Quantum Interference

Signatures of Quantum Interference Effects on Charge Transport Through a Single Benzene Ring**

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Until recently, single-molecule conduction experiments have mostly been described in terms of a nonresonant tunneling process where the molecule acts as a tunneling barrier.^[1–3] In this description, the width and height of the energy barrier, and the electronic coupling between the molecule and the electrodes are the main parameters that characterize the efficiency of charge transport. Electron transfer through a molecule then depends exponentially on the length of the conductance pathway and this has indeed been observed in many experiments.^[1,3–7] However, such a simple tunneling picture disregards quantum interference effects that can strongly influence transport at the molecular scale.^[8,9] Therefore, these effects are a subject of growing scientific interest, both theoretically^[10-15] and experimentally.^[16-20] One of the simplest systems where quantum interference effects in charge transport are expected is a single benzene ring.^[8] It has been shown theoretically that a benzene ring connected between two electrodes in a para-configuration should have a conductance that is several orders of magnitude higher than that of a *meta*-configuration.^[13,21] This can be understood in terms of transport along different pathways through the benzene ring. These pathways can be either spatial or orbital pathways. Interference of transport components along these different pathways can lead to constructive or destructive interference.^[10,11,13,22]

Interference effects on charge transport have been considered experimentally in two classes of molecules. In

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Figure 1. a) Structures of molecules used in this study. The *para*-(blue) and *meta*- (red) coupled benzene rings are coupled to the thienyl anchoring units (green) by ethynyl spacers (black). b) Layout of a mechanically controlled break-junction (MCBJ) setup. Inset: scanning electron micrograph of a MCBJ device.

the first class, the molecule consists of an anthraquinone with thiol anchoring groups.^[16–18] In the second class, the coupling between the molecule and the electrode is through either a thiol^[20,23] or a methyl thio-ether^[19] that is directly connected to a phenyl ring. This phenyl ring is coupled to the rest of the molecule in either a *para*- or a *meta*-configuration, and large differences in conductance between these two situations have been observed. A disadvantage of the latter systems is that the anchoring is very close to the place in the molecule where interference effects occur. This can introduce alternative conductance pathways that can obscure the quantum interference effects.^[24]

Herein, the effect of quantum interference on charge transfer through a single benzene ring is studied by considering a series of specifically designed molecules represented in Figure 1 a. The central part of the molecule is a benzene ring to which anchoring units are connected either in *para*- or *meta*-configuration. The anchoring groups consist of thienyl rings that are connected through an ethynyl spacer to provide some distance between the benzene ring, where the interfer-

ence occurs, and the electrodes. To examine the effect of the geometry of the anchor unit, the linkage position of the thienyl group (2- or 3-position) was also varied.

The low-bias conductance and formation of the singlejunctions molecule was explored using the mechanically controlled break-junction (MCBJ) technique. The MCBJ device, clamped in a three-point bending configuration, is shown in Figure 1b. By driving the pushing rod against the bottom part of the MCBJ device, the gold constriction is stretched until it breaks, leaving a pair of sharp electrodes separated by a nanometer-scale gap. Once the bridge is broken, atomicsized gold contacts were repeatedly formed and broken by moving the electrodes towards



Figure 2. Two-dimensional trace histograms constructed from 500 consecutive breaking traces taken at ambient conditions and 0.1 V bias for junctions exposed to a 1 mm solution of a) 1, b) 3, c) 2, and d) 4 in chloroform. Regions of high counts represent the most probable breaking behavior of the contact. The black curves are examples of individual breaking traces.

and away from each other at a speed of 9 nm s^{-1} . Simultaneously, the conductance G = I/V was measured with a bias voltage of 0.1 V applied across the electrodes. Details concerning the experimental procedures are given in the Supporting Information together with the synthetic procedures for molecules 1–4.

