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The Chameleonic Nature of Electron Transport through π-Stacked Systems

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This paper shows that the symmetry breaking effects involved in chemisorbing π-stacked benzene rings to metallic electrodes can have a significant impact on the transport properties. Fully eclipsed stacks may not be optimal; rather stacks designed to favor interactions between particular sites lead to increased transport. Conversely, in the case of transport through an infinite stack of benzene rings, where the full 6-fold symmetry of the system is preserved, maximal overlap of the rings in the fully eclipsed structures maximizes transport.

Molecules have been investigated for use as electronic components in two contexts. Molecular electronics has looked at single molecules bound in junctions to (often) metallic electrodes. Conversely, organic electronics has focused on molecular films as active layers, often in organic transistors or photovoltaics. While the relationship between chemical structure and electronic functionality may be, in many cases, transferable between these two contexts, we show that this is not always the case. The properties of a molecular structure employed in these different environments can be influenced significantly by the nature of the connection to the leads.

All transport calculations were performed using gDFTB,[1−5] although some of the results are reproduced in the Supporting Information using density functional theory in combination with an exchange-correlation functional specifically suited to intermolecular interactions. In both cases these methods provide a description of the coherent tunneling regime and consequently any departure from this in real systems (such as sequential incoherent hopping steps) will not be captured. The calculation details are included in the Supporting Information.

A series of π-stacked molecules with thiol substituents for binding to gold electrodes is shown in Figure 1. The systems are designated with a number (1, 2, or 3) indicating how many phenyl rings are present and a letter (P or M) indicating whether the electrodes are attached with either *para*- or *meta*-type substitution. These systems can be considered as even alternant hydrocarbons,[6] with stars placed on every second atom and with no nearest neighbors being either both starred or unstarred. In the case of the stacked systems, the starring continues across nearest neighbors in the stack as has been discussed previously in the case of magnetic systems.[7]

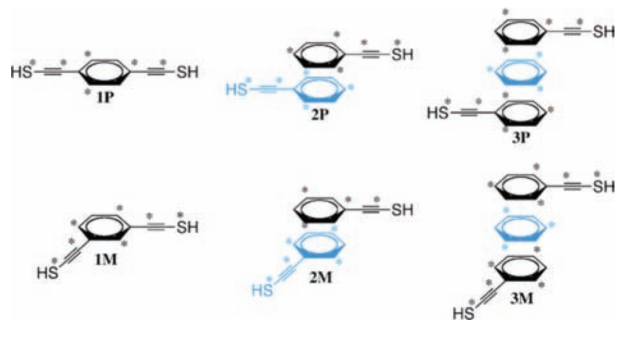

Figure 1. A series of thiol-substituted benzene systems for transport calculations with gold electrodes. The systems are all even alternant hydrocarbons and are marked with stars to show when alike (low) or disjoint (high) coupling is expected. In each case, adjacent layers are colored differently for clarity.

When the terminal sulfurs are both starred, this indicates "*alike*" coupling and is known to result in weak transmission with *meta*-substituted benzene being the prototypical example. The alternative is "*disjoint*" coupling, which leads to high levels of transport, with *para*-substituted benzene being the counterpart example. The spin coupling in biradical molecules similar to **2P** and **2M** (with radical substituents in the place of the binding groups) has been measured[8,9] with a high-spin groundstate observed in the "*para*" substituted system and low-spin ground state for the "*meta*" substituted system.

In single molecule transport, *alike* coupling provides destructive interference features, frequently near the Fermi energy of the electrodes, and, consequently, a significant reduction in the observed current. The electronic transmission as a function of the electron injection energy for the molecules in Figure 1 is shown in Figure 2. In each case the gold Fermi energy (which we set to −5.0 eV) is marked with a dashed line.

