

Signatures of Room-Temperature Quantum Interference in Molecular Junctions

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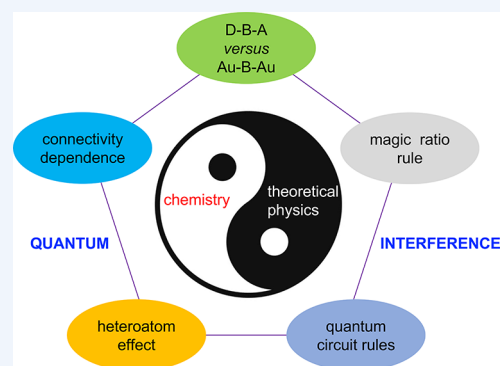
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CONSPECTUS: During the past decade or so, research groups around the globe have sought to answer the question: “How does electricity flow through single molecules?” In seeking the answer to this question, a series of joint theory and experimental studies have demonstrated that electrons passing through single-molecule junctions exhibit exquisite quantum interference (QI) effects, which have no classical analogues in conventional circuits. These signatures of QI appear even at room temperature and can be described by simple quantum circuit rules and a rather intuitive magic ratio theory. The latter describes the effect of varying the connectivity of electrodes to a molecular core and how electrical conductance can be controlled by the addition of heteroatoms to molecular cores. The former describes how individual moieties contribute to the overall conductance of a molecule and how the overall conductance can change when the connectivities between different moieties are varied. Related circuit rules have been derived and demonstrated, which describe the effects of connectivity on Seebeck coefficients of organic molecules. This simplicity arises because when a molecule is placed between two electrodes, charge transfer between the molecule and electrodes causes the molecular energy levels to adjust, such that the Fermi energy (E_F) of the electrodes lies within the energy gap between the highest occupied molecular orbital and lowest unoccupied molecular orbital. Consequently, when electrons of energy E_F pass through a molecule, their phase is protected and transport takes place via phase-coherent tunneling. Remarkably, these effects have been scaled up to self-assembled monolayers of molecules, thereby creating two-dimensional materials, whose room temperature transport properties are controlled by QI. This leads to new molecular design strategies for increasing the on/off conductance ratio of molecular switches and to improving the performance of organic thermoelectric materials. In particular, destructive quantum interference has been shown to improve the Seebeck coefficient of organic molecules and increase their on/off ratio under the influence of electrochemical gating. The aim of this Account is to introduce the novice reader to these signatures of QI in molecules, many of which have been identified in joint studies involving our theory group in Lancaster University and experimental group in Bern University.



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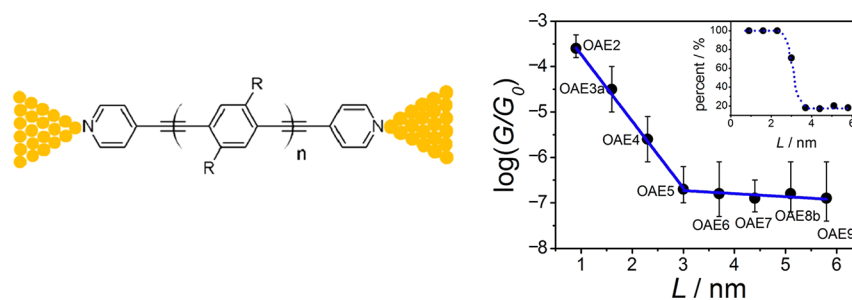


Figure 1. Crossover from phase-coherent tunnelling to incoherent hopping. Adapted with permission from ref 34. Copyright 2013 American Chemical Society.

to Self-Assembled Molecular-Electronic Films. *J. Am. Chem. Soc.* **2020**, *142*, 8555–8560.⁴ It is the first report of constructive QI-boosted thermoelectricity of anthracene-based molecular films guided by MRR. It represents a critical step forward for future high-performance thermoelectric devices.

INTRODUCTION/BACKGROUND

Interference is a generic property of all waves, including electromagnetic waves, sound waves, gravitational waves, and water waves. It refers to the fact that when two or more waves are superposed to create a combined wave pattern, they can either superpose constructively, resulting in a large combined amplitude, or destructively, resulting in a small combined amplitude. The term ‘quantum interference (QI)’ is used to describe interference of de Broglie waves. In the context of molecular electronics, QI is relevant, provided the energy of an electron passing through a molecule is well-defined and not changed as it passes through the molecule. This means that the phase of the wave function of an electron passing through a molecule is also well-defined, in which case, transport is said to be “phase coherent”. It is timely to clarify design principles for controlling QI effects in single molecules as a prerequisite of exploiting such effects in nanoscale devices formed from self-assembled monolayers of molecules.^{1–4} Much effort has been devoted to detection, manipulation, and application of QI effects in charge transport through single-molecule junctions.^{5,6} Research groups in Lancaster and Bern universities have collaborated in studies of room-temperature, molecular-scale QI effects for over a decade, through the European Union networks FUNMOLS⁷ and MOLESCO.⁸ In part, these studies were stimulated by the potential impact of QI on the electronic and thermoelectric performance of single-molecule junctions and self-assembled monolayers (SAMs).⁹ The aim of this Account is to outline the new concepts and strategies for controlling QI that have emerged from these collaborations and also to discuss how certain “quantum circuit rules”, describing single-molecule electrical conductance can impact on the nearby field of electron transfer in donor–acceptor molecules.