In the experiments reported here, each molecule (1-4) was deposited by pipetting a 2 µL droplet of a freshly prepared 1 mm solution in chloroform onto the MCBJ device. To exclude artifacts resulting from contaminant species adsorbed on the gold surface, the characterization of the MCBJ device was first performed for pure chloroform. The breaking traces measured for pure chloroform do not show any other conductance signatures other than observed for an empty device in air (Figure S10). After characterization of the pure solvent, a droplet containing molecules dissolved in chloroform is added to the MCBJ device. This is accompanied by the appearance of characteristic conductance features that indicate the formation of molecular junctions (see Figure S9 in Supporting Information). The spread of conductance values found in this study is comparable to those found for dithiol-terminated oligophenylene-ethynylene molecules,^[25] confirming that the thienyl units act as anchoring groups that are mechanically stable and allow the formation of molecular junctions with clear conductance features.

Figure 2 represents two-dimensional trace histograms^[26] constructed from sets of 500 consecutive breaking traces measured after the deposition of a solution containing the molecules (1–4). In these trace histograms, the individual breaking traces have been shifted along the horizontal electrode displacement-axis to fix the rupture of the one-atom gold contact at zero. The color scale indicates the number of counts found at each conductance value for a certain electrode displacement. The areas with high counts

denote the most probable evolution during the formation of the molecular junctions.

The low-bias conductance of para-coupled benzene was systematically studied using thienyl anchoring groups that are coupled either through the 2- or the 3-position to provide a quantitative assessment of the effect of the anchoring groups. We found that the conductance value of 2 is slightly lower than that of 1 and that the conductance plateaus of 2 are more horizontal than those for 1 (see the Supporting Information). This shows that for both anchoring groups stable molecular junctions are formed with distinguishable conductance values. The decrease in conductance by a factor of three when going from 1 to 2 indicates that the conductance is limited by the details of binding to the electrodes and the corresponding charge injection into the molecule. A conductance difference of a factor three in molecules 1 and 2 was obtained by fitting a Gaussian function through the peaks in the one-dimensional conductance histograms as described in Supporting Information.

The individual breaking traces for the *meta*-coupled molecules **3** and **4** show clear plateaus (see Figure S11 in Supporting Information), but in a conductance region that is at least one order of magnitude lower than for the *para*-molecules (see the black individual breaking traces in Figure 2 b,d). In the two-dimensional trace histograms, a slanted region of high counts is found for **3** in the 10^{-5} G₀ region, whereas the conductance for molecule **4** (Figure 2 d) is even lower and approaches the limit of the resolution of the setup. The slanted regions of high counts are assigned to the averaging of individual traces, each showing distinct conductance plateaus of different lengths. Remarkably, a recent study^[18] shows similar 2D histograms in which linear conjugated molecules show slanted regions. Possible



Figure 3. a) Calculated transmission through the π -systems of molecules 1 (solid line) and 3 (dashed line) in the wide band limit. b) Amplitude (top) and phase (bottom) of the transmission through the HOMO and LUMO of 1. c) Amplitude (top) and phase (bottom) of the transmission through the HOMO and LUMO of 3.

explanations for this difference may be found in a stronger energy dependence of the transmission function for molecules with destructive quantum interference effects (see Figure 3) combined with small changes in the work function associated with (slightly) different binding configurations, or in a configuration dependence of the *p*-orbital overlap with the electrodes.^[27,28]

The dramatic reduction of the conductance through a meta-coupled benzene ring (molecules 3 and 4) as compared to para-coupled benzene (molecules 1 and 2) can be interpreted as a form of quantum interference. Theoretically, the charge propagation through molecules can be described as a transmission through different molecular orbitals in the Landauer formalism.^[13] We have calculated the transmission through molecules 1-4 using the non-equilibrium Green's function method with a density functional theory (DFT) calculation of the ground-state electron density. In Figure 3, the calculated transmission through the π -systems of molecules 1 and 3 in the wide band limit is shown. At energies between the HOMO and LUMO energies, the transmission of **3** is more than an order of magnitude smaller than that of **1**, with an anti-resonance occurring at -4.38 eV, where the transmission drops to zero. This anti-resonance is caused by destructive interference between transmissions through different orbitals. In the non-equilibrium Green's function formalism it is possible to separate the total transmission into contributions from the individual molecular orbitals. Since these contributions are complex (i.e., they have an amplitude and a phase), an interference effect can arise when transmission through different orbitals are combined.

