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Heteroatom-Induced Molecular Asymmetry Tunes Quantum Interference in Charge Transport through Single-Molecule Junctions

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This manuscript is dedicated to the memory of Professor Thomas Wandlowski.

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ABSTRACT

We studied the interplay between quantum interference (QI) and molecular asymmetry in charge transport through a single molecule. Eight compounds with five-membered core rings were synthesized and their single-molecule conductances were characterized using the mechanically controllable break junction (MCBJ) technique. It is found that the symmetric molecules are more conductive than their asymmetric isomers and there is no statistically-significant dependence on the aromaticity of the core. In contrast, we find experimental evidence of destructive QI in five-membered rings, which can be tuned by implanting different heteroatoms into the core ring. Our findings are rationalized by the presence of anti-resonance features in the transmission curves calculated using non-equilibrium Green's functions. This novel mechanism for modulating QI effects in charge transport via tuning of molecular asymmetry will lead to promising applications in the design of single-molecule devices.

1. INTRODUCTION

Quantum interference (QI) effects have recently attracted great interest in studies of the charge transport at the single-molecule scale.[1-6] As determined by the phases of the partial de Broglie waves traversing different paths,[7-9] QI provides a unique way to tune the single-molecule conductance by orders of magnitude without incorporating substituent groups, extending molecular length or changing the surrounding environment of the molecule. To date most reports of QI in cyclic molecules have been restricted to compounds with central six-membered rings.[10-14] Although it has not been observed experimentally, QI in central five-membered rings is

suggested to be a promising way to vary the molecular topology and increase structural diversity of single-molecule devices.[15]

The incorporation of heteroatoms into a central difunctionalized five-membered π-system leads to the structural asymmetry of the molecular junctions. Parks et al demonstrated that through modification of the symmetry of a single-molecule junction by axially stretching the molecule, the spin states, magnetic anisotropy, and thus the electron flow through the junction can be tuned.[16] Our recent studies also suggest that an asymmetric pyridine (2,4-disubstituted) modifies the pattern of QI within the core of the molecular backbone and promotes charge transport through single-molecule junctions.[17] Therefore, five-membered heterocyclic cores provide a logical diversification of the known structural platforms and enable an investigation of the interplay of QI effects and structural asymmetry of the core unit in charge transport through single-molecule junctions.

