths of the Büttiker probes. The simulation results suggest that increasing the coupling strength leads to a larger source–drain current, which is consistent with our theoretical analysis. When the coupling strength is enhanced, more electrons go into the Büttiker probes and lose their phases upon exit. As a

result, the destructive interference is suppressed, and the source–drain current is enlarged.

Next, the Büttiker probes are placed at position 6a and 12b of the perylene ring, as shown in Figure 3a. One would expect

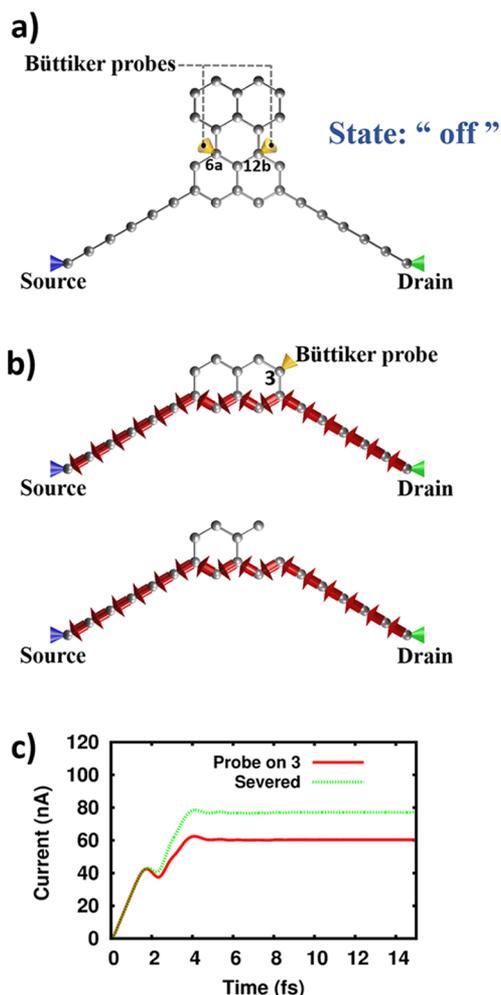


Figure 3. Currents when different numbers of Büttiker probes are placed at different locations of the perylene or naphthalene molecule. (a) When the probes are placed at positions 6a and 12b, the molecular junction is at the off state. (b) Comparison between the steady-state local currents of the naphthalene junction when a Büttiker probe is placed at position 3 and the one in which the atom at position 3 is removed. The time-dependent currents through the electrodes of the two structures are shown in (c).

inhibition of destructive QI and switching on of the device. Unfortunately, from the results shown in Figure 3a, we observe that the Büttiker probes do not work at all. Similar results are obtained when the upper naphthalene ring is removed, which is to exclude the interference between the two subsystems. Careful study of the local current distribution in Figure 2b reveals that electrons tend to avoid the pathway with Büttiker probes involved. This is reasonable because the other pathway is fully coherent and leads to ballistic transport if taken alone. Therefore, the role that the Büttiker probe plays is to introduce local resistance and hinder the passage of electrons. To confirm this, we prepare two 2,7-linked naphthalene structures, as shown in Figure 3b. In one of them, a Büttiker probe is connected to position 3 with a coupling strength as strong as 32 eV. As a comparison, we remove the atom at position 3 in the

other structure to mimic the extreme case of local resistance. In the latter case, the cross-conjugated stem³⁵ on the longer branch of the benzene ring prevents the formation of destructive QI and therefore allows the current to pass through the electrodes. The steady-state local currents are shown in Figure 3b, and the time-dependent currents through the electrodes are shown in Figure 3c. It is observed that the features of both the steady-state and time-dependent currents through the electrodes in the two cases are quite similar. The animations in the Supporting Information also clearly reveal the resemblance between the developments of the local currents in the two cases. These results confirm further that a Büttiker probe may be treated as a local resistor, and to first-order approximation, we may simply sever the bonds around Büttiker probes when predicting the conductance of multiring structures. As an example, we go back to Figure 3a. After severing the bonds around the Büttiker probes, the remaining structure is an alkene chain with three side chains each composed of one C–C bond, as indicated by the pink area in the Abstract graphic. Each of the side chains induces destructive interference due to the phase of π gained through detouring to it. As a result, the system is at the off state and explains everything.