Within the Theory of Molecular-Scale Transport group in Lancaster University, interest in molecular-scale QI effects was born out of earlier work on electron transport through hybrid superconducting nanostructures,¹⁰ which led to the discovery of novel interference phenomena.^{11,12} This led to descriptions of thermoelectricity¹³ and resonant transport¹⁴ in hybrid superconductors, which formed a basis for investigating these effects in single molecule junctions a decade or so later. The computer codes used to probe transport in superconducting

nanostructures were later generalized to describe material-specific electron transport in transition metal multilayers¹⁵ and carbon nanotubes and underpinned the subsequent development of the SMEAGOL quantum transport code, with colleagues in the University of Oviedo and Trinity College Dublin¹⁶ and, more recently, the GOLLUM code.¹⁷ The underlying theory leading to these density-functional-theory-based quantum-transport simulation tools is described in a recent textbook.¹⁸

Within the experimental groups at the University of Bern, research in the field of single-molecule electronics was born out of previous work, such as the study of redox-active tetrathiafulvalene molecules incorporated into metal-molecule-metal junctions within a two-dimensional nanoparticle assembly. Successive oxidation–reduction cycles showed a clear switching behavior of the molecular junction conductance.¹⁹ Also, of greatest interest was the search for suitable anchor groups that would allow direct and robust binding of a π -conjugated molecular framework to gold electrodes. This investigation led to the discovery of an in situ desilylation process that yielded robust Au–C σ -bonds.^{20–22} Of great importance was the discovery of a versatile synthesis protocol leading to benzodifuran derivatives,²³ which opened a way to exploit the molecular conductances of these redox-active π -conjugated molecules in different configurations and in response to different stimuli.^{24–28} As another example, the conductance of an organoborane wire in a single-molecule junction was studied in response to Lewis acid–base interactions.²⁹ Consistent with electron transfer through molecules, a variety of synthetic methods have been developed in Bern to obtain π -conjugated donor-bridge-acceptor (D-B-A) systems, with a focus on addressing some key issues about photoinduced charge and energy-transfer processes that are closely related to energy topics such as renewable energy conversion and energy storage.³⁰ Particularly, such D-A systems have been shown to be effective in noncovalent functionalization of nanographene³¹ as well as in the chemical or optical control of intramolecular charge flow.^{32,33} Clearly, single-molecule junction (M-B-M) experiments, in which the molecular wires are confined by anchoring groups between two electrodes, provide a useful tool to understand the role of the bridge between the D and A units.

The collaborations described below are a result of combining these two rather diverse backgrounds to undertake projects at the interface between physics and chemistry.

SIGNATURES OF SINGLE MOLECULE QUANTUM INTERFERENCE

Our joint collaborations were based on the fact that electron transport through sufficiently short molecules is phase coherent, even at room temperature. For short enough molecules, this is clearly demonstrated.^{34,35} For example, Figure 1 shows that the electrical conductance G of a series of oligo(aryleneethynylene) (OAE) molecules initially varies as $G \sim e^{-\beta L}$, where L is the molecular length. This is a signature of phase-coherent tunnelling. However, as L increases beyond 3 nm, the conductance crosses over to a more classical behavior $G \sim 1/L$, associated with incoherent hopping.

The above progress in characterizing transport through single molecules underpinned our first joint experimental and theoretical study, designed to find evidence of destructive quantum interference (DQI) associated with cross-conjugated oxygen atoms in anthraquinones.³⁶ This was presented in the ref 36 and followed by further confirmations.³⁷ These studies were stimulated by theoretical predictions of DQI transmission dips due to cross-conjugated oxygen atoms in fluorenones.³⁸ From a theoretical viewpoint, the presence of DQI is signaled by the presence of dips in the transmission coefficient $T(E)$ describing the probability that an electron of energy E can pass from one electrode to another via a molecule, which bridges the gap between the two electrodes in a single-molecule junction, as shown in Figure 2. The black dashed line shows