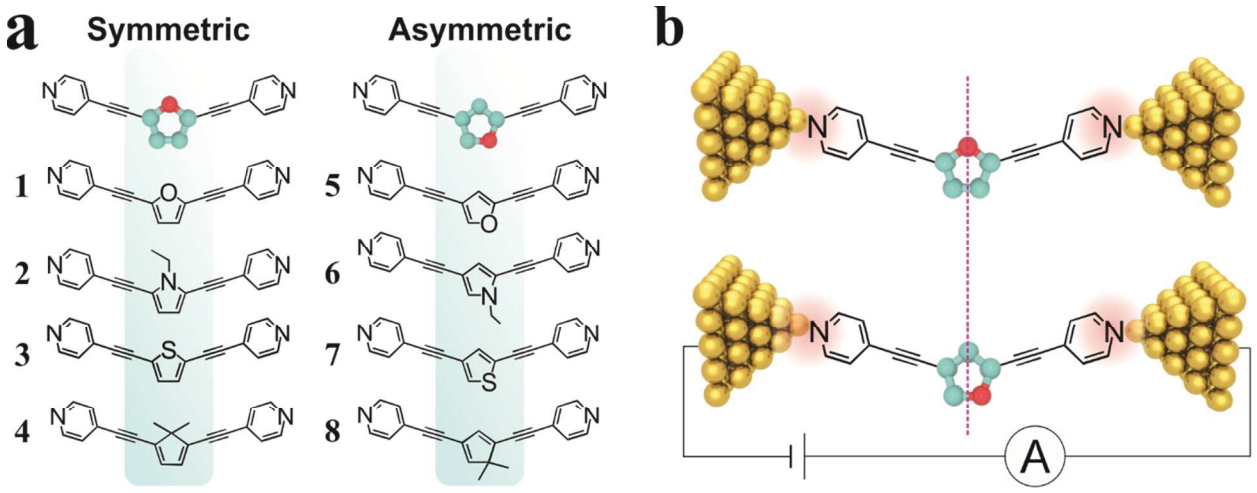


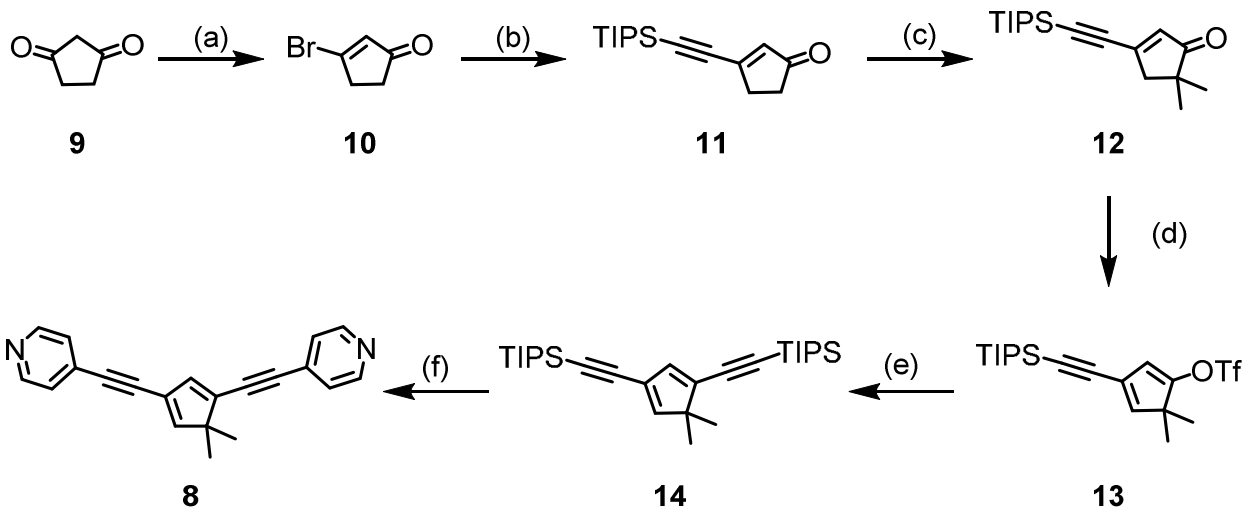
Figure 1. (a) Molecules with five-membered core units studied in this work. (b) Schematic of a molecular junction. The vertical dashed line shows the symmetry (top structure) and asymmetry (bottom structure) with respect to the core unit.

Herein we study the single-molecule conductances of a series of eight compounds of the type X-Y-X. As shown in Figure 1a and Figures S3-1 and S3-2 in the SI, the furan (**1**, **5**), pyrrole (**2**, **6**), thiophene (**3**, **7**) and cyclopentadiene cores (**4**, **8**) are rigid and planar. There are three notable features in their molecular design: (i) all of the molecules have terminal pyridyl anchoring units (X) at both ends; (ii) each molecule has one of four different five-membered core units (Y), and (iii) the core is either symmetrically substituted (i.e. 2,5-difunctionalized; **1-4**) or asymmetrically substituted (i.e. 2,4-difunctionalized; **5-8**). These compounds provide a unique opportunity to investigate two issues. First, whether the QI effect is general for other conjugated systems, besides those previously studied with aromatic six-membered central rings.[10-14] Second, what is the interplay between QI and structural asymmetry in charge transport through five-membered core units?

