Supporting information for:

Effect of Aromaticity and Connectivity on the Conductance of Five-membered Rings

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Contents

1   Validity of assumptions

As explained in the paper, in order to calculate the conductance we make a variety of assumptions. Here, we investigate the validity of the assumptions. We first describe the method we use to obtain the effective Hamiltonian for a full junction and proceed to evaluate the validity of these assumptions by comparing to results obtained for a more realistic system.

1.1   Method for realistic junction

We performed a calculation on a full junction which contains electrodes and linker groups. We chose to look at the furan derivative studied experimentally by Chen et al.[S1] We modelled the experiment with the junction shown in figure S1(a). The junction contains 10 layers of 4x4 Au(111) with trimer tips on both sides of the slab. The molecule is bound to the trimer via the lone-pairs on the Ns. The outer layers of Au, the trimer atoms and molecular atoms were relaxed to within 0.03 eV/Å for a variety of cell lengths employing periodic boundary conditions in order to find the cell length that corresponded to a minimum on the potential energy surface. We used the same setting as in the paper to allow for direct comparison.

We took the geometry of the central five-membered furan molecule, added hydrogens to

the carbons bound to the linker groups, and relaxed the geometry of the molecule while constraining the nuclei of all other atoms but the two added hydrogens. From this geometry we performed a new DFT calculated and constructed the p_z orbitals as for the gas phase molecules in the paper. Since the two extra hydrogens are not present in the junction, we removed the components of the p_z orbitals on the basis functions centered on the added hydrogens. We then evaluated the corresponding overlap matrix of the molecular junction for the four p_z orbitals and noted that although constructed to be mutually orthogonal, the missing components along the hydrogens meant that there were overlaps of up to 0.1.Orthogonality of the p_z orbitals is crucial in order to Gram-Schmidt orthogonalize the non-p_z orbitals onto the the p_z orbitals. This is necessary to retain the full span of the basis, including "unoccupied" contributions to the transmission which can be important for destructive interference in the band gap. We therefore Löwdin orthogonalized the four p_z orbitals with respect to each other before we Gram-Schmidt orthogonalized basis functions centered on the atoms of furan atoms until the full span of the junction basis was recovered. The Löwdin orthogonalization, however, comes at the expense of reduced of localization of the p_z orbitals, which might affect the validity of our further assumptions. Figure S1(b) shows the obtained p_z orbitals which indeed look like p_z orbitals.

Another DFT calculation was performed on bulk Au in order to evaluate the overlap and coupling between principal layers of Au in the leads. From the resulting Hamiltonians and overlap matrices the self-energy of the junction in the presence of repeating principal layers of Au on both sides of the junction could be obtained using a heavily modified version of the ASE transport calculator. By using the method of transition regions as outlined by Thygesen and Rubio[S2] we reduced the active region to that of the central furan molecule corresponding to the one studied in the main paper but without hydrogens. Having obtained the lead self energies we constructed $\mathbf{g}_m^r$ as described in the main paper. From the lead self-energy and $\mathbf{g}_m^r(E)$ we could construct $\mathbf{\Sigma}^m(E)$. From these, we constructed G_{pq}^r where the indices p and q are the p_z orbitals centered on the atoms bound to the linker groups. Having calculated

the p_z orbitals, Hamiltonians, overlap matrices and self energies for a realistic junction, we can compare them to those we made assumptions about in the paper.
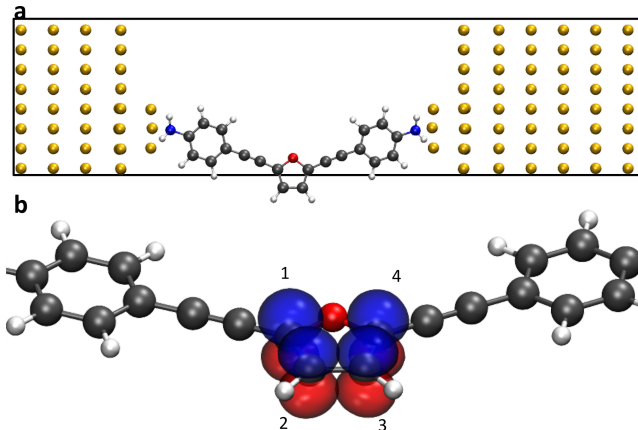

Figure S1: a) Geometry of realistic junction. Box indicates unit cell. b) Löwdin orthogonalized p_z orbitals evaluated at isovalue 0.1. Numbers indicate ordering of basis functions.

