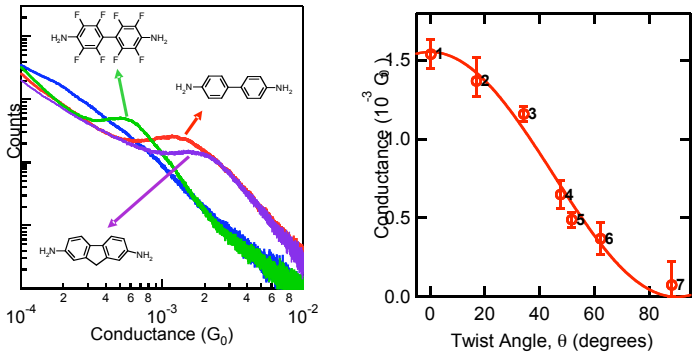
NANO HIGHLIGHT
Toward Design Rules for Conduction in Single Molecules

NSF NSEC Grant CHE-0641523
PIs: **James T. Yardley, Ronald Breslow, Tony Heinz**
Columbia University

Over the past decade there have been a number of reports of measurement of the electrical conduction for a single molecule covalently bound to metallic electrodes. These experiments have been difficult and have generally been confined to a limited number of chemical compounds and electrodes. Building on the pioneering experiment developed by Tao and coworkers [1], a team of researchers at the Columbia Nanocenter led by Dr. Latha Venkataraman and including Prof. Ronald Breslow, Prof. Colin Nuckolls, Dr. Mike Steigerwald, and Dr. Mark Hybertsen have discovered that for molecular diamine systems, which bind strongly to gold, they observe well-defined electrical conductance values which can be measured directly for a wide variety of molecules. This discovery has allowed this group to carry out a systematic investigation of the conductance for individual organic diamine molecules for a wide variety of molecular structures. Thus for example they have shown that for simple alkyl and aryl amines, the observed molecular conductance follows a tunneling model, exhibiting exponential decrease in conductance with increasing molecular length [2]. Conduction for alkyl molecules is lower than for aryl molecules and conductance decays more rapidly with length for alkyl molecules.

The team has also explored conductance in a series of molecules based on a simple biphenyl structure in which they experimentally control twist angle through manipulation of the molecular structure. The experimental measurements for a series of molecules show a clear decrease in single molecule conductance with increasing twist angle (θ), following a $\cos^2\theta$ dependence as shown in the figure here [3]. We may understand these results in terms of electron transfer theory: For biphenyls, as the twist angle between the two rings increases, the degree of π-conjugation between them decreases. The molecular conductance, which is proportional to the electron transfer rate, therefore scales as the square of the π-overlap. The group is continuing to investigate the influence of molecular substitution on molecular conductance as well as new molecule-electrode systems.

Measured distribution of conductance values for three molecules based on the biphenyl structure and plot of average conductance versus twist angle for seven molecules with $\cos^2\theta$ fit.



References.
[1] B. Q. Xu and N. J. J. Tao. Science **301**, 1221-1223 (2003)
[2] Latha Venkataraman, Jennifer E. Klare, Iris Tam, C. Nuckolls, Mark Hybertsen and Michael Steigerwald. "Single-Molecule Circuits with Well-Defined Molecular Conductance". Nano Letters **6**, 458-462 (2006).
[3] Latha Venkataraman, Jennifer E. Klare, C. Nuckolls, Mark Hybertsen and Michael Steigerwald. "Dependence of single-molecule junction conductance on molecular conformation". Nature **442**, 904-907 (2006).