

Determination of the Molecular Electrical Properties of Self-Assembled Monolayers of Compounds of Interest in Molecular Electronics

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In this communication we report preliminary results with a tuning fork-based scanning probe microscope (SPM) technique combined with current–voltage (i – V) measurements, for the rapid characterization and screening of monolayer films in an inert atmosphere. We studied self-assembled monolayers (SAMs) of a variety of molecules with different structures that are being considered for possible application in molecular electronic devices and devised a high throughput analysis method for their characterization.

There is currently a high level of interest in the electrical properties of isolated molecules especially in the use of unconventional substances and single molecules or SAMs to construct electronic devices.^{1–3} Advances in synthetic supramolecular chemistry, coupled with recent developments in device fabrication techniques and scanning probe techniques,⁴ allow single molecules to be manipulated and investigated electronically. Synthetic chemistry is mature enough to offer a huge range of molecular structures with different properties. A challenge has been to develop reliable and fast screening methods to characterize electronic properties of molecules and to be able to correlate the electrical behavior of the molecules with their structure.

A few initial efforts have used long molecular wires across lithographically patterned proximal gold-coated probes separated by approximately 10 nm, but these studies were unreliable and not suitable for molecules shorter than the array gap.^{1,3} The Langmuir–Blodgett technique was also used to prepare a single molecular layer which was sandwiched between Al and Ti/Al contacts to form a device.⁵ Other efforts employed a nanopore arrangement or mechanically controllable break junctions⁶ where electronic measurements were performed between adjustable proximal point contacts. Still others have been performed in nanopores on a structure⁷ that has a metal top contact formed by vacuum evaporation, an active SAM, and a metal bottom contact. These techniques have provided interesting results, but the preparation of such nanostructures is time-consuming and fabrication-intensive. An attractive approach is to utilize a conducting atomic force microscope (AFM) tip⁸ as one of the contacts to form a metal–molecule–metal junction. We show here that a

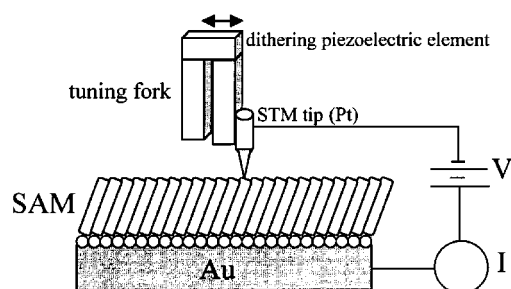


Figure 1. Schematic representation of the measurement and formation of the metal–molecule–metal junction with a tuning fork-based SPM tip contacting the SAM on Au (not to scale). Ar atmosphere.

tuning fork-based scanning probe microscope (SPM)⁹ for rapid probe positioning combined with i – V measurements can be used to characterize and screen a large variety of molecules with different electrical properties.

In the work reported here the molecules of interest were assembled on a flat gold substrate and then studied by this technique in a controlled environment. The basic principle of the device is illustrated in Figure 1. The tip, sharpened by electrochemical etching, as used for STM tips, is attached to a small tuning fork. The tuning fork is excited by an attached piezoelectric element, generally oscillating in the region of 33 to 100 kHz, and is used for rapid approach of the tip to the SAM. When the tip just contacts the SAM surface, the amplitude and frequency of the oscillation decrease, and this can be used to sense the presence of a surface. This same technique is used with many near-field scanning optical microscopy (NSOM) instruments to maintain tip position. Thus, the tip can be moved to the substrate and positioned fairly rapidly. The tip is then retracted slightly (about 10 nm) and moved to a different location on the SAM. The potential of the tip is swept with respect to the substrate over the desired potential range, and the current is recorded, as the tip is again approached toward the SAM, this time in small steps (e.g., 2 Å). Before the tip contacts the molecules in the SAM, essentially no current flows. Upon contact, when the potential across the SAM containing electron-donating or electron-withdrawing groups attains a characteristic bias voltage, a current flows through the film. The magnitude of the current that flows in the i – V curve is a function of the conductance of the molecules.

The synthesis of the compounds reported here and the preparation and characterization of the SAM have been described elsewhere^{10,11} (see Supporting Information). The i – V measurements were made in an argon atmosphere on seven compounds (Table 1).¹² Figure 2 shows typical i – V characteristics of compounds **I**, **II**, and **IV** when the tip first contacts the surface of a SAM. For the alkythiol (**I**) only the expected tunneling behavior at biases beyond about ± 4.8 V is seen (Figure 2A).

Figure 2B shows the i – V curve of a SAM of 2'-ethyl-4,4'-bis(phenylethynyl)-1-benzenethiolate (**II**) on gold. When the negative scan reaches about 2.8 V, a peaked current response of a few pA is observed. This type of response has been observed previously in similar studies with nanopore junctions and has been

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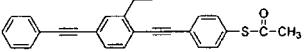
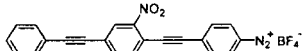
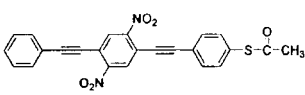
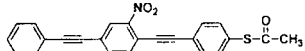
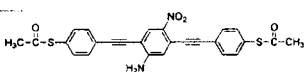
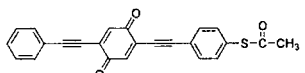
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(12) The number of molecules contacting the tip estimated from the tip radius (~5 nm), the van der Waals radius (~0.35 nm) of the molecules for a deformation depth of 0.2 nm of the SAM was about 35.