While the interference in the π-system transport through **1M** is not evident in the total transmission, due to the residual σ-system transport, a pronounced interference feature is evident near the Fermi energy in **2P** and **3M**. Consequently, there is lower transport through **2P** than **2M** in this region, a result that might at first appear unintuitive if the differences between "*meta*" and "*para*" substitution were naively extended to stacked systems. This relationship is reversed again in **3P** and **3M** with the same trend as the single molecule systems.

By appreciating that the starring assignments across the stack are set by which sites are nearest neighbors, it is possible to design structures with spatial dislocation between the rings in **2P** and **2M**, making both systems exhibit *disjoint* coupling. Figure 3 shows two structures (**2P max.** and **2M max.**) where spatial dislocation is used to favor overlap between selected sites, rather than overlap of the

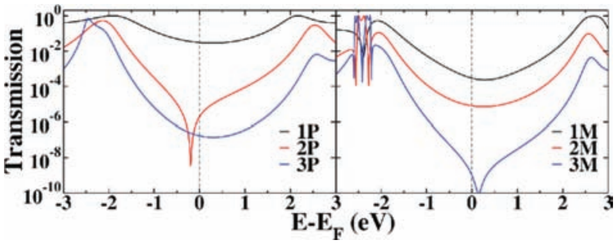

Figure 2. Transmission through the π-stacked molecules in Figure 1. The Fermi energy is marked with a dashed line.

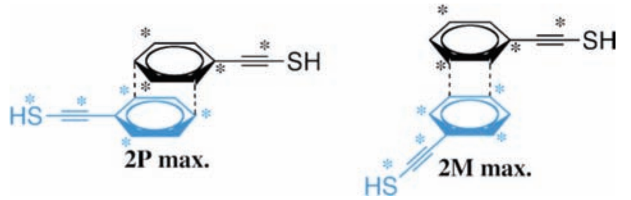

Figure 3. Structures of two systems with spatial dislocation optimizing the overlap between selected sites (highlighted with a dashed line) and resulting in overall disjoint coupling.

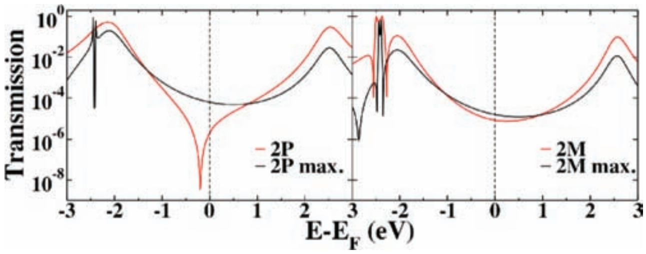

Figure 4. Transmission through the fully eclipsed (red) and dislocated (black) π-stacked systems. In both instances the transmission near the Fermi energy is increased in the dislocated structures; however the absence of the interference feature in **2P max.** makes this effect particularly dramatic.

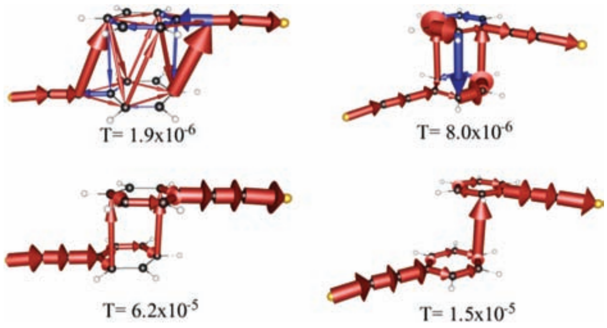

Figure 5. The local transmission at the Fermi energy through **2P** and **2M** (top: left and right) and **2P max.** and **2M max.** (bottom). Local contributions are normalized with red arrows indicating contributions in the direction of the net current and blue arrows indicating contributions in the opposite direction. The total transmission is shown below each plot. The dislocated structures favor select sites leading to higher transmission and a simpler picture of the local contributions.

benzene rings as a whole. Both of these systems are now predicted to exhibit the higher levels of transmission, previously only seen in **2M**.