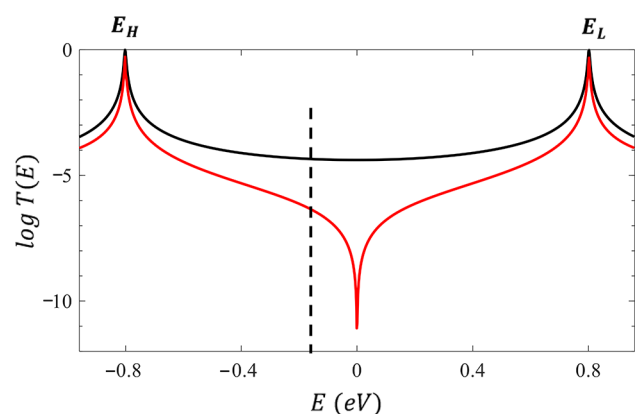


Figure 2. Generic plots of the transmission coefficient $T(E)$ versus electron energy E from two different single-molecule junctions. The black curve corresponds to a single-molecule junction displaying CQI, whereas the sharp dip in red curve is typical of a junction exhibiting DQI. Data are from ref 39.

the location of the Fermi energy E_F of the electrodes and the electrical conductance G of such a junction (in units of $G_0 = 2e^2/h$) is approximately equal to the intersection between the black dashed line and a transmission curve; i.e. $G \approx G_0 T(E_F)$. From an experimental viewpoint, DQI leads to the suppression of electrical conductance and is revealed by comparing the measured electrical conductances of appropriate homologous series of molecules, as shown in Figure 3.

In both cases shown in Figure 2, high values of $T(E)$ (i.e., transmission resonances) occur at energies E_H and E_L corresponding to energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Typically, when a molecule is placed between two metallic electrodes, charge is transferred on or off the molecule, such that the Fermi energy lies between E_H and E_L , i.e., E_F

typically lies within the HOMO–LUMO gap and not close to a transmission resonance. This is why the behavior of $T(E)$ within the HOMO–LUMO gap is relevant experimentally. If E_F is close to the dip in the red curve, DQI suppresses G , which could help to lower the “off-conductance” of molecular switches, whereas tuning the HOMO or LUMO energies E_H and E_L to be close to E_F yields high G . Additionally, the Seebeck coefficient S is proportional to the slope of $\log T(E)$ at $E = E_F$ and therefore for high-performance thermoelectricity, where high values of G and S are needed, careful tuning of energy levels to yield a high slope at E_F and high $T(E_F)$ is desirable.

The top left panel of Figure 3 shows a series of studied molecules, in which 9 is nonconjugated while 7 and 8 are linear- and cross-conjugated, respectively. As expected, the bottom left panel shows that the broken π -conjugation in 9 leads to a rather low conductance compared to its conjugated counterpart 7, but surprisingly, the cross-conjugated anthraquinone compound 8 has an even lower conductance. Figure 3D of the right panel shows that the low conductance of 8 arises, because the transmission coefficient of 8 possesses a DQI dip near the Fermi energy.

MAGIC RATIO THEORY

The above study led us to ask how electrical conductance depends on the connectivity of a molecular core to external electrodes. For example, 4 and 6 (Figure 3) possess the same naphthalene core, but the triple bonds connecting them to the external electrodes are connected to different carbon atoms within the core. Similarly, 5 and 7 (Figure 3) possess the same anthracene core, but with different connectivities to the electrodes. To take advantage of the fact that the connectivity to a central core can be varied with atomic accuracy and to describe how connectivity controls QI in molecules, we developed a rather intuitive “magic ratio theory” of transport through the π system of polycyclic aromatic hydrocarbons (PAHs).^{1,40,41} This theory describes qualitatively the connectivity dependence of $T(E)$ near the middle of HOMO–LUMO gap by constructing a “magic number table” with entries labeled m_{ij} and noting that the electrical conductance G_{ij} of a molecule with connectivity i, j is proportional to $|m_{ij}|^2$. (See section S2 of the Supporting Information for more details.)

As an example,⁴⁰ Figure 4 shows pyrene cores, P1 and P2, connected to electrodes with two different connectivities, $i, j = 2, 5'$ and $i, j = 5, 1'$. The bottom right panel shows the magic number table for pyrene and reveals that $m_{5,1'} = -1$, whereas $m_{2,5'} = -3$. Consequently, magic ratio theory predicts their conductance ratios to be

$$G_{2,5'}/G_{5,1'} = (m_{2,5'}/m_{5,1'})^2 = (3/1)^2 = 9 \quad (1)$$

The bottom left panel shows their measured conductance histograms, whose most-probable conductances are in a ratio of $G_{2,5'}/G_{5,1'} = 7.9$, in close agreement with magic ratio theory.