1.2 Evaluation of the validity of assumptions

Figure S2(a) shows the calculated transmissions for the realistic junction. The full black line shows the full calculated transmission in the direct basis before any basis rotations have been performed. The dashed red line shows the full transmission calculated after the rotation to the basis which includes the p_z orbitals and reducing the central region to that of only the central furan ring. This shows that our rotation preserves the full transmission as it must. The primary assumption in the paper is that $T(E) \approx \Gamma^L_{pp} G^r_{pq} \Gamma^R_{qq} G^a_{qp}$, where p and q are the indices of the two p_z orbitals. This term is plotted as the green line. This line follows the full transmission closely inside the band gap. At the Fermi energy, the term reproduces 81 % of the total transmission. This indicates that the approximation used in the paper is reasonable - especially considering that the p_z orbitals prior to Löwdin orthogonalization had mutual overlaps of up to 0.1 eV which must result in somewhat reduced localization after Löwdin localization. In the paper we calculate the conductance assuming the Fermi energy to be in the middle of the molecular band gap. From the transmission we see that the HOMO-LUMO gap is off-set by roughly 0.5 eV with respect to our assumption. Using different

binding groups may change this off-set in both positive and negative direction as has been shown by thermo-power measurements[S3] and also calculations.[S4] This should be considered when evaluating trends for specific binding groups. Figure S2(b) shows the spectral density of the p_z orbitals calculated for our realistic junction. Shown in full lines are those calculated for the realistic junction and shown in dashed lines are those assumed in the main paper. This shows that our assumption about spectral density is accurate for low bias. Figure S2(c) shows three different matrix elements which we make assumption about in the main paper. Again, full lines indicate the result calculated for the realistic junction and the dashed lines indicate those calculated for the gas phase molecule. We see that the parameter $\tilde{H}_{22}(E)$ is off-set by roughly 0.5 eV as expected due to the off-set in Fermi energy discussed above. The molecular self-energy term $S_{11}^m(E)$ however, follows closely that calculated for the gas phase molecule. The matrix element $\tilde{H}_{11}(E)$ differs for the realistic junction by roughly 1 eV at the Fermi energy. This indicates that the lead self-energy contains a real contribution of roughly 0.5 eV which we neglect in our calculation of the conductance in the paper. However, we also see that that because the molecular self-energy is almost constant within the band gap the sign change of $\tilde{H}_{11}(E)$ within the band gap indicates that the lead self-energy changes sign within the band gap. Since our DFT method grossly underestimates the band gap, one could imagine that for higher more realistic band gaps, the real part of the lead self-energy is much smaller at the Fermi energy because the molecular resonances are further away. We therefore believe our assumptions about these elements to be realistic.