The transmission through these systems is shown in Figure 4 with the transmission through **2P** and **2M** for comparison. In both cases, the dislocated structures have higher transmission near the Fermi energy than their fully eclipsed counterparts, although the change is very minor for **2M**. In the case of **2P** this change is particularly dramatic as the destructive interference feature is absent in **2P max**.

While off-resonant transmission near the Fermi energy increases with dislocation, resonant transmission decreases. Both systems have resonant peaks between 2 and 3 eV above and below the Fermi energy that no longer approach unity in the dislocated structures. The behavior near the Fermi energy would dominate in a measurement of the low-bias conductance; however, the resonant behavior is interesting to note in comparison with transport through stacked benzene rings in the absence of metallic electrodes.

It is also possible to calculate the components of the transmission between pairs of atoms in the molecule, known as the local transmission,[5,10,11] which is shown in Figure 5 and confirms the behavior hypothesized from the starring arguments. In the fully eclipsed structures, the local transmission is somewhat complicated with components in the direction of net current (red) and in the reverse direction (blue). Further, in both cases cyclic currents are present, which is evidence of interference effects.[11,12] In contrast, the dislocated structures show simple local transmission. The transmission across the stack is dominated by either one or two components between the sites favored by the overlap of the dislocated structures. Interestingly, although there are two sites favored by the dislocation in **2M max.**, only one participates in the transport as the other is *meta* to the binding groups and thus there is no electronic coupling to this site.

The symmetry breaking effect of the binding groups means that not all sites in the ring are equal in terms of electronic coupling. This is well-known in the context of single benzene rings;[13] however the consequences for transport in stacked systems are somewhat less obvious. There is only strong electronic coupling to sites *ortho* and *para* to the injection site. In the relatively simple case of two stacked rings there is the additional requirement of good coupling from these sites to the sites in the second ring that are *ortho* or *para* to the binding group out of the molecule. In all the cases with relatively high transmission, **2M**, **2P max.**, and **2M max.** this condition is fulfilled. In the case of **2P** it is not and consequently there is low transmission through this system near the Fermi energy.

In organic electronics, where molecules are not generally chemisorbed through binding groups to the electrodes, electronic coupling matrix elements are generally calculated rather than electronic transmission. The comparison of these two approaches can be made directly for π-stacked systems;[14] however here we simply study analogous systems relevant in the context of organic electronics. To see the influence of the symmetry breaking, the transport through four systems of benzene rings, without metallic electrodes, was considered. The structures of these systems are shown in Figure 6 and have been chosen to highlight the role of nearest neighbor coupling in these stacks. The systems range from the fully eclipsed (six nearest-neighbor interactions across the stack) to a system with significantly reduced spatial overlap (one site and two site nearest neighbor interactions across the stack). These systems were calculated with periodic boundary conditions, and parts of the stack are used to constitute the "electrodes" and the "molecule" for the purposes of the formalism; full details are given in the Supporting Information.

The transmission through these systems is shown in Figure 7, and it is immediately clear that the transport characteristics differ substantially from the systems bound to metallic electrodes. The transmission is plotted on a linear scale as the off-resonant transport near the Fermi energy that characterizes the measurable range in molecular junctions is essentially nonexistent. In the molecular junction, the nonzero density of states in the gold electrodes allows for electronic injection over a wide range between the molecular resonances. Conversely, when the system is comprised of molecules alone there are bands of transmission that emerge from the mutual broadening of the molecular resonances, but this broadening occurs over a relatively limited range. As distinct from calculations in molecular junctions where transmission rarely exceeds unity by any appreciable extent, the resonant bands in these systems show transmission peaking at two over a considerable range. In all of the dislocated systems (**1S**, **2Sa**, and **2Sb**) the range over which the resonant transmission reaches its local maximum is significantly reduced as compared with the fully eclipsed structures. While this is in contrast with the off-resonant behavior in the molecular

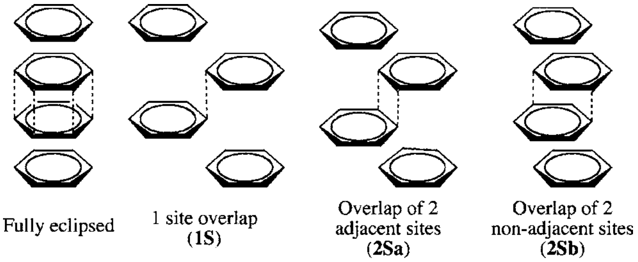

Figure 6. Four systems considered for an infinite stack of benzene rings. Spatial dislocation takes the fully eclipsed structure (left) to systems where only one or two sites are strongly interacting between rings.