As a second example,⁴¹ Figure 5 shows an anthanthrene core connected to electrodes with two different connectivities, $i, j = 1, 5'$ and $i, j = 7, 2'$, indicated by red and blue lines, respectively. The bottom left panel shows the magic number table for anthanthrene and reveals that $m_{7,2'} = -9$, whereas $m_{1,5'} = -1$. Consequently, magic ratio theory predicts their conductance ratio to be

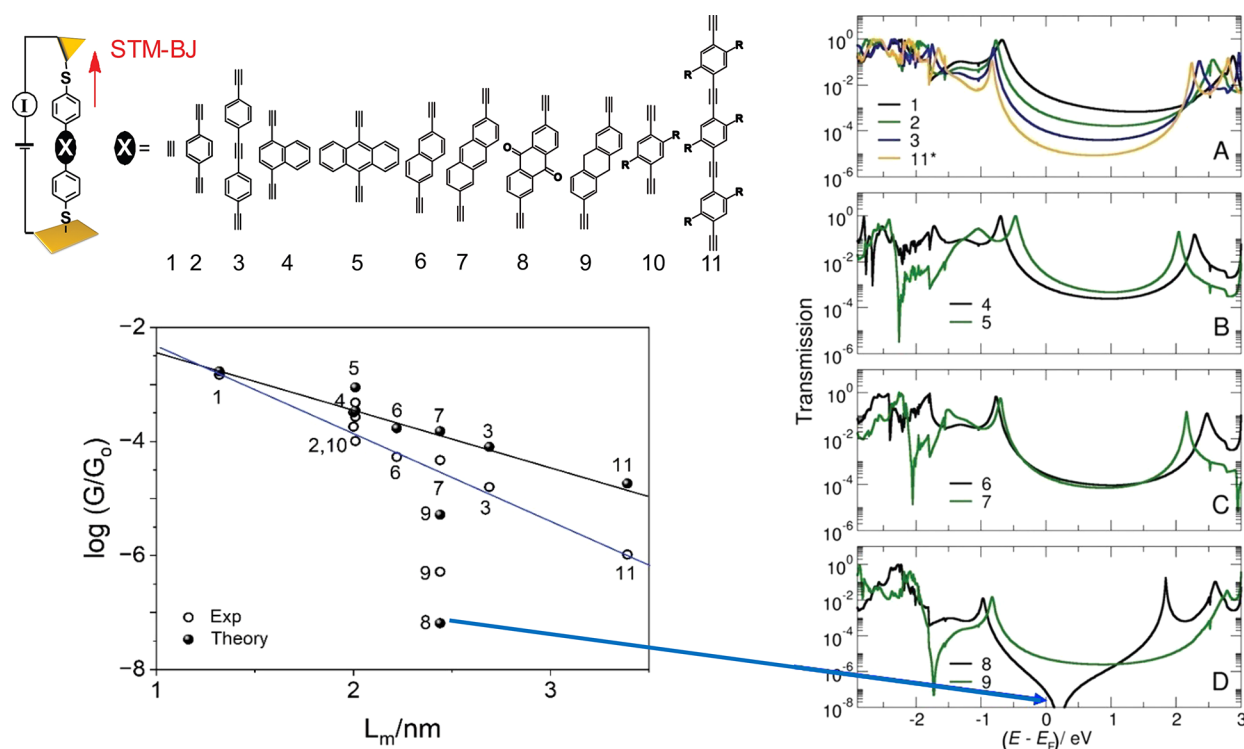


Figure 3. A Bern–Lancaster study of DQI. Adapted with permission from ref 37. Copyright 2012 American Chemical Society.

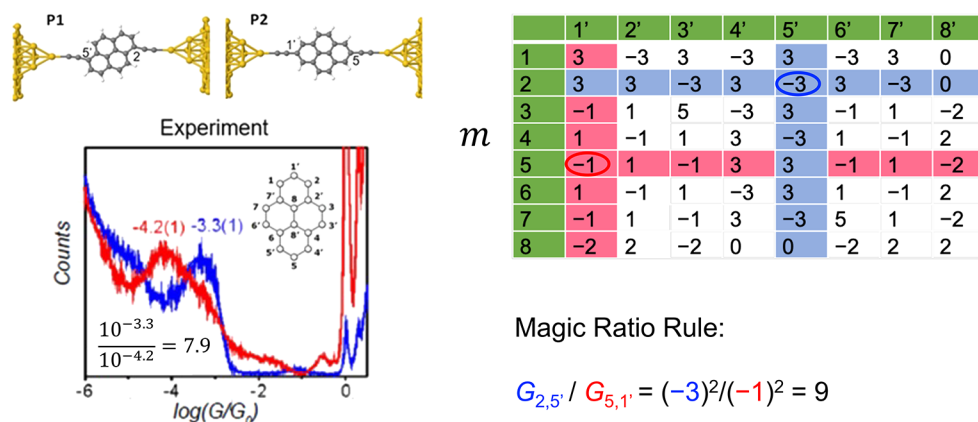


Figure 4. Experimental verification of magic ratio theory for pyrene. Adapted with permission from ref 40. Copyright 2015 American Chemical Society.

$$G_{7,2'} / G_{1,5'} = (m_{7,2'} / m_{1,5'})^2 = (9/1)^2 = 81 \quad (2)$$

The bottom right panel shows their measured conductance histograms, whose most-probable conductances are in a ratio of $G_{7,2'} / G_{1,5'} = 79$. Again, this is in close agreement with magic ratio theory and in agreement with a density functional theory (DFT) calculation of $T(E)$ for these junctions, shown in the top right panel (Figure 5).

