

NANOSCALE MOLECULAR OPTOELECTRONICS

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Project Area and Objectives:

Molecular electronics aims to use molecules as electronic components; switches, amplifiers, sensors etc. The goal is to exploit the flexibility of synthetic chemistry and hopefully circumvent the limitations of conventional solid-state fabrication.

Our group brings together expertise from experimental and theoretical physics, engineering, organic chemistry and photochemistry with the aim of building devices based on what we have learned from our work in artificial photosynthesis.

The first steps have been made in making reliable, well-characterized connections to simple single molecules, and we are moving on to study molecules with switching capabilities and negative differential resistance (NDR) and molecules with interesting opto-electronic properties.

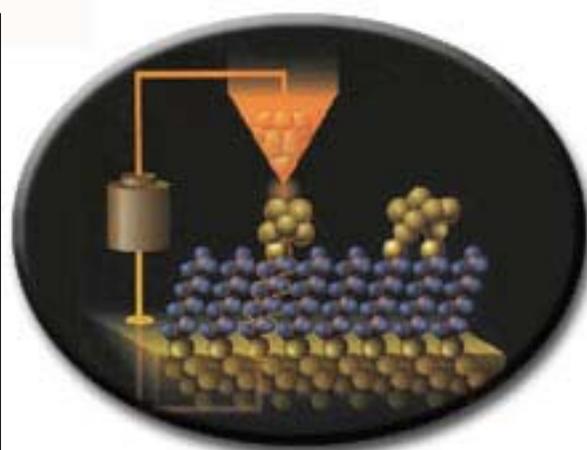
The first step - contacting single molecules:

The geometry of the metal-molecule interface and the number of molecules in a junction are matters of considerable uncertainty; electronic measurements on DNA have found it to be an insulator, semiconductor, metal and superconductor! Even well controlled break-junction measurements on small molecules yield conductivities that differ from theoretical predictions by several orders of magnitude.

We have overcome many uncertainties about the nature of the metal-molecule-metal junction by using conducting atomic force microscopy (CAFM) combined with self-assembled nanodevices, as illustrated in Figure 1.

A molecule, carrying reactive sulfur groups (thiols) at each end is inserted into a vacancy in a molecular-monolayer film using solution chemistry. The bottom thiol forms a covalent bond with the bottom gold surface while the top thiol is contacted by a second solution phase reaction in which a gold nanocrystal attaches to the top thiol group. The film is then scanned (in a controlled liquid environment) with a

Fig 1: A gold-coated CAFM probe is pushed into a gold nanocrystal covalently-attached to one end of an octanedithiol molecule. The other end is covalently-attached to a gold surface



CAFM probe to locate the gold top contacts. The gold AFM probe is pushed into the gold nanocrystal to complete the circuit. A single molecule is now wired into an electrical circuit. The results are dramatic [2]. It turns out that, for small *n*-alkanes, one, two, three or more molecules can fit into the film-vacancies and form bonds with both contacts. Thus, current-voltage curves are found to be multiples of a fundamental curve; the *i-v* characteristic of a single molecule. A histogram of these relative conductances shows sharp peaks at integer values, as

shown in Figure 2. Thus, the i-v curve of a single molecule can be found unambiguously. We have developed solid-state electronic structure calculations based on DFT to handle the metal-molecule-metal problem [3, 4] and find much better agreement between theory and experiment. The improved agreement comes almost completely from the factor 1000 increase in experimentally-measured currents obtained with our new method.

Do we really understand our data?

The gap between first-principles calculations and experiment has been narrowed enormously, but a detailed examination of a series of molecules[5] reveals significant areas of disagreement (factors of five or so in conductivity and discrepancies in the value of the electronic decay length). These problems may be resolved when charging (Coulomb blockade) of the gold nanocrystals is accounted for properly and experiments are underway to settle this issue.

Moving on to functional molecules

Negative differential resistance devices:

Phenylethynylbenzene oligomers, with, and without, a reducible nitro group (Fig, 3) were examined in the nanojunctions. These experiments showed that negative differential resistance occurs in single molecules and that it requires the nitro group[6].

