

# Can We Understand the Molecule in Molecular Electronics?

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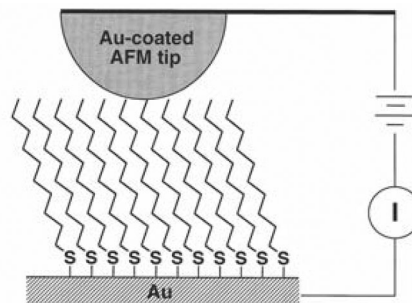
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The idea of molecular electronics is certainly an appealing one.<sup>[1,2]</sup> As feature sizes in inorganic semiconductor circuits are pushed smaller and smaller, it is inviting to extrapolate this push to the ultimate component size, the individual molecule. The goal of molecular electronics, to use individual molecules as the component elements in an integrated circuit, is appealing for at least two reasons. The first, already mentioned, is the ultimately small size of a molecular circuit element. The second is the enormous range of synthetic possibilities suggested by the use of organic molecules as electronic components. The skill of the synthetic chemist in designing molecules with particular geometric and electronic structures ought to allow the tuning of properties of appropriately designed circuit elements. This tuning would allow much broader control of circuit properties and device applications, while pushing the very limits of feature size in the designed device.

Of course “in principle” is almost always different than “in practice”. To take just a single area of importance in determining the relevant properties of organic molecules as electronic components, the metal/molecule/metal junction is perhaps the most interesting and the most studied.<sup>[3]</sup> One must be able to wire the components repeatably and reliably, and if the idea of tuning component properties synthetically is to be realized, this is the area where it must first be shown. While there have been many studies addressing this specific question, there is not agreement yet on whether the intrinsic properties of the molecule (structural conformation, length, HOMO–LUMO gap, alignment with the Fermi level, etc.) actually control the rate of charge transport across such a junction.

This lack of agreement is perhaps not too surprising given the difficulty of actually measuring the property (conductivity) of the metal/molecule/metal junction. Two general approaches have been developed to attempt this measurement.<sup>[2]</sup> The first tries to make reliable measurements on individual molecules appropriately attached to very small scale metal electrodes. Attachment is usually by way of a covalent linkage of the molecule to the metal electrode; thiol or amine linkages to noble metals are popular ap-

proaches here. Mechanical break junctions can be used, wherein a nanoscopic wire is mechanically pulled apart in the presence of a solution of the junction-forming molecules to be studied. As the broken wires are moved closer together, one or a few of the relevant molecules will bridge the gap and current–voltage measurements can be made across the junction.<sup>[4]</sup> Another method uses electromigration to thin a lithographically deposited wire in the presence of the relevant molecules until a junction is formed at the break, again consisting of one or a few molecules whose conductivity can be measured.<sup>[5]</sup> The other general approach is to take advantage of the property of self-assembly of organic molecules on solid surfaces, and to establish a metal/molecule/metal junction using the self-assembly substrate as one electrode in the junction geometry (Figure 1).<sup>[6]</sup> Methods for attaching the other electrode have included vapor deposition



**Figure 1.** Schematic of metal/molecule/metal junction using the SAM approach. Reproduced with permission from Ref. [6]; copyright American Chemical Society.

of the top conductor (which often results in shorts at monolayer defects), the use of a scanning tunneling microscopy tip as the second electrode, conductive probe (CP) AFM for the top electrode, or the use of hanging mercury drops or other approaches to make contact with the monolayer without damaging the device.

Results of these sorts of studies have been interesting to say the least. Work by Venkataraman and co-workers,<sup>[7]</sup> using mechanical break junctions and amine linkages to gold electrodes, has shown clear and statistically significant differences in conductivity of a series of substituted 1,4-diaminobenzene molecules. Substituents that donate electrons to the

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benzene ring increase conductance of the bridge molecule, while electron-withdrawing groups decrease conductance. The same group has also examined the effect of the twist angle in break junction measurements of a series of diamino biphenyl molecules.<sup>[8]</sup> As the angle defining the twist between the two benzene rings increases, the measured conductivity decreases, as the opportunity for conjugation across the molecule junction is disrupted. Jiang, Scoles, and co-workers, using the self-assembled monolayer (SAM) approach and CP/AFM, noted significant differences in conductivity between monolayers of benzenethiol and 4-ethylbenzenethiol.<sup>[9]</sup> Their approach used a direct differential comparison of nanografted monolayers, using the same CP/AFM tip, under the same solvent and loading conditions. Their work also identified a myriad of difficulties for these measurements, including substrate roughness, purity and order in the SAM, the size, shape, and contamination of the tip region, wear of the probe tip during measurement, applied tip force, and solvent or ambient conditions, all of which affect the quality and repeatability of measurements using SAM junctions with scanning probe top contacts. They noted that tip contamination appears as the largest source of error in metal/molecule/metal junction conductivity measurements.<sup>[10]</sup>

Both of these groups, and others, seem to have shown that the fundamental concept of molecular electronics, that the electronic and geometric structure of the component molecule can be tuned to control the properties of the device component, is likely valid. One reads with some surprise then, the recent publication by Yoon and co-workers,<sup>[11]</sup> which claims that “The rate of charge tunneling through self-assembled monolayers is insensitive to many functional group substitutions”, to quote their title.<sup>[11]</sup> On close examination, their conclusions appear to be well supported by their data. They also use a self-assembled monolayer/top contact approach for these measurements. The junction they describe uses a very flat substrate (template stripped Ag), a thiol-bound monolayer of constant thickness but with varying tail groups, and a top contact made with liquid metal GaIn eutectic, protected by a layer of Ga<sub>2</sub>O<sub>3</sub>. This work showed that for a series of monolayers with aliphatic, aromatic, and heteroaromatic tail groups, there was no measureable difference in conductivity across the junction. This observation is in spite of the significant differences in electronic structure of the tail groups, which included substituted benzene, thiophene, pyridine, naphthylene, cyclohexane, adamantane, and norbornene rings in the series.

These authors have taken great care to address the difficulties inherent in these junction measurements. They use a very flat substrate, the SAM on the Ag substrate is more upright than on the Au substrate typically used, the monolayers are stiffened by hydrogen bonding between intermediate amide linkers, and the eutectic GaIn top contact provides conformal contact to the self-assembled monolayer on the micron scale. The presence of the Ga<sub>2</sub>O<sub>3</sub> layer protects the top

contact, prevents (or minimizes) tip contamination, and provides a constant distance tunneling gap making the contact repeatable and robust. Making measurements using this method is also rapid enough that significant numbers of measurements on a monolayer junction can be made in a reasonable time, thus providing statistical significance to the measurements, and the ability to compare, “based on a physical organic design”,<sup>[11]</sup> a large series of substituted monolayers. Thus, there appears to be a conflict with conclusions reached in earlier work, such as that cited above.

Is this conflict the result of a significant difference in actual systems being measured? Perhaps we do not yet understand the nature of the top contact. It is certainly different from the covalent linkage that comprises the bottom contact in the SAM approach or both the bridge contacts in the break junction methods. Perhaps the thickness dependence of the conductivity dominates any possible change that the electronic structure of the tail group may make to the overall conductivity, in this case. It is interesting to note that the same group, using the same approach, did find an odd-even effect in the variation in conductivity of a series of long chain aliphatic monolayers.<sup>[12]</sup> Does this say that organic molecules cannot perform as components in molecular electronic devices? Clearly, more research is necessary before workers in this field will have a distinct understanding of the behavior of these possible molecular electronic components. However, with the research highlighted here, it appears that the tools are in place to carry out the measurements which can answer these questions, and that will lead to this understanding.

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