2. EXPERIMENTAL SECTION

The synthesis and detailed characterization of compounds **1-8** are given in the SI. The general synthetic strategy to the symmetrical target structures **1-4** was as follows. The core-unit 2,5-disubstituted with bromine (thiophene, pyrrole, and furan) or triflate (cyclopentadiene) was reacted with two equivalents of TIPS-protected acetylene under Sonogashira conditions. After a two-pot reaction sequence of desilylation with tetrabutylammonium fluoride and subsequent Sonogashira coupling with 4-iodopyridine, compounds **1-4** were obtained in good yields. The synthesis of the asymmetric isomers **5-8** was more challenging. This was especially the case for derivative **8** (Scheme 1) as the formation of C-C bonds at the 2,4-positions of cyclopentadiene under mild conditions, to our knowledge is not known in the literature. It is worth noting that the

alkyne units at C(2) and C(4) were attached sequentially: this strategy should, therefore, be versatile for the attachment of different functionality at these positions.



Scheme 1. Synthesis of **8.** Reagents and Conditions: (a) PPh_3, Br_2, TEA, CH_2Cl_2, 0 °C to rt, 2 h, 71%; (b) $PdCl_2(PPh_3)_2$, CuI, TIPSA, DIPA, 10 min, 94%; (c) LiHMDS, MeI, THF, -78 °C to rt, 12 h, 64%; (d) KHMDS, Comins' reagent, THF, -78 °C to rt, 12 h, 87%; (e) TIPSA, $PdCl_2(PPh_3)_2$, CuI, TEA, THF, rt, 4 h, 91%; (f) TBAF (1 M in THF), THF, rt, 30 min, then 4-iodopyridine, $PdCl_2(PPh_3)_2$, CuI, THF, DIPA, 40 °C, 12 h, 61% (over two steps).

The mechanically controllable break junction (MCBJ) technique was used to measure the single-molecule conductances of compounds **1-8**. A schematic drawing of the molecular junction is shown in Figure 1b, while details of the electrical characterization are reported in our previous paper.[18] Briefly, we use an Au wire tip of 99.99% purity for the in-situ fabrication of nanometer-sized separation. The target compounds were pre-pared as 0.2 mM solutions in TMB (mesitylene) as solvent. The experiments were carried out in ambient conditions at room

temperature by employing a homebuilt *I-V* converter with a sampling rate of 10 *k*Hz. For each conductance histogram, at least 1,000 individual curves were collected without any data selection.

3. RESULTS AND DISCUSSION

Figures 2a and 2c display individual conductance traces of **1-4** and **5-8** recorded during the opening process of the MCBJ operation. The corresponding conductance histograms are given in Figures 2b and Figure 2d, respectively. Figures 2a-f are plotted in a semi-logarithmic scale in order to cover the whole measuring range, and the conductance values are reported in units of the conductance quantum ($G_0=2e^2/h$). As shown in Figure 2a, after an abrupt jump from the sudden rupture of the last gold-gold atomic contact, clear conductance plateaus were observed which could be attributed to the single molecular junctions.