Optically-active molecules: Reliable current voltage measurements of a carotenoid molecules (figure 4) are now complete. Subject to some uncertainty associated with the charging (Coulomb blockade) effect, the conductivity is well described by conventional tunneling theory. Thus, the electrochemical contribution owing to oxidation of the unsaturated backbone (hole current) is not dominant. It will be interesting to see what happens to electronic transport when the molecule is illuminated.

Molecular Switches: All the molecules examined to date (including simple alkane dithiols) show stochastic on-off switching. Comparison of the switching rates with, and without, covalently attached top contacts shows that the bottom gold-thiol contact also fluctuates, causing a universal and intrinsic “electronic blinking”. This is a fundamental limitation on the utility of single molecule devices.

Educational Activities: The collaboration provides a fertile interdisciplinary training ground. Three PhD’s have or will shortly graduate (Cui, Tomfohr and Zarate) with experience spanning chemistry, physics and engineering. Several REU students have completed projects. Graduate students from across the campus attend monthly “nano-lunches”. Faculty and students from several departments spanning two colleges, together with Motorola scientists attend group meetings every two weeks.

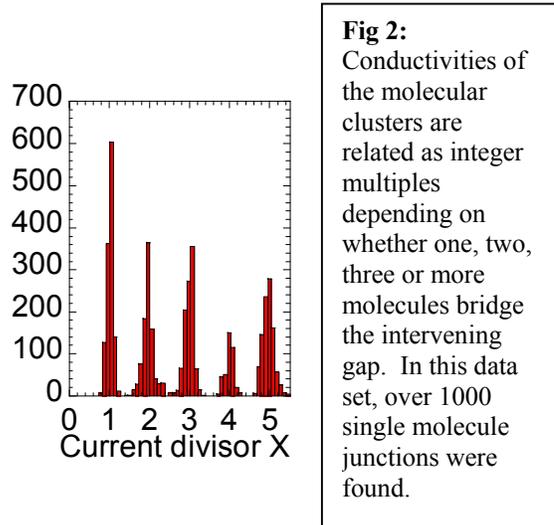
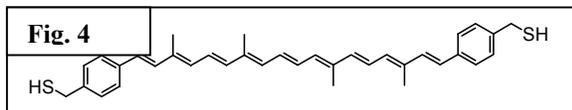
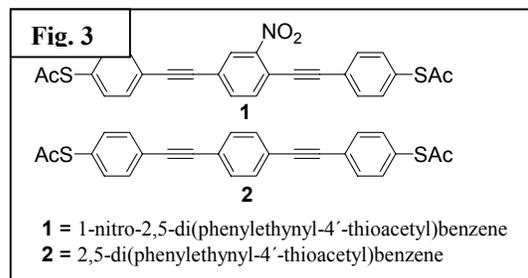
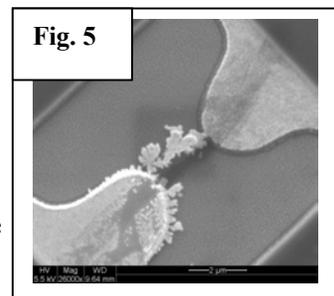


Fig 2: Conductivities of the molecular clusters are related as integer multiples depending on whether one, two, three or more molecules bridge the intervening gap. In this data set, over 1000 single molecule junctions were found.



The Major Challenge; A target for Collaborations: The major challenge facing us (and many others) is to translate the present level of reliability into a system that can be fabricated on a chip. There is a basic-science need for junctions suitable for variable temperature measurements. It is also an essential step in developing technology. We are building nanojunctions using the electrochemical methods developed by Nonjain Tao; an example of a junction with a sub nm gap is shown in Fig. 5. It is clear from the growth morphology that the geometry is far from well defined! We are also investigating electromigration methods (with the help of the Cornell group). But it is hard to see how metal-molecule-metal junctions can be well defined on the atomic scale in self-assembled systems like this. There must be a better way! We have well calibrated molecules and would like to work with nano-junction fabricators to see if well defined, manufacturable devices can indeed be produced.



References

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