

# Materials Science & Engineering

## Doctoral Defense

### Contact and Length Dependences in Single-Molecule Electronics

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## abstract

Understanding charge transport in single molecules covalently bonded to electrodes is a fundamental goal in the field of molecular electronics. In the past decade, it has become possible to measure charge transport on the single molecule level using the STM break junction method. Measurements on the single molecule level shed light on charge transport phenomena which would otherwise be obfuscated by ensemble measurements of groups of molecules. This thesis will discuss three projects carried out using STM break junction.

In the first project, the transition between two different charge transport mechanisms is reported in a set of molecular wires. The shortest wires show highly length dependent and temperature invariant conductance behavior, whereas the longer wires show weakly length dependent and temperature variant behavior. This trend is consistent with a model whereby conduction occurs by coherent tunneling in the shortest wires and by incoherent hopping in the longer wires. We support our measurements with calculations and investigate the evolution of the molecular junction during the pulling process.

The second project reports controlling the formation of single-molecule junctions by means of electrochemically reducing two axial-diazonium terminal groups on a molecule, thereby producing direct Au-C covalent bonds in-situ between the molecule and gold electrodes. Step length analysis shows that the molecular junction is significantly more stable, and can be pulled over a longer distance than a comparable junction created with amine anchoring bonds. The stability of the junction is explained by the calculated lower binding energy associated with the direct Au-C bond compared with the Au-N bond.

Finally, in the third project we investigate the role that molecular conformation plays in the conductance of oligothiophene single-molecule junctions. We measured ethyl substituted oligothiophenes and find temperature dependent conductance and transition voltage behavior for molecules with between two and six repeat units. While the molecule with only one repeat unit shows temperature invariant behavior. We perform density functional theory simulations to show that at higher temperatures the oligomers with multiple repeat units assume a more planar conformation, which increases the conjugation length and decreases the effective energy barrier of the junction.



July 23, 2013; 4:00 PM; ERC 490