To test our findings further, we explore several scenarios for the 2,7-linked naphthalene system. First, we place a Büttiker probe at position 1. Severing the bonds around the Büttiker probe results in a para-linked benzene molecule, and constructive interference follows, which leads the current to pass through. Indeed, we observe in Figure 4a the two parallel local currents with nearly equal strength through the branches of the benzene ring. In another case where a Büttiker probe is placed at position 4, severing the two bonds leaves a circuit composed of a meta-linked benzene and a cross-conjugated stem, both of which exhibit destructive interference and forbid

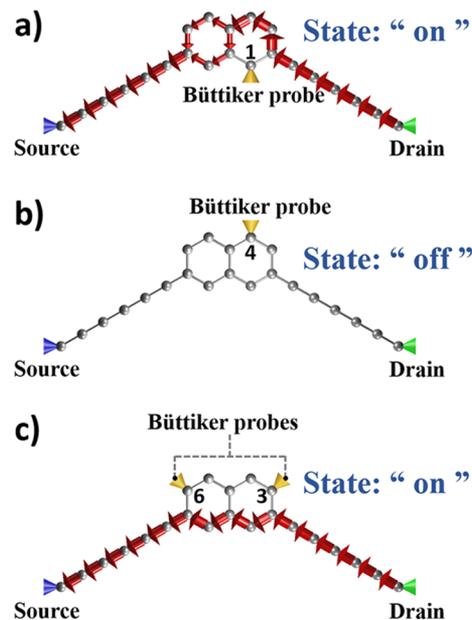


Figure 4. Steady-state local currents of the naphthalene junction with different numbers of Büttiker probes placed at different locations. (a) When a probe is placed at position 1, the molecular junction is switched on. (b) The molecular junction is at the off state when a probe is placed at position 4. (c) When two probes are placed at positions 3 and 6, the molecular junction is switched on again.

electric current. As can be seen in Figure 4b, no current flows through the electrode at steady state. When two Büttiker probes are placed at positions 3 and 6, no cross-conjugated structure is generated after severing the bonds, and therefore, we observe current along the shorter path in Figure 4c.

In conclusion, time-dependent simulations are carried out on a 2,5-linked perylene molecular junction to explore design principles for future QuIETs. We find the following: (1) Large π -conjugated systems may be divided into several subsystems if their connections induce destructive QI. The overall conductance is determined by the subsystems directly connected to electrodes. (2) A Büttiker probe may be seen as a resistor whose strength depends on the coupling amplitude between the probe and the molecule. To first-order approximation, the bonds adjacent to the Büttiker probe may be severed, and the remaining structure determines the conductance of the entire molecule.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.8b01185.

Details of the methodology to calculate the time-dependent current, the effect of varying the coupling strength of the Büttiker probes, and the response of the transient current to switching on/off the Büttiker probes for a 2,5-linked perylene-based molecular junction (PDF)

Animation of the time-dependent local currents of the naphthalene junction with a Büttiker probe at position 3 (MPG)

Animation of the time-dependent local currents of the naphthalene junction with atom 3 removed (MPG)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Sautet, P.; Joachim, C. Electronic interference produced by a benzene embedded in a polyacetylene chain. *Chem. Phys. Lett.* **1988**, *153*, 511–516.
- (2) Patoux, C.; Coudret, C.; Launay, J.-P.; Joachim, C.; Gourdon, A. Topological Effects on Intramolecular Electron Transfer via Quantum Interference. *Inorg. Chem.* **1997**, *36*, 5037–5049.
- (3) Stadler, R.; Forshaw, M.; Joachim, C. Modulation of electron transmission for molecular data storage. *Nanotechnology*. **2003**, *14*, 138.
- (4) Stadler, R.; Ami, S.; Joachim, C.; Forshaw, M. Integrating logic functions inside a single molecule. *Nanotechnology* **2004**, *15*, S115.
- (5) Sols, F.; Macucci, M.; Ravaoli, U.; Hess, K. Theory for a quantum modulated transistor. *J. Appl. Phys.* **1989**, *66*, 3892–3906.