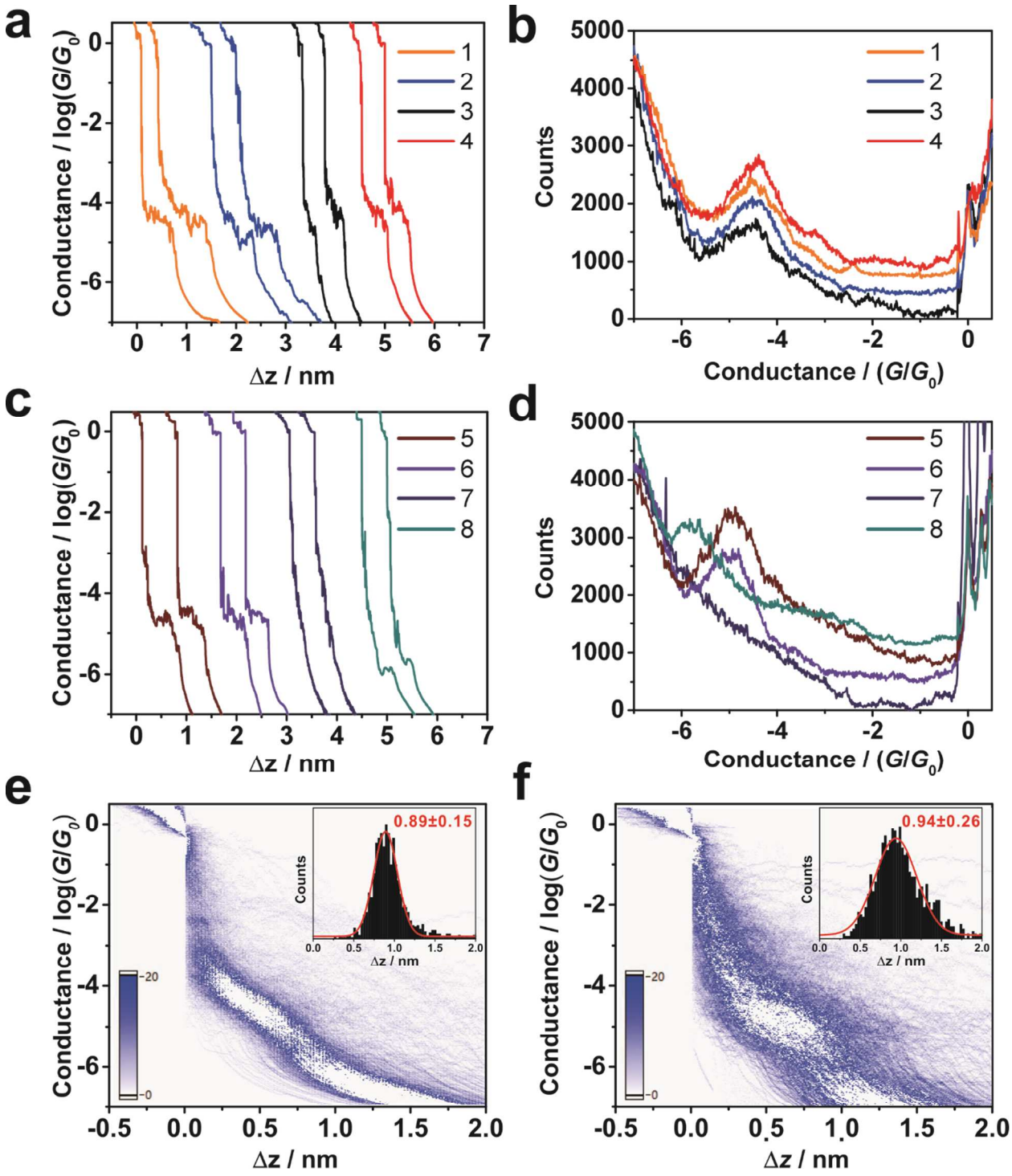


Figure 2. Typical conductance traces for compounds **1-4** (a) and **5-8** (c), respectively. One-dimensional conductance histograms for compounds **1-4** (b) and **5-8** (d), respectively. Two-

dimensional conductance-distance clouds of compounds **1** (e) and **5** (f), respectively. The curves in (b) and (d) are shifted for clarity, while the original histograms are given in the **SI**.

Table 1. Single-molecule conductances and lengths measured in MCBJ measurements.

Compounds	Measured Conductance / $\log(G/G_0)$[a]	Measured Length / nm
1	-4.54±0.37	1.39±0.15
2	-4.57±0.54	1.38±0.18
3	-4.63±0.36	1.36±0.16
4	-4.49±0.60	1.38±0.13
5	-4.94±0.40	1.44±0.26
6	-5.03±0.35	1.47±0.23
7	<-6[b]	/
8	-5.85±0.34	1.40±0.16

[a] Error bars are based on the Gaussian fitting of conductance all-data-point one-dimensional histograms. The conductance of the symmetric isomers **1-4** divided by the conductance of the corresponding asymmetrical isomers **5-8**, respectively, gives the following values: **1**/**5** = 2.5; **2**/**6** = 2.9; **3**/**7** = >23.4; **4**/**8** = 22.9. [b] This is an assumed value, not a measured value. As discussed in the text, we conclude that the conductance of molecule **7** is below the instrumental sensitivity of our *I-V* converter, i.e., $<10^{-6}$ G_0.