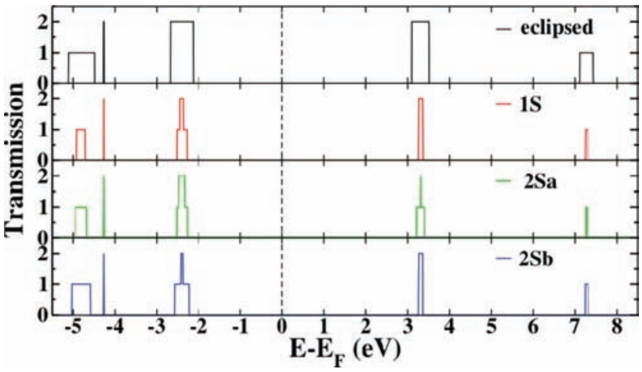

Figure 7. Transmission for the systems shown in Figure 6. The transmission is plotted on a linear scale as off-resonant transport is suppressed due to the limited range of the molecular density of states. In all cases, spatial dislocation decreases the energy window over which the maximum resonant transmission is observed compared with the fully eclipsed structure.

junctions, where dislocation increased transmission, it is in keeping with the trends observed for the resonant transport as well as those observed in prior work on electron transfer.[15,16]

Finally, it is possible also to plot the local transmission through these systems, shown in Figure 8. This reveals the simplicity and high symmetry of the local transmission through the eclipsed structure, an image in accordance with an intuitive picture of the electronic interaction between two stacked benzene rings. The dislocated structures show transmission predominantly through the sites with maximum spatial overlap but also more complicated features. In contrast with the symmetry broken systems in molecular junctions, spatial dislocation leads neither to increased transport nor to simplicity in the patterns of the local transport.

Transport through π-stacked systems offers a rich array of properties for future study. The effects of symmetry breaking in these systems cannot be ignored as they have a direct bearing on the nature of the electronic coupling and the favored interactions in the resulting structures. Systems that may be ideal candidates for single molecule studies in transport junctions may be unsuitable as components of an active organic film, and the converse may also hold true. The nature of the charge injection into the stacked system will influence the role that symmetry plays and therefore should be carefully considered in molecular design.

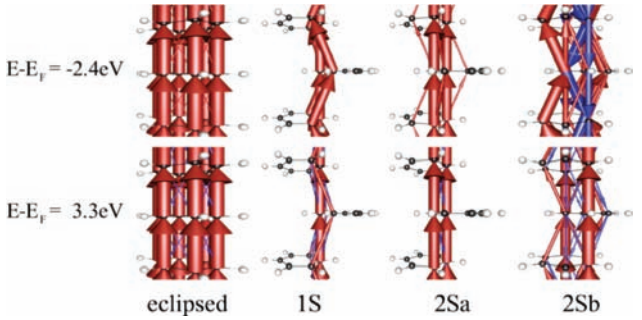

Figure 8. Local transmission through the four stacked benzene structures calculated near the transmission resonances. The local transmission through the fully eclipsed structure reflects the full 6-fold symmetry of the system.

Acknowledgment. We thank David Q. Andrews for helpful comments. This work was supported as part of the ANSER Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award Number DE-SC0001059. C.H. would like to thank the German Research Foundation (DFG) for generous support through a postdoctoral research fellowship.

Supporting Information Available: Full details of calculation method, calculations using density functional theory, geometries of the molecular systems used in all calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA102434M