The positions of the orbital resonances and the amplitudes of the transmissions are approximately the same for both molecules. However, the phase of the transmission through the LUMO differs by π for **1** and **3**, while the phase of the HOMO is the same (see Figure 3b and c). This results in

constructive interference for 1 when the transmissions through the HOMO and LUMO are combined. For 3, the phase shift results in destructive interference between the HOMO and LUMO transmission, as evident from the antiresonance in the full transmission plot (Figure 3a). It should be noted that also the HOMO-1 and LUMO + 1 orbitals contribute to the transmission within the HOMO-LUMO gap, however the phase behavior of these orbitals is the same as for the HOMO and LUMO; i.e., constructive and destructive interference for 1 and 3, respectively (see Supporting Information). This analysis therefore clearly confirms the possibility of constructive and destructive interference playing a role in the molecules studied experimentally.

In a complementary study we have also performed similar measurements of *para*- and *meta*-coupled (oligo-phenylene vinylene) OPV3 derivatives covalently connected to gold electrodes by thiol groups. The conductance histograms show a similar difference in conductance between the *para*- and *meta*-coupled central benzene ring as reported here. Theoretical calculations again assign the lower conductance for the *meta*-coupled molecule to destructive interference between LUMO- and HOMO-mediated transport. This observation therefore confirms that the coupling to the central benzene ring determines the occurrence of quantum interference effects and not the spacers or anchoring groups.

In conclusion, we have shown that the conductance through a single *meta*-coupled benzene ring is more than an order of magnitude lower than through a *para*-coupled benzene. Reproducible conductance traces were recorded using thienyl anchoring units that are coupled to the benzene ring through an ethynyl spacer. Non-equilibrium Green's function calculations show that interference effects that are related to the phase of the transmission function may be at the origin of the observed large differences in conductance. The results open up new opportunities for the design of single-molecule devices based on quantum interference effects, for instance switching devices that operate through a "chemical gating" unit.^[11]

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- [3] R. L. McCreery, Chem. Mater. 2004, 16, 4477-4496.
- [4] S. H. Choi, B. Kim, C. D. Frisbie, *Science* 2008, 320, 1482–1486.
 [5] R. L. McCreery, A. J. Berggren, *Adv. Mater.* 2009, 21, 4303–4322.

D. M. Adams, L. Brus, C. E. D. Chidsey, S. Creager, C. Creutz, C. R. Kagan, P. V. Kamat, M. Lieberman, S. Lindsay, R. A. Marcus, R. M. Metzger, M. E. Michel-Beyerle, J. R. Miller, M. D. Newton, D. R. Rolison, O. Sankey, K. S. Schanze, J. Yardley, X. Zhu, J. Phys. Chem. B 2003, 107, 6668–6697.

^[2] P. P. Edwards, H. B. Gray, M. T. J. Lodge, R. J. P. Williams, Angew. Chem. 2008, 120, 6860–6868; Angew. Chem. Int. Ed. 2008, 47, 6758–6765.