The emergence of conductance plateaus in Figure 2a results in the discernible peaks in Figure 2b, which are centered at the very similar values of $10^{-4.54\pm0.37}$ G_0, $10^{-4.57\pm0.54}$ G_0, $10^{-4.63\pm0.36}$ G_0, and $10^{-4.49\pm0.60}$ G_0 for compounds **1-4**, respectively. The plateaus and peaks are attributed to the most favorable microscopic configuration of the molecular junctions, which were further verified by the location of the intensive cloud in the corresponding two-dimensional conductance-distance histograms, as shown in Figures 2e and 2f for compounds **1** and **5**. The comparable data for the other compounds and pure solvent are given in the SI. Based on the above-mentioned data analysis, Table 1 summarizes the single-molecule conductances and the lengths of

compounds **1-8** obtained from MCBJ measurements, where the length was calibrated by adding 0.5 nm considering the snap-back effect.[18] In Table 1, error bars are based on the Gaussian fitting of the one-dimensional conductance histograms and the plateau displacement distributions. For compound **7** there is no distinct plateau in the individual trace, or peak in the conductance histogram, implying that the single-molecule conductance is out of the measuring range of our *I-V* converter, i.e., it is lower than 10^{-6} G_0. We emphasize that we repeatedly attempted to measure the conductance of molecule **7** with the same result on each occasion. In these experiments, all the aspects of the instrumentation were checked, such as the notched-wire chip, the mechanical components, as well as the *I-V* converter. Compound **7** is stable to storage under ambient laboratory conditions, so decomposition of the molecules cannot explain this unexpected result. We cannot prove that molecule **7** is binding in the junction, but there is no logical reason why it should not bind, given that all the other seven molecules clearly do bind and reproducibly give measurable conductance data.

The data show that for the symmetric compounds **1-4** there is no statistical variation of conductance with the bridging atom (S, N, O or C). It is instructive to compare these results with the work of Chen et al on a series of compounds having similar structures to **1**, **3**, and **4**.[19] The only difference is that each compound studied by Chen et al was wired to gold electrodes by aminophenyl anchors, while the compounds studied here are wired by pyridyl anchors. The molecular lengths in both studies are similar. Amino anchors lead to HOMO-dominated conductances,[20] while pyridyl anchors lead to LUMO-dominated conductances,[21] respectively. For the amino anchors the clear trend in conductance was cyclopentadiene > furan > thiophene. This led Chen et al to conclude that "aromaticity decreases single-molecule junction conductance".[19] However, we conclude that for the symmetrical compounds **1-4** the pyridyl

anchor dominates the conductance, and there is no statistically-significant dependence on the aromaticity of the core. Transport between the electrodes can occur through a continuous linearly-conjugated "butadiene-type" pathway involving the four sp^2-hybridized carbon atoms in **1-4**. We also note that the single-molecule conductances of our pyridyl compounds are consistently lower than for the amino anchored analogs due to the different anchoring groups.[22]

