

## Nanoscale Electronic Structure Measurements in Organic Systems

A team of NIST and University of Maryland researchers are developing a scanning tunneling microscope (STM) technique that can provide information on localized electronic structure in molecular and organic systems based on tip height ( $Z$ ) versus voltage measurements ( $Z$ - $V$ ). Knowledge of interfacial electronic structure at organic-metal and organic-organic heterojunctions is a prerequisite for the development of a wide range of organic electronic applications, including organic light emitting diodes, organic photovoltaics, and field effect transistors.

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Photoelectron spectroscopies can provide information about interfacial electronic structure at organic-metal and organic-organic heterojunctions and have been used extensively for this purpose. However, many advanced applications depend on nanostructured materials and it is desirable to access electronic structure information at nanometer length scales. One technique employed for this purpose is scanning tunneling spectroscopy (STS). Current versus voltage ( $I$ - $V$ ) curves are acquired with subnanometer resolution over a fixed location using a scanning tunneling microscope (STM). To perform the measurement the STM tip height is fixed (tip feedback is disengaged) and the voltage between the tip and sample is varied. Current increases occur whenever the voltage corresponds to filled or empty (depending on the bias direction) electronic level. This technique, however, has limitations for molecular/organic systems due to the rapidly increasing current in the system as the voltage is ramped through the experimentally interesting regime. This can lead to breakdown of the molecule/organic or induced molecular motion and make measurements at high bias extremely difficult.

The NIST/U. of MD research team are investigating an alternative technique to provide information on localized electronic structure in molecular and organic systems based on tip height ( $Z$ ) versus voltage measurements ( $Z$ - $V$ ). [1,2]

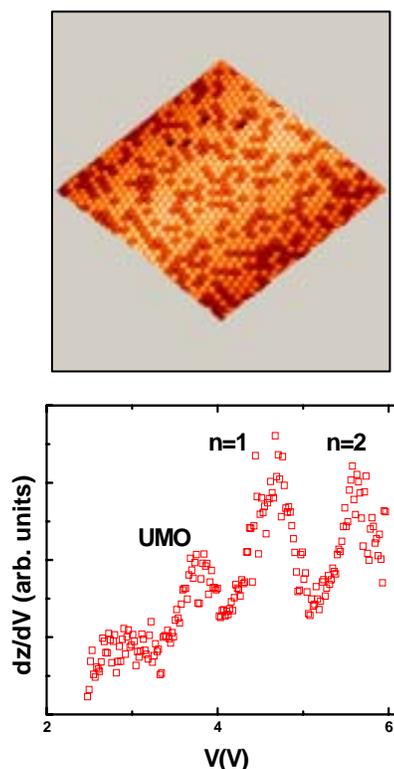
[1] G. Binnig, K.H. Frank, H. Fuchs, N. Garcia, B. Reihl, H. Roher, F. Salvan, and A.R. Williams, *Phys. Rev. Lett.* 55 (1985) 991.

[2] S.F. Alvarado, P.F. Sedler, D.G. Lidzey, and D.D.C. Bradley, *Phys. Rev. Lett.* 81 (1998) 1082.

In this case, the STM tip feedback is engaged at a chosen current setpoint. The voltage in the tunneling gap is then varied as in the  $I$ - $V$  measurement but the feedback now keeps the current constant, causing the tip to retract abruptly at voltages corresponding to molecular resonances. The exponential dependence of the tunneling current on the tip-sample separation leads to small variations in  $Z$  which are monitored. The constant current negates the limitations of  $I$ - $V$  spectroscopy noted above.

Knowledge of interfacial electronic structure at organic-metal and organic-organic heterojunctions is a prerequisite for the development of a wide range of organic electronic applications, including organic light emitting diodes, organic photovoltaics, and field effect transistors.

The figure below shows STM images of one monolayer of  $C_{60}$  on  $Ag(111)$  and corresponding localized unoccupied electronic structure measured using  $Z$ - $V$  spectroscopy. UMO=unoccupied molecular orbital;  $n=1, 2$  are tentatively assigned to image state resonances.



The figures provide sample STM data and preliminary Z-V measurements for thin layers of C<sub>60</sub> and pentacene grown on a silver substrate. These molecular materials are of interest for a variety of applications, including photovoltaics and organic field effect transistors.

*STM measurement of 2 and 3 monolayer regions of pentacene coexisting on Ag(111) and Z-V localized spectroscopy over the second layer region.*

**Future Work:** Z-V spectroscopy will be used to investigate the localized electronic structure in the vicinity of interfaces between C<sub>60</sub> and pentacene and other organic donor-acceptor systems of interest for photovoltaic applications. This information can then be correlated directly to molecular resolved structural information to determine the impact of molecular structure at the interface on donor-acceptor band offsets.