- [6] L. Venkataraman, J. E. Klare, I. W. Tam, C. Nuckolls, M. S. Hybertsen, M. L. Steigerwald, *Nano Lett.* 2006, 6, 458–462.
- [7] B. Xu, N. J. Tao, *Science* **2003**, *301*, 1221–1223.
- [8] P. Sautet, C. Joachim, Chem. Phys. Lett. 1988, 153, 511-516.
- [9] M. Magoga, C. Joachim, Phys. Rev. B 1999, 59, 16011.
- [10] A. A. Kocherzhenko, F. C. Grozema, L. D. A. Siebbeles, J. Phys. Chem. C 2010, 114, 7973–7979.
- [11] A. A. Kocherzhenko, L. D. A. Siebbeles, F. C. Grozema, J. Phys. Chem. Lett. 2011, 2, 1753–1756.
- [12] T. Markussen, R. Stadler, S. Thygesen, Nano Lett. 2010, 10, 4260–4265.
- [13] G. C. Solomon, D. Q. Andrews, T. Hansen, R. H. Goldsmith, M. R. Wasielewski, R. P. Van Duyne, M. A. Ratner, *J. Chem. Phys.* **2008**, *129*, 054701.
- [14] G. C. Solomon, D. Q. Andrews, R. P. Van Duyne, M. A. Ratner, J. Am. Chem. Soc. 2008, 130, 7788–7789.
- [15] G. C. Solomon, C. Hermann, T. Hansen, V. Mujica, M. A. Ratner, *Nat. Chem.* **2010**, *2*, 223–228.
- [16] C. M. Guédon, H. Valkenier, T. Markussen, K. S. Thygesen, J. C. Hummelen, S. J. van der Molen, *Nat. Nanotechnol.* 2012, 7, 305– 309.
- [17] D. Fracasso, H. Valkenier, J. C. Hummelen, G. C. Solomon, R. C. Chiechi, J. Am. Chem. Soc. 2011, 133, 9556–9563.
- [18] W. Hong, H. Valkenier, G. Meszaros, D. Z. Manrique, A. Mishchenko, A. Putz, P. M. Garcia, C. J. Lambert, J. C. Hummelen, T. Wandlowski, *Beilstein J. Nanotechnol.* **2011**, *2*, 699– 713.

- [19] S. V. Aradhya, J. S. Meisner, M. Krikorian, S. Ahn, R. Parameswaran, M. L. Steigerwald, C. Nuckolls, L. Venkataraman, *Nano Lett.* **2012**, *12*, 1643–1647.
- [20] S. Ballmann, R. Hartle, P. B. Coto, M. Mayor, M. Elbing, M. R. Bryce, M. Thoss, H. B. Weber, arXiv:1203.4128v1 2012.
- [21] S.-H. Ke, W. Yang, Nano Lett. 2008, 8, 3257-3261.
- [22] D. M. Cardamone, C. A. Stafford, S. Mazumdar, *Nano Lett.* 2006, 6, 2422–2426.
- [23] M. Mayor, H. B. Weber, J. Reichert, M. Elbing, C. Von Hanisch, D. Beckmann, M. Fischer, *Angew. Chem.* 2003, *115*, 6014–6018; *Angew. Chem. Int. Ed.* 2003, *42*, 5834–5838.
- [24] G. C. Solomon, D. Q. Andrews, M. A. Ratner, in *Charge and exciton transport through molecular wires*, (Eds.: L. D. A. Siebbeles, F. C. Grozema), Wiley-VCH, Weinheim, **2011**, pp. 19–52.
- [25] V. Kaliginedi, P. Moreno-Garcia, H. Valkenier, W. Hong, V. M. Garcia-Suarez, P. Buiter, J. L. H. Otten, J. C. Hummelen, C. J. Lambert, T. Wandlowski, J. Am. Chem. Soc. 2012, 134, 5262– 5275.
- [26] C. A. Martin, D. Ding, J. K. Sorensen, T. Bjornholm, J. M. van Ruitenbeek, H. S. J. van der Zant, *J. Am. Chem. Soc.* 2008, *130*, 13198–13199.
- [27] I. Diez-Perez, J. Hihath, T. Hines, Z. S. Wang, G. Zhou, K. Mullen, N. J. Tao, *Nat. Nanotechnol.* 2011, 6, 226-231.
- [28] J. S. Meisner, M. Kamenetska, M. Krikorian, M. L. Steigerwald, L. Venkataraman, C. Nuckolls, *Nano Lett.* 2011, 11, 1575–1579.