Compounds **5-8** have isomeric structures and comparable lengths with **1-4**. However, the single-molecule conductance values of **5-8** are consistently lower than that of the series **1-4** as listed in Table 1, giving the direct evidence of destructive QI. This is logical based on a simple resonance structure analysis of the cores disubstituted at the 2,4 positions,[23] suggesting the QI rule in the conventional six-membered rings is also valid for five-membered rings. In contrast to **1-4**, there is only weak effective coupling through the system in **5-8** as these molecules do not offer a linearly conjugated pathway between the two leads. Connecting the substituents at the 2,4-positions of the core (compounds **5-8**) corresponds to cross-conjugation,[4,24] thus resulting in destructive QI. This finding is reminiscent of data for six-membered phenyl core units, where destructive QI has been observed in the case of non-conjugated *meta* couplings,[10-14] and of our recent work with polycyclic core units, which established that the resonance energy of the core influences single-molecule conductance.[25] In the present case, there is no effective conjugated pathway in molecules **5-8**, therefore, the heteroatom in **5-7**, or the sp^3 carbon atom in **8**, plays a more important role in determining the conductance than in series **1-4**.

For compounds **5-8**, the electronegativity decreases in the sequence O (3.44) > N (3.04) > S (2.58) ≈ C (2.55) from the periodic table of electronegativity by the Pauling scale, thus for the studied compounds, the degree of asymmetry decreases in the sequence **5** > **6** > **7** ≈ **8**. The degrees of asymmetry are tuned by the electronegativity of the heteroatom in **5-7**, or the sp^3

carbon atom in **8**. As listed in Table 1, the lowest conductance values are obtained for **7** and **8**, where the heteroatoms have the lowest electronegativities, suggesting a strong correlation between the molecular asymmetry, electronegativity and single-molecule conductance.

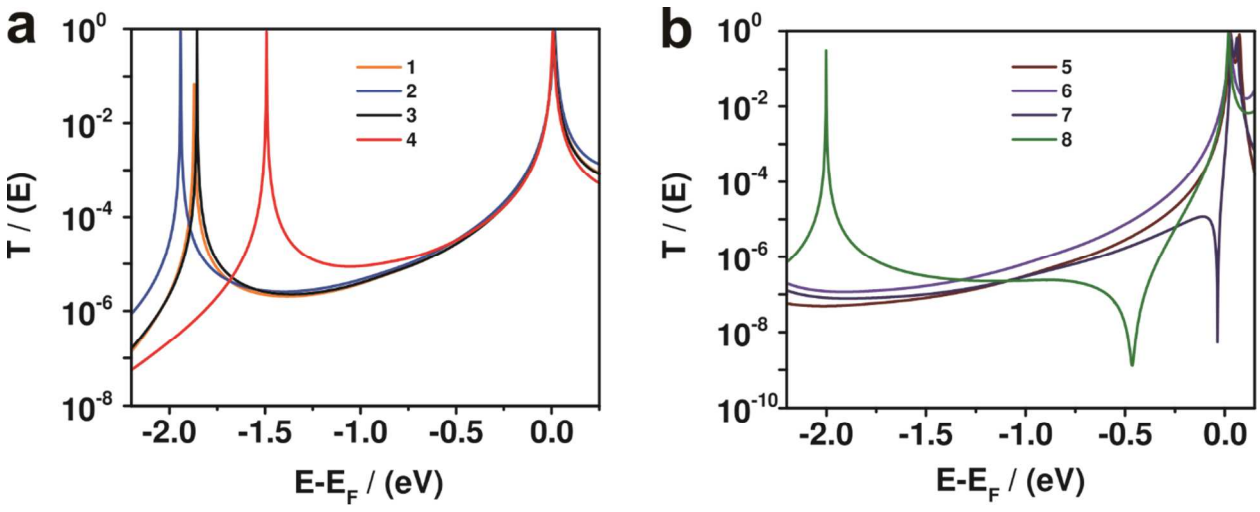


Figure 3. DFT results of the transmission coefficients for (a) compounds **1-4** and (b) **5-8**.