It should be noted that the above molecules are represented by bipartite lattices, in which atoms labeled by unprimed integers are connected to atoms labeled by primed integers only. Consequently, $m_{ij} = 0$ when i, j are both primed or both unprimed integers, and therefore, these connectivities correspond to DQI.

THE EFFECT OF HETEROATOM SUBSTITUTION

Magic number tables can also be used to predict the effect of heteroatom substitution into a PAH core.^{2,42,43}

As an example, if a heteroatom is added to site k , where $k = 3$ in the right panel of Figure 6, then the new magic number table m_{ij}^{new} for the heteroatom-substituted core is related to the bare pyrene magic number table m_{ij} by

$$m_{ij}^{new} = m_{ij} + m_{ik}\epsilon m_{kj} \quad (3)$$

In this equation ϵ represents the perturbative effect of the heteroatoms on site k . In view of the bipartite nature of pyrene, for $k = 4$, which is unprimed:

- (1) If both i, j are unprimed, then $m_{ij} = 0$ and the unsubstituted pyrene exhibit DQI, and also, $m_{ik} = m_{kj} = 0$ and $m_{ij}^{new} = m_{ij} = 0$. Therefore, the heteroatom has no effect and DQI persists.

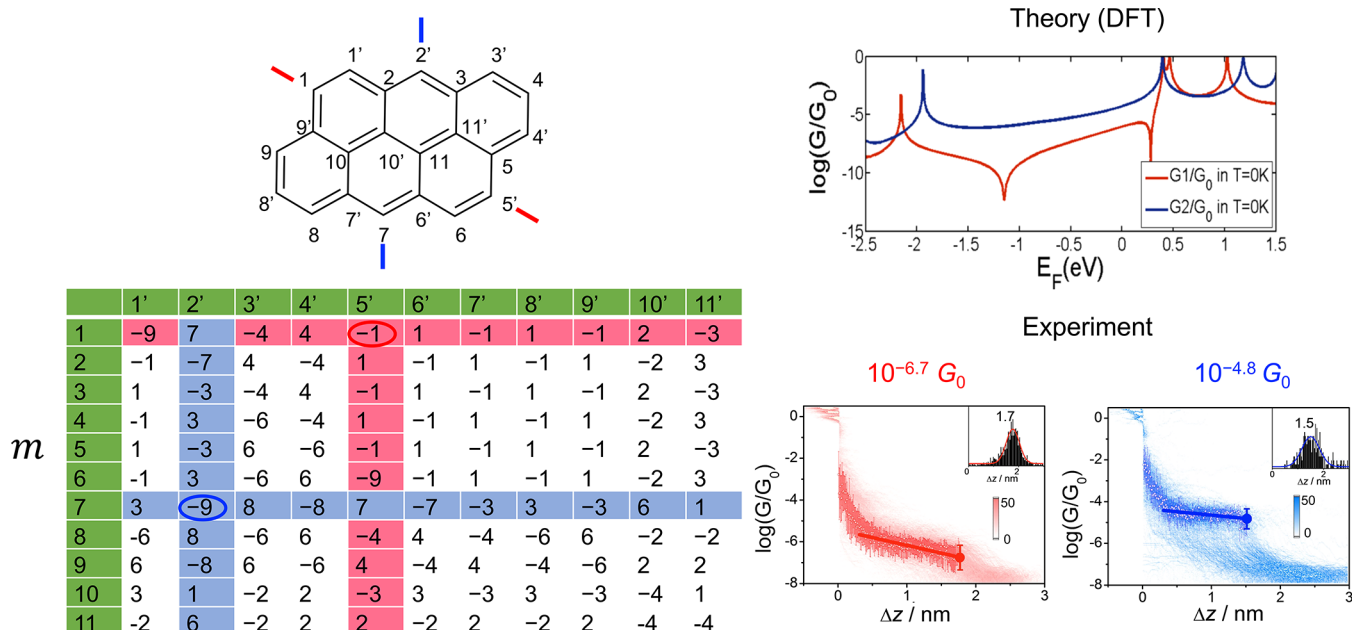


Figure 5. Experimental verification of magic ratio theory for anthanthrene. Adapted with permission from ref 41. Copyright 2015 American Chemical Society.