2   Correlation of c with aromaticity

Figure S3 shows the NICS reported in the literature for our molecules versus our parameter c evaluated in the middle of the band gap. The value for the ketone is taken from a separate reference,[S5] but the others are taken from the same reference.[S6] Ordering the molecules in terms of c and NICS therefore gives the same result.
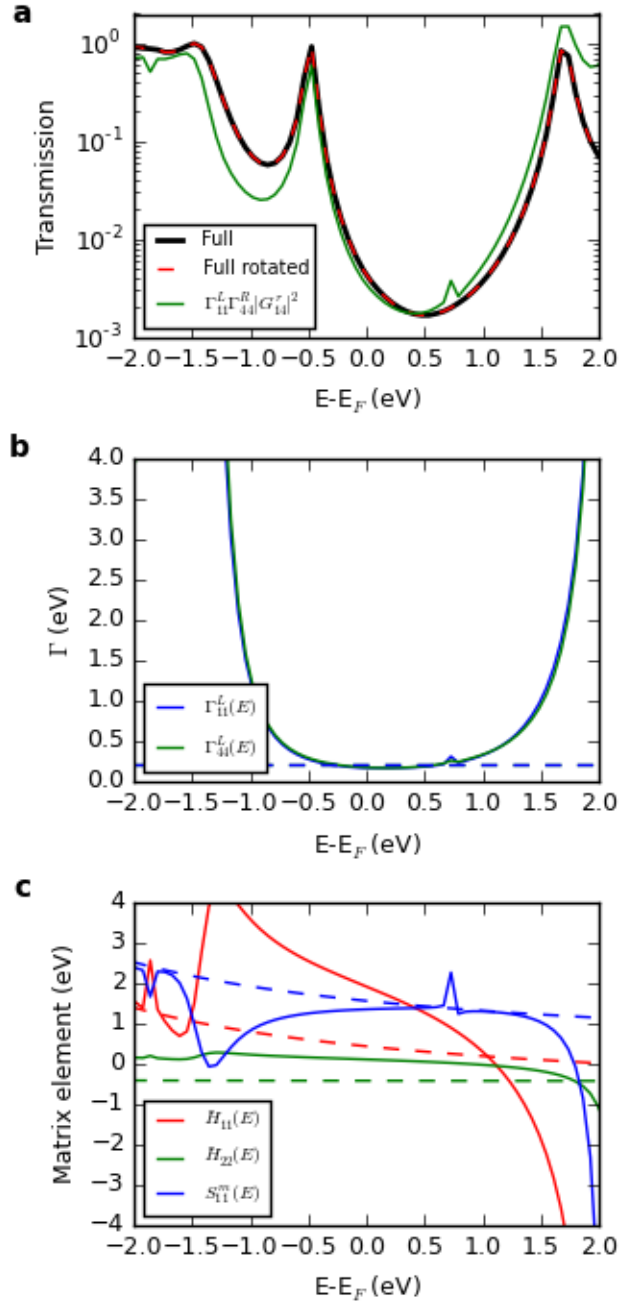
Figure S2: a) Transmission for realistic junctions. Black: Full transmission in direct basis. Red: Full transmission in basis rotated to basis which includes p_z orbitals and central region reduced to furan molecule. Green: Contribution to the full transmission from p_z orbitals. b) Spectral density of the two p_z orbitals. Full line: full calculation with realistic junction. Dashed line: Wide-band approximation used in paper. c) Elements of effective Hamiltonian. Full lines: Calculated for realistic junction. Dashed line: Calculated for gas phase molecule.
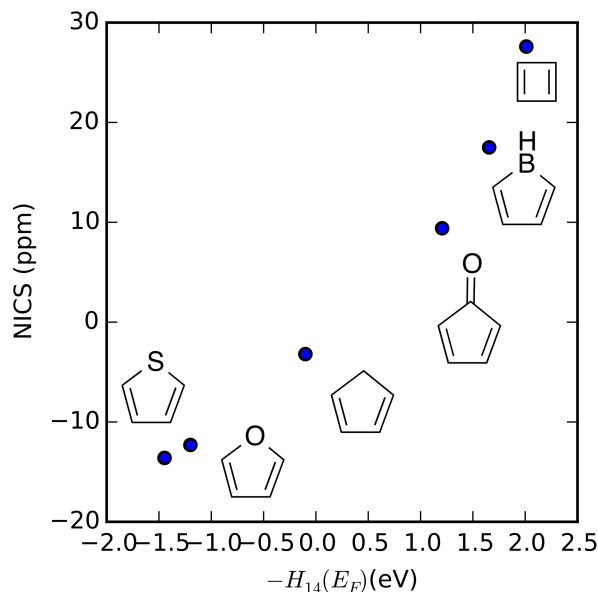
Figure S3: NICS value reported in the literature versus the effective coupling between sites 1 and 4 at the center for band gap.

3 Realistic calculation on ketone

The low conductance observed experimentally for the ketone is not reproduced by our DFT calculations. This is seen in figure S4 which shows the calculated transmission evaluated at the Γ point for the structures shown in the insert. It is seen that the ketone shows high conductance in the band gap but exhibits a destructive interference feature just outside the band gap which DFT is known to underestimate.

References

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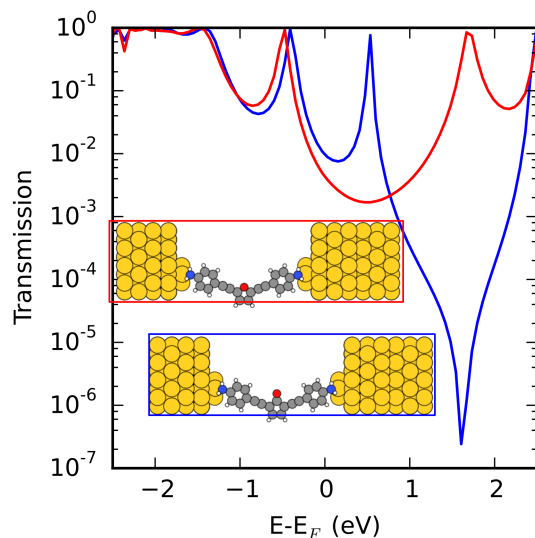(S2) Thygesen, K. S.; Rubio, A. Conserving GW scheme for nonequilibrium quantum trans-

Figure S4: Calculated tranmission for the structures in the insert. Furan derivative: red box. Ketone derivative: blue box.

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