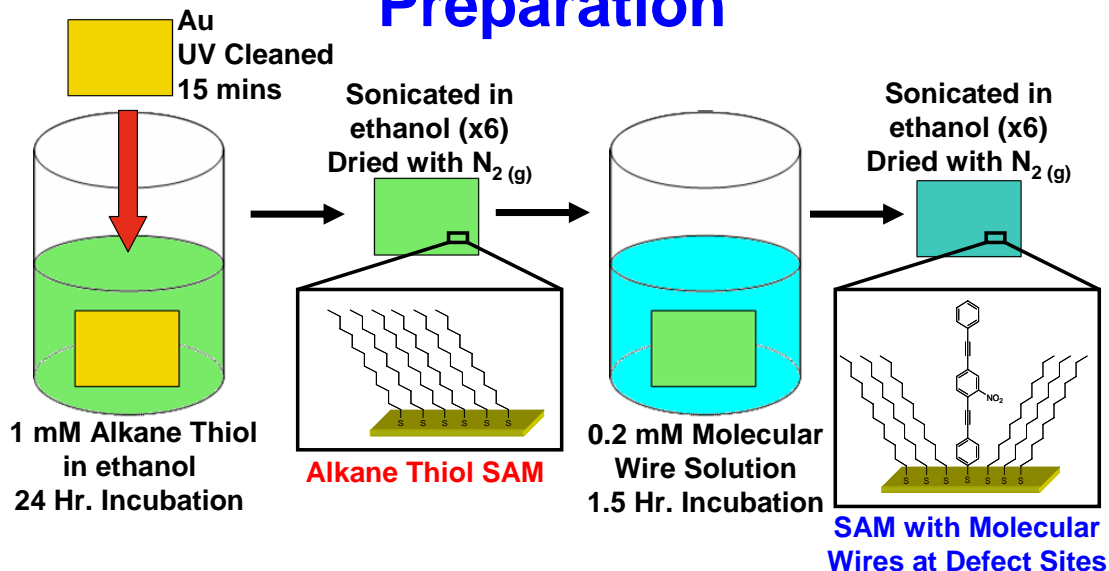
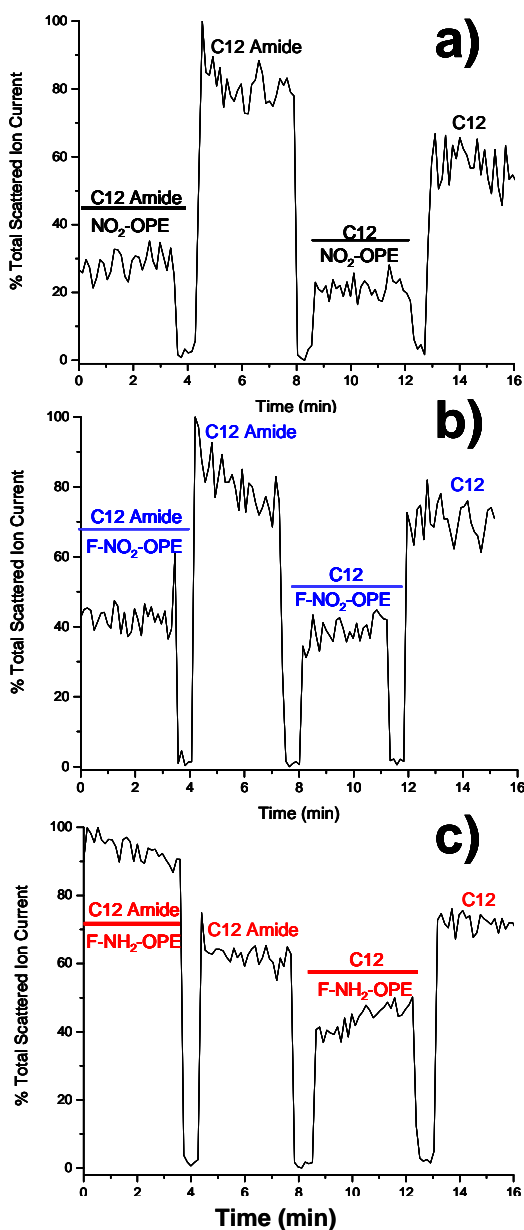


# Characterizing Electron Transfer Properties of Molecular Wires through Ion-Surface Collisions

Molecular electronics has become an emerging field as silicon based device miniaturization approaches physical limitations. Molecular devices are comprised of components analogous to traditional electronics such as wires, capacitors, and transistors but are built from molecular materials. Characterizing even the simplest molecular components poses many challenges. Investigating the conductivity of molecular wires by traditional methods requires manufacturing full devices with metal contacts at both ends of the molecular wires. This is time consuming and device performance can obscure fundamental conductance measurements. Tandem mass spectrometry can overcome these obstacles allowing ions to collide on wire doped surfaces. These surfaces provide a single metal contact and impinging ions permit electron transfer through the wires which can be monitored as ion neutralization. This project is a collaboration with Dr. James M. Tour's group at Rice University, Houston, TX [www.jmtour.com](http://www.jmtour.com). The schematic below shows the generic process for forming molecular wire doped SAM films.

## Molecular Wire Doped Self-Assembled Monolayer (SAM) Preparation





Total ion currents (TICs) of alkyl thiols and alkyl thiols doped with molecular wires a) NO<sub>2</sub>-OPE, b) F-NO<sub>2</sub>-OPE, and c) F-NH<sub>2</sub>-OPE.

In both C12 and C12 amide SAMs, NO<sub>2</sub> containing wires neutralize a greater percentage of the incident ion beam when compared to the matrix SAM alone indicating greater electron transfer through the wires than the insulating matrix SAMs. This is recorded as a decrease in the overall TIC intensity as is shown in **a** and **b**.

When NH<sub>2</sub> containing molecular wires are embedded in alkyl thiol SAMs, the ion neutralization phenomenon is influenced by the nature of the embedding matrix. For wires in a C12 SAM, a less rigid matrix, a greater proportion of the incoming ions are neutralized than in the C12 SAM alone. In a more rigid matrix of C12 amide however, the ion neutralization observed is reversed when compared to NO<sub>2</sub> containing wires due to the opposite orientation of the interface dipole of the molecular wire. This difference allows less ion neutralization and an increase in the TIC as shown in **c**.

By interrogating these surfaces with MS/MS, additional chemical information is collected simultaneously with wire conductivity. Methyl abstractions by projectile ions are indicative of CH<sub>3</sub> terminated SAMs and methyl reaction quotients can be calculated based on the appearances of addition products in mass spectra.

For all molecular wire doped films, methyl reactions are reduced when compared to the alkyl SAMs alone. This reaction process is a competing pathway with ion neutralization and confirms the electron transfer effects of the incorporated wires. These experiments show promise as an innovative technique to compare the conductivity and performance of molecular wires. By using tandem mass

spectrometry, full device construction is not necessary, making this a rapid screening process for molecular wire candidates.