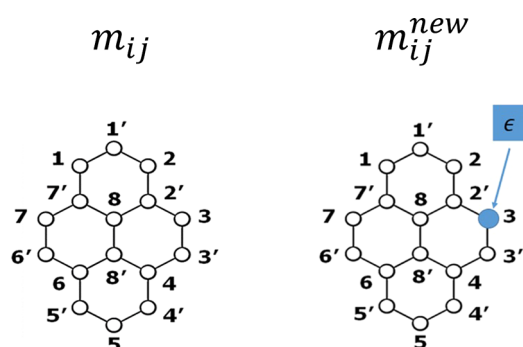


Figure 6. Left: A pyrene core. Right: A heteroatom added to position 3 of the pyrene core.

- (2) If only one of i, j is unprimed, then for most choices $m_{ij} \neq 0$, and the unsubstituted pyrene exhibits constructive quantum interference (CQI), and also at least one of m_{ik} or $m_{kj} = 0$ and $m_{ij}^{new} = m_{ij}$. Therefore, the heteroatom again has no effect.

- (3) If both i, j are primed, then $m_{ij} = 0$ and the unsubstituted pyrene exhibits DQI, and also $m_{ij}^{new} = m_{ij}m_{kj}$ which can be nonzero, leading to the alleviation of DQI.

This predictive nature of magic ratio theory was verified experimentally in the ref 2.

UPSCALING QUANTUM INTERFERENCE TO SELF-ASSEMBLED MONOLAYERS

More recently, it has been demonstrated that these single-molecule QI effects can be translated into self-assembled monolayers,^{3,4,44} thereby creating two-dimensional materials, whose electronic and thermoelectric properties are controlled by room-temperature quantum interference. For example, the above anthanthrene core was used to form a SAM in a graphene-based transistor, and the large conductance ratio in eq 2 was found to persist, though with a modified value.³ Similarly, the conductance ratio in anthracene-based SAMs with different connectivities was again predicted by magic ratio theory.

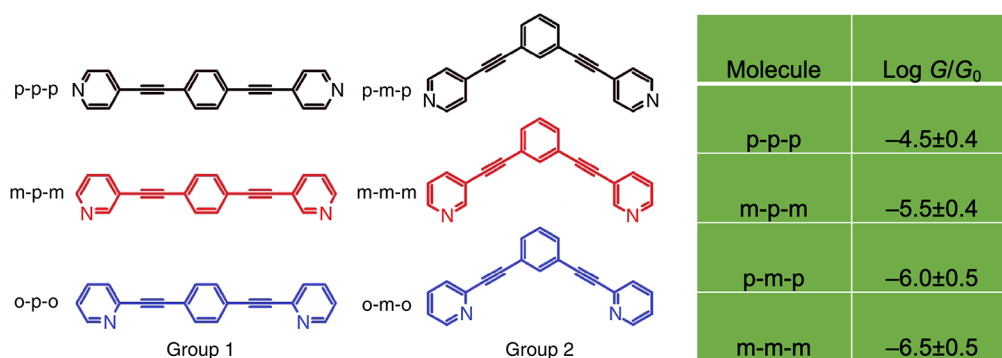


Figure 7. Left: Molecules with different connectivities to terminal groups and central ring. Right: Experimental conductance values reported. Adapted with permission from ref 45. Copyright 2015 Nature Portfolio.

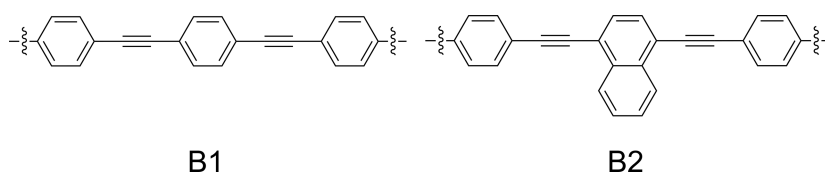


Figure 8. Two molecular backbones forming single-molecule junction systems or donor–acceptor systems in Table S1.

■ QUANTUM CIRCUIT RULES FOR ELECTRICAL CONDUCTANCE

A further manifestation of QI in single molecule junctions led us to identify quantum circuit rules for combining conjugated moieties connected in series within linear molecules.⁴⁵ The underlying theory leading to these rules is discussed in section 12.6 of the textbook mentioned in ref 21. Their origin lies in the fact that electron transport takes place via phase-coherent tunnelling within the HOMO–LUMO gap. The molecules in Figure 7 were studied.⁴⁵ They have the property that the nitrogen of the terminal pyridyl group preferentially connects to the gold electrodes, and therefore, electrons are injected into the molecule via the N in the left pyridyl ring, pass through the central ring, and exit through the N of the rightmost ring. For group 1, the central ring is *para*-connected, while for group 2, it is *meta*-connected. Their connectivity-dependent electrical conductances were predicted and measured to satisfy the following circuit rule, which captures the effect of changing the connectivity to both the central phenyl ring and the terminal groups:

$$G_{ppp}G_{mmm} = G_{pmp}G_{mpm} \quad (4)$$

In the above expression, G_{ppp} , G_{mmm} , G_{pmp} , and G_{mpm} are the electrical conductances of molecules *p-p-p*, *m-m-m*, *p-m-p*, and *m-p-m*, respectively. The “rule” of eq 4 means that a permutation of *para* vs *meta* connectivities in otherwise identical molecules has no influence on conductivity as long as the sum of *meta* and *para* connections in both molecules remains the same.