To investigate the interplay between structural asymmetry and QI in molecules wired between two electrodes, we calculated the transmission coefficient T(E) of electrons with energy E passing from one electrode to another through molecules shown in Figure S3-2, using the Gollum transport code.[26] Figure 3 shows the calculated T(E) of compounds **1-8** using the material specific mean field Hamiltonian obtained from the SIESTA implementation of density functional theory (DFT).[27] For molecules with pyridyl terminal groups, it is known that DFT incorrectly places the Fermi energy close to the LUMO resonance (at E-E_F = 0 in Figure 3). This causes DFT to overestimate the conductance and therefore to achieve agreement with experiment, the Fermi energy should be shifted away from the LUMO towards the middle of the HOMO-LUMO gap (near E-E_F = -1 eV in Figure 3).[21] Such a shift is consistent with

thermopower measurements of pyridyl-terminated molecules, whose positive Seebeck coefficients indicate that the Fermi energy lies in the tail of the LUMO, (in the range -1 eV < E-E_F < 0 in Figure 3).[28] For the symmetric compounds, Figure 3 shows that the T(E) values of **1-4** in the LUMO dominated regime -1 eV < E < 0 are quite similar, in good agreement with the experimental findings, that for the series **1-4** the conductances are almost the same. Nevertheless, in other cases the conductances of *para* compounds with pyridyl may be sensitive to the heteroatoms. For instance, recently we measured the conductances of a series of *para* compounds with polycyclic core units, i.e., dibenzothiophene, carbazole, dibenzofuran and fluorene cores, where the conductance varies as the heteroatom changes because the transmission around the LUMO peak is sensitive to the heteroatoms.[25]

As shown in Figure 3b, in the same energy regime -1 eV < E < 0, the calculated T(E) of **5-8** is significantly lower than that of **1-4**. Furthermore, for compounds **7** and **8**, sharp drops in the transmission curve, i.e., the anti-resonance features, are observed in the tail of the LUMO peaks. The presence of these anti-resonances correlates with the lower measured conductances for these compounds. In contrast, for **5** and **6**, as shown in Figure 3b, there are no anti-resonances within the HOMO-LUMO gap, which correlates with the higher conductances that are measured experimentally. The absence of anti-resonance features within the HOMO-LUMO gap suggests that the high electronic asymmetry of the core unit, which originates from the greater electronegativities of the heteroatoms, moves the anti-resonance features out of the HOMO-LUMO gap of the molecular junction, and thus QI has a minor effect on the charge transport through single-molecule junctions. These theoretical results and our experimental findings suggest that molecular asymmetry affords a novel approach to tuning destructive QI and charge transport through single-molecule junctions.

4. CONCLUSIONS

To conclude, we investigated the synergistic effect of molecular symmetry and QI on the charge transport through single-molecule junctions with five-membered core rings. The study of 5-membered ring cores is a new and promising way to increase structural diversity of single-molecule devices. It was found that for the symmetric 2,5-disubstituted series **1-4**, the pyridyl anchors dominate the conductance and there is no statistically significant variation with core unit. In contrast, the conductances of the asymmetric 2,4-disubsituted series **5-8** are significantly lower than those of the symmetric **1-4** series, reflecting the presence of destructive QI. More importantly, the control of molecular asymmetry via the heteroatoms provides the tuning of destructive QI in the charge transport through single-molecule junctions. DFT calculations reveal that for asymmetric molecules, the electronegativity of the heteroatoms can be used to move anti-resonance features into or out of the HOMO-LUMO gap, which controls the destructive QI effect. Our work establishes a route for the design of building blocks through incorporating heteroatoms into molecular structure, and further demonstrates a novel yet simple strategy for tuning QI in single-molecule electronics via asymmetry. This has promising applications in the design of future molecular-electronic components

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Author Contributions

[#]Yang Yang, Markus Gantenbein and Afaf Alqorashi contributed equally to this work.

Notes

The authors declare no competing financial interests.

SUPPORTING INFORMATION

The Supporting Information is available free of charge on the ACS Publications website at DOI: Synthesis and characterization of compounds **1-8**; methods and results for the single-molecule conductance measurements of solvent and compounds **1-8**; computational methods for calculating the transmission coefficients.

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