- (6) Mayor, M.; Weber, H. B.; Reichert, J.; Elbing, M.; von Hänisch, C.; Beckmann, D.; Fischer, M. Electric Current through a Molecular Rod—Relevance of the Position of the Anchor Groups. *Angew. Chem., Int. Ed.* **2003**, *42*, 5834–5838.

- (7) Baer, R.; Neuhauser, D. Phase Coherent Electronics: A Molecular Switch Based on Quantum Interference. *J. Am. Chem. Soc.* **2002**, *124*, 4200–4201.

- (8) Pickup, B. T.; Fowler, P. W. An analytical model for steady-state currents in conjugated systems. *Chem. Phys. Lett.* **2008**, *459*, 198–202.

- (9) Ke, S.-H.; Yang, W.; Baranger, H. U. Quantum-Interference-Controlled Molecular Electronics. *Nano Lett.* **2008**, *8*, 3257–3261.

- (10) Arroyo, C. R.; Tarkuc, S.; Frisenda, R.; Seldenthuis, J. S.; Woerde, C. H. M.; Eelkema, R.; Grozema, F. C.; van der Zant, H. S. J. Signatures of Quantum Interference Effects on Charge Transport Through a Single Benzene Ring. *Angew. Chem.* **2013**, *125*, 3234–3237.

- (11) Solomon, G. C.; Herrmann, C.; Hansen, T.; Mujica, V.; Ratner, M. A. Exploring local currents in molecular junctions. *Nat. Chem.* **2010**, *2*, 223–228.

- (12) Liu, X.; Sangtarash, S.; Reber, D.; Zhang, D.; Sadeghi, H.; Shi, J.; Xiao, Z.-Y.; Hong, W.; Lambert, C. J.; Liu, S.-X. Gating of Quantum Interference in Molecular Junctions by Heteroatom Substitution. *Angew. Chem., Int. Ed.* **2017**, *56*, 173–176.

- (13) Borges, A.; Xia, J.; Liu, S. H.; Venkataraman, L.; Solomon, G. C. The Role of Through-Space Interactions in Modulating Constructive and Destructive Interference Effects in Benzene. *Nano Lett.* **2017**, *17*, 4436–4442.

- (14) Nozaki, D.; Toher, C. Is the Antiresonance in Meta-Contacted Benzene Due to the Destructive Superposition of Waves Traveling Two Different Routes around the Benzene Ring? *J. Phys. Chem. C* **2017**, *121*, 11739–11746.

- (15) Hansen, T.; Solomon, G. C.; Andrews, D. Q.; Ratner, M. A. Interfering pathways in benzene: An analytical treatment. *J. Chem. Phys.* **2009**, *131*, 194704.

- (16) Chen, S.; Zhou, W.; Zhang, Q.; Kwok, Y.; Chen, G.; Ratner, M. A. Can Molecular Quantum Interference Effect Transistors Survive Vibration? *J. Phys. Chem. Lett.* **2017**, *8*, 5166–5170.

- (17) Cardamone, D. M.; Stafford, C. A.; Mazumdar, S. Controlling Quantum Transport through a Single Molecule. *Nano Lett.* **2006**, *6*, 2422–2426.

- (18) van Dijk, E. H.; Myles, D. J. T.; van der Veen, M. H.; Hummelen, J. C. Synthesis and Properties of an Anthraquinone-Based Redox Switch for Molecular Electronics. *Org. Lett.* **2006**, *8*, 2333–2336.