The measured values of G_{ppp} , G_{mmm} , G_{pmp} , and G_{mpm} are shown in the Table of Figure 7. These satisfy

$$\begin{aligned} \log G_{ppp}G_{mmm} &= \log G_{ppp} + \log G_{mmm} = -4.5 - 6.9 = -11.4 \\ \text{and } \log G_{pmp}G_{mpm} &= \log G_{pmp} + \log G_{mpm} = -5.5 - 6.0 = -11.5 \end{aligned}$$

which is in close agreement with eq 4.

A more general extension of this rule was proposed and verified theoretically through DFT simulations, which also established a related circuit rule for Seebeck coefficients of organic molecules. Further experimental verifications of this rule were recently presented.⁴⁶

■ QUANTUM CIRCUIT RULES FOR ELECTRON-TRANSFER RATES OF DONOR ACCEPTOR SYSTEMS

So far, the discussion has been confined to charge transport across molecular wires in break junction (M-B-M) experiments where molecules are attached to external electrodes. In this section, we ask if quantum circuit rules are also valid for experiments of electron transfer across the bridge in solvated donor-bridge-acceptor (D-B-A) molecules. A relationship between electron-transfer rates and electrical conductance was discussed earlier,^{47–49} where it was noted that the two phenomena differ because they take place at different energies

under two different environmental conditions. The former involves the reorganization energy and the localization of the electron on the donor and acceptor species, while the latter does not. This issue remains an unresolved complex topic as only a few papers have been published, showing that the trends observed in the electron-transfer rates across the bridges of the D-B-A systems are reflected well in the trends of conductance values of the same bridges embedded in M-B-M junctions.^{29,48,50} The absolute values yielded in these two sets of experiments are not comparable. Now the question arises “Given that the tunnelling energy barrier is mainly associated with the electronic properties of D and A in the D-B-A systems and electronic coupling of molecules to electrodes through anchor groups in the M-B-M junctions, respectively, should conductance ratios apply to electron-transfer rates in order to cancel out this effect?” In other words, through the molecular wires B1 and B2 are conductance ratios comparable to the ratios of electron-transfer rates?

To address this issue, we have collected a series of data distributed into two tables (Supporting Information) showing transfer-rate ratios and conductance ratios for a series of molecular systems with bridges of the same molecular length. For example, in Table S1, we show results for the backbones in Figure 8, denoted B1 and B2. The electrical conductances of systems formed from these two molecular backbones with different anchor groups to electrodes are shown in Table S1, along with a unique label for each pair of measurements. Similarly, electron-transfer rates of systems formed from these two molecular backbones with different donor and acceptor terminal groups are shown, along with a unique label for each pair of donor–acceptor systems. For each pair of single-molecule conductances in Table S1, the conductance ratio B_1/B_2 can be calculated, and similarly for each pair of transfer rates, the transfer-rate ratio (also denoted B_1/B_2) can be calculated, as shown in the fifth column of the Table S1. In Figure 9, these ratios are shown as blue and orange stars,

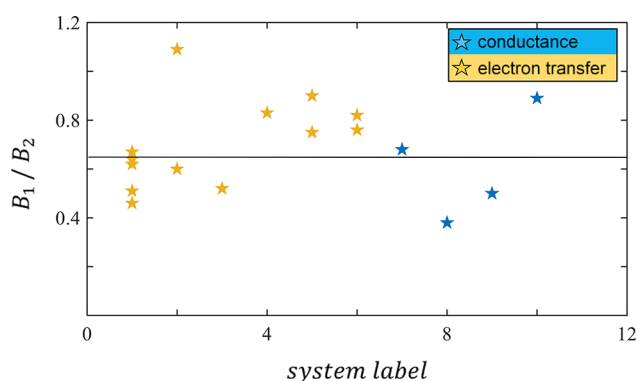


Figure 9. A comparison between electron-transfer rate ratios and conductance ratios, orange and blue stars respectively, using the data and system labels shown in Table S1. The black line is a guide to the eye.