Table 1. Structures and Negative Threshold Tip Bias (V_{TH}) for Electric Conduction of Several Compounds^a

compound	structure	V_{TH} (V)
I	<chem>CH3(CH2)11SH</chem>	~ -4.8
II		-2.79 ± 0.15
III		-1.64 ± 0.20
IV		-1.76 ± 0.15
V		-2.25 ± 0.10
VI		-2.09 ± 0.09
VII		-1.58 ± 0.15

^a V_{TH} values reported here are taken as the average of the first negative peak voltage of 15 to 25 i - V curves for each compound (standard deviation shown). The acetate groups are removed during the deposition using NH_4OH to afford the free thiol. The diazonium salt probably affords the gold-aryl bond upon loss of N_2 ; however, further characterization is needed.

called a negative differential resistance (NDR) effect.⁷ The current flow through the film corresponds to the onset of conduction, and the shape of the response is different than the tunneling behavior seen with **I**. Similarly a scan to positive tips bias, either initially or after the scan to negative values, results in the appearance of an anodic peak at about 2.9 V.

At a bias voltage between -2.6 and 2.6 V, the molecules are nonconductive. The presence of the dinitro substituents in the central ring in **IV** modifies dramatically the voltammetric response of the molecule. With electron-withdrawing and electroactive nitro groups the threshold tip bias (V_{TH}) for electron conduction shifts to a less negative value as compared to that for **II**. This i - V curve also clearly shows several current peaks in the negative bias region, which are sometimes observed in the reverse scan (not shown). These peaks are probably related to the well-known multielectron redox activity of dinitro compounds. With this compound, an initial scan to positive tip bias does not show a peak; however, an anodic peak appears after the scan to negative bias. Some of the negative V_{TH} for several compounds are summarized in Table 1. The compound with a central quinone structure (**VII**) had the least negative V_{TH} of the compounds listed.

Note also that the linking group to the gold substrate affects the measured response via contact impedance differences at the molecule/metal junction. The diazonium salt (**III**) shows a smaller barrier for interfacial electron transfer as compared with the same compound with a thiol linkage (**V**). Several compounds, for example, **III**, **IV**, and **VII**, showed distinct multiple cathodic peaks (see, e.g., Figure 2C). It was possible to obtain reasonably reproducible mechanical contact between the tip and the SAM

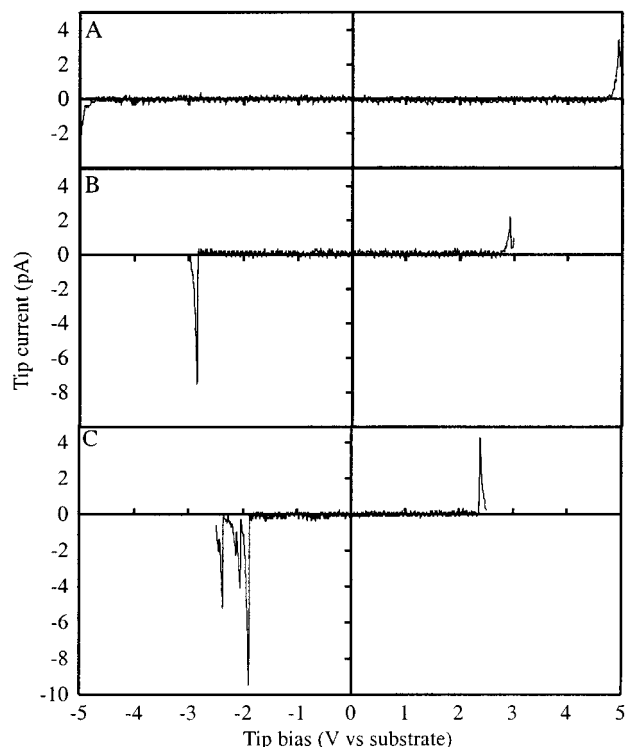


Figure 2. i - V characteristics of compounds (A) **I**, (B) **II**, and (C) **IV** when the tip is barely in contact with the surface of a SAM. Potentials represent tip bias vs gold, and all scans were taken from 0 V first toward negative bias and then to positive values.

to study the effect of force (or tip/substrate gap) on the i - V behavior (Figure S1). Three i - V curves were recorded as the tip approached the surface in 2 \AA steps of a SAM of **II** on gold. V_{TH} for this compound was apparently not highly sensitive to the tip/substrate gap, although the magnitude of the current was.

In summary, we have shown that it is possible to make stable electrical and mechanical contact to SAMs by tuning fork-based SPM tips. The resulting junctions of some compounds show peak-shaped i - V curves (an NDR effect), which agree well with results reported previously.⁷ Like conducting probe AFM, this technique is promising as a method for fast characterization and screening of molecules with different electronic properties in a SAM configuration for possible application in molecular electronic devices. We are currently exploring this technique and characterizing additional compounds. By compiling data for a wide range of molecules, it should be possible to establish a useful correlation between molecular structure and electronic properties.

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Supporting Information Available: Synthesis and preparation of SAMs, i - V curves of **II**, and additional references (PDF). This material is available free of charge at <http://pubs.acs.org>.

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