- (19) Stadler, R. Quantum interference effects in electron transport through nitrobenzene with pyridil anchor groups. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2009**, *80*, 125401.

- (20) Walczak, K. The role of quantum interference in determining transport properties of molecular bridges. *Cent. Eur. J. Chem.* **2004**, *2*, 524–533.

- (21) Washburn, S.; Webb, R. A. Aharonov-Bohm effect in normal metal quantum coherence and transport. *Adv. Phys.* **1986**, *35*, 375–422.

- (22) Büttiker, M. Role of quantum coherence in series resistors. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *33*, 3020–3026.

- (23) D'Amato, J. L.; Pastawski, H. M. Conductance of a disordered linear chain including inelastic scattering events. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1990**, *41*, 7411–7420.

- (24) Kilgour, M.; Segal, D. Inelastic effects in molecular transport junctions: The probe technique at high bias. *J. Chem. Phys.* **2016**, *144*, 124107.

- (25) Chen, S.; Zhang, Y.; Koo, S.; Tian, H.; Yam, C.; Chen, G.; Ratner, M. A. Interference and Molecular Transport—A Dynamical View: Time-Dependent Analysis of Disubstituted Benzenes. *J. Phys. Chem. Lett.* **2014**, *5*, 2748–2752.

- (26) Kwok, Y. H.; Xie, H.; Yam, C. Y.; Zheng, X.; Chen, G. H. Time-dependent density functional theory quantum transport simulation in non-orthogonal basis. *J. Chem. Phys.* **2013**, *139*, 224111.

(27) Zheng, X.; Chen, G.; Mo, Y.; Koo, S.; Tian, H.; Yam, C.; Yan, Y. Time-dependent density functional theory for quantum transport. *J. Chem. Phys.* **2010**, *133*, 114101.

(28) Zheng, X.; Wang, F.; Yam, C. Y.; Mo, Y.; Chen, G. Time-dependent density-functional theory for open systems. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *75*, 195127.

(29) Zhang, Y.; Yam, C. Y.; Chen, G. Dissipative time-dependent quantum transport theory. *J. Chem. Phys.* **2013**, *138*, 164121.

(30) Darwish, N.; Díez-Pérez, I.; Da Silva, P.; Tao, N.; Gooding, J. J.; Paddon-Row, M. N. Observation of Electrochemically Controlled Quantum Interference in a Single Anthraquinone-Based Norbornyl-ogous Bridge Molecule. *Angew. Chem.* **2012**, *124*, 3257–3260.

(31) Koole, M.; Thijssen, J. M.; Valkenier, H.; Hummelen, J. C.; van der Zant, H. S. J. Electric-Field Control of Interfering Transport Pathways in a Single-Molecule Anthraquinone Transistor. *Nano Lett.* **2015**, *15*, 5569–5573.

(32) Markussen, T.; Schiötz, J.; Thygesen, K. S. Electrochemical control of quantum interference in anthraquinone-based molecular switches. *J. Chem. Phys.* **2010**, *132*, 224104.

(33) Rabache, V.; Chaste, J.; Petit, P.; Della Rocca, M. L.; Martin, P.; Lacroix, J.-C.; McCreery, R. L.; Lafarge, P. Direct Observation of Large Quantum Interference Effect in Anthraquinone Solid-State Junctions. *J. Am. Chem. Soc.* **2013**, *135*, 10218–10221.

(34) Markussen, T.; Stadler, R.; Thygesen, K. S. The Relation between Structure and Quantum Interference in Single Molecule Junctions. *Nano Lett.* **2010**, *10*, 4260–4265.

(35) Solomon, G. C.; Andrews, D. Q.; Hansen, T.; Goldsmith, R. H.; Wasielewski, M. R.; Van Duyne, R. P.; Ratner, M. A. Understanding quantum interference in coherent molecular conduction. *J. Chem. Phys.* **2008**, *129*, 054701.