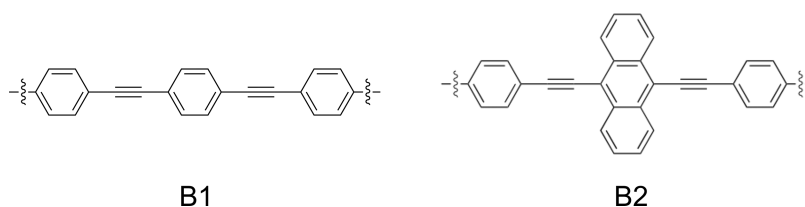


Figure 10. Two molecular backbones forming single-molecule junction systems or donor–acceptor systems in Table S2.

respectively, and clearly fall into a rather narrow range. The deviation of one point for the system 2 is larger, which originates from a marked solvent dependence of electron-transfer rates for the series of B1 with respect to the series of B2. This is not unexpected as differences in the relaxation rates for populations and coherences of the bridge states can be affected by the environment.⁴⁸ Remarkably, the values for conductance ratios are found to be comparable with those obtained for transfer-rate ratios.

A similar scatter plot for the molecular backbones shown in Figure 10 is depicted in Figure 11. Again, the conductance

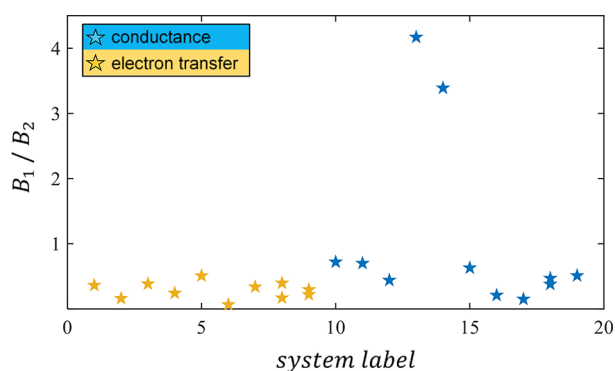


Figure 11. A comparison between electron-transfer rate ratios and conductance ratios, orange and blue stars respectively, using the data and system labels shown in Table S2.

ratios are found to be comparable with those obtained for transfer-rate ratios, and except for the systems labeled 13 and 14, they fall into a rather narrow range. The anomaly appears to occur in the system 13 with pyridyl anchoring groups, which can be attributed to the change in the electronic properties of B1 and B2 by the replacement of two benzene rings with two pyridine rings. In contrast, the large deviation of the ratio for the system 14 with the protected acetyl thiol anchoring groups is probably due to the experimental uncertainty as a result of conformational fluctuations of the molecule in the junction, different experimental setups, and methods for data analysis for single-molecule junctions.

A detailed interpretation of the anomalies is a challenge, as different experimental parameters have to be taken into account in photoinduced electron transfer and charge transport through the single-molecule junctions. Despite this, the ratio of electron transfer rates is likely independent of the donor–acceptor couple used and since this appears to be useful in predicting the corresponding conductance ratio in single-molecule junctions (vice versa), it merits further consideration.

CONCLUSION AND PERSPECTIVE

In this Account, we have outlined the new concepts and strategies for controlling QI that have emerged from recent

joint experimental and theoretical studies. As illustrated in Figure 3, signatures of quantum interference can be revealed by comparing measurements on homologous series of related molecules, and as demonstrated in Figures 4 and 5, quantum interference can be controlled by varying the connectivity of electrodes to the central molecular core. These studies provide evidence that electron transport is phase coherent, even at room temperature and can lead to new designs of self-assembled molecular layers, whose room-temperature transport properties are controlled by quantum interference. Quantum circuit rules for electrical conductance are expected to be valid when transport takes place in the vicinity of the middle of the HOMO–LUMO gap. This condition for validity is similar to the condition that leads to a generic $\cos^2\theta$ dependence of conductance on the dihedral angle θ between two neighboring conjugated rings; this θ dependence is valid, provided the Fermi energy is near the gap center, whereas this trend is broken when the Fermi energy lies close to the HOMO or LUMO.⁵¹ Mechanisms for tuning the Fermi energy relative to HOMO and LUMO levels have been discussed by a number of authors,^{52,53} including surface dipole effects, vacuum level shifts, and charge-transfer complexation. Such interactions shift the energy levels of the molecule relative to the contact Fermi level.

Remarkably, these nonclassical quantum circuit rules appear to have approximate validity when describing the ratio of electron-transfer rates in D-B-A systems, as discussed above.

For the future, this is an exciting and expanding area of research and has been the subject of a few recent reviews.^{5,54} The implementation of controlled QI holds great promise of a real breakthrough in energy applications and molecular electronics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.accounts.2c00726>.

Transfer-rate ratios and conductance ratios for a series of molecular systems in Tables S1 and S2 as well as magic ratio theory and counting rules (PDF)

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Notes

The authors declare no competing financial interest.

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