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Characterization of the Conductivity of Organic Thiols by Field Emission Microscopy and Field Emission Spectroscopy

S. T. Purcell,*,[†] N. Garcia,[‡] Vu Thien Binh,[†] L. Jones, II,[§] and J. M. Tour[§]

Contribution from the Laboratoire d'Emission Electronique, DPM, UA CNRS, Université Claude Bernard Lyon 1, 69622 Villeurbanne, France, Fisica de Sistemas Pequeños, Consejo Superior de Investigaciones Cientificas, Universidad Autonoma de Madrid, 28049 Spain, and Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

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Abstract: The conducting properties of two organic thiols (5-mercapto-2,2′-bithiophene and 4-mercaptobiphenyl) deposited by the self-assembly method on Pt tips have been characterized in ultrahigh vacuum by field emission microscopy and spectroscopy. It was shown that these two molecular species can be successfully adsorbed from solution on the Pt tip. The presence of the molecules causes a large decrease in the required field emission voltages by a factor of ~3–5. Measurement of the total energy distributions of the emitted electrons showed that the electrons are emitted from a narrow band which is not pinned at the Fermi level but which shifts to lower energy with increased applied field. The molecules thus appear more like an insulator than a conductor. Significant current-induced heating of the molecules was found: for example, $\Delta T \approx 80$ K for 0.3 nA. Taken together these properties pose problems for the use of these and similar one-dimensional molecules as current-carrying connections in proposed nanoscale electronic applications. However, when used in the subpicoampere range, the current through the wire may be sustainable and dissipation small. In general, these experiments open a door to exploring other molecules.

Introduction

One of the most important points for the construction of nanostructure-based devices is the finding of wires at the nanometer scale that can be assembled and connected for communication between the nanostructures. For this purpose one could envisage the possibility of connecting the structures by thin metallic wires (~1 nm diameter). However, this will be a tremendously demanding task. A proposed alternative is to search for organic one-dimensional elongated molecules that can self-assemble and have enough conductivity to transfer electrons between the nanostructure devices.[1]

A class of possible candidates for interconnection molecules are long-chain organosulfur compounds which form robust, ordered monolayer films on Au,[2] particularly those compounds terminated with thiols.[3,4] These have been shown in extensive studies to adhere with a strong covalent bond between the sulfur head group and the Au surfaces when deposited in solution and to have their long axes oriented away from the substrate surface. These properties may make the self-assembling of these molecules as interconnections at prepared sites on the nanostructures possible if appropriate techniques and geometries can be found for controlling their positioning. However, despite an intense research effort in this field, the important qualities of the conductivity and the dissipation of heat in the molecules are as yet unknown.[1a] This is largely due to the experimental difficulty of attaching electrodes to the nanometric scale molecules. In this paper we present studies by the field emission (FE) technique in ultrahigh vacuum of the conductivity and current-induced-heating of one-dimensional thiol molecules of ~10 Å length deposited on preprepared and characterized Pt field emitters. This method has the crucial advantage of eliminating the difficult connection of a second electrode to the molecule.

Experimental Section

Preparation of Organic Thiols. 5-Mercapto-2,2′-bithiophene[5] (defined as thiol A; see Figure 1a) was prepared by the following sequence of reactions. (1) 2,2′-Bithiophene was converted to 5-bromo-2,2′-bithiophene with *N*-bromosuccinamide in a mixture of acetic acid and chloroform. (2) Lithium halogen exchange on 5-bromo-2,2′-bithiophene with *n*-butyllithium followed by quenching with trimethylsilyl chloride afforded 5-(trimethylsilyl)-2,2′-bithiophene which was (3) treated with *n*-butyllithium and then dimethyl disulfide to afford 5-(methylthio)-5′-(trimethylsilyl)-2,2′-bithiophene. (4) Treatment with sodium methanethiolate in *N,N*′-dimethyl-*N,N*′-propyleneurea (DMPU) afforded the desired 5-mercapto-2,2′-bithiophene. All the intermediates as well as the final product were purified by flash chromatography on silica gel. The final product was >99% pure, and it had the following spectral characteristics: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (dd, J = 5.0, 1.1 Hz, 1 H), 7.19 (dd, J = 3.6, 1.2 Hz, 1 H), 7.05 (ABq, J = 3.6 Hz, $\Delta\nu$ = 6.6 Hz, 2 H), 7.00 (dd, 5.1, 3.6 Hz, 1 H), 3.54 (s, 1 H) (the NMR was recorded in the presence of triethylamine to convert the conjugately added dimer to the monomer[6]); LRMS calcd for $C_8H_6S_3$ 198, found 198. The length of this molecular system is approximately 10 Å.

[†] Université Claude Bernard Lyon 1.

[‡] Universidad Autonoma de Madrid.

[§] University of South Carolina.

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(1) (a) Workshop on Nanoscience: Transport in nanoscale structures, May 25–28, 1993, Seattle, WA; Everitt, H. O., Ed.; sponsored by the U.S. Army Research Office. This booklet contains a discussion on properties and characterization of molecular wires and clusters cooordinated by R. P. Andres, N. Garcia, and G. Whitesides where the problem and necessity of finding one-dimensional organic conducting wires to connect nanostructures is discussed. (b) See also: Mirkin, C. A.; Ratner, M. A. *Annu. Rev. Phys. Chem.* **1992,** *43,* 719–754.

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(3) Porter, M. D.; Bright,T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987,** *109,* 3359–68.

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(6) Ponticello, G. S.; Habecker, C. N.; Varga, S. L.; Pitzenbeger, S. M. *J. Org. Chem.* **1989,** *4,* 3223.

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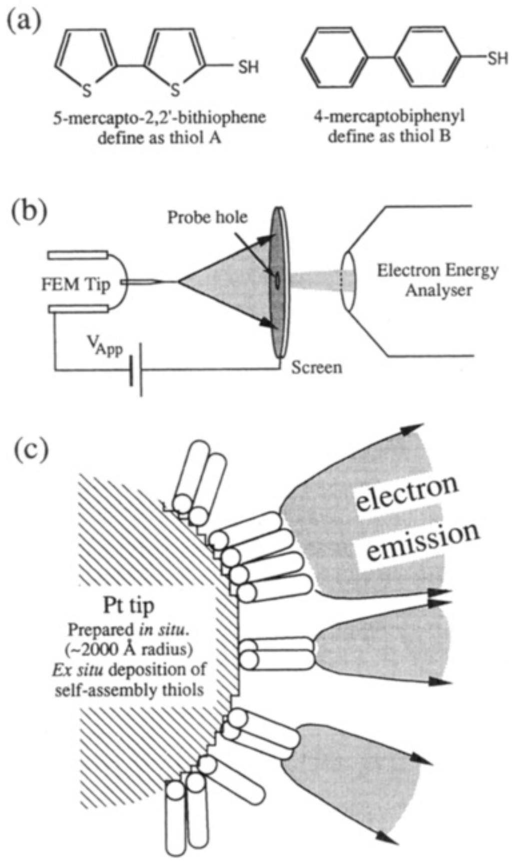

Figure 1. (a) Organic thiols used in the experiment. (b) Experimental setup for the measurement of the electron energy distributions. Not shown are the mechanical and electrical deflections which allow selection of the emission zone that passes through the probe hole. (c) Schematic depiction of the field emission from a tip with adsorbed thiol molecules.

4-Mercaptobiphenyl[7] (defined as thiol B; see Figure 1a) was prepared according to the following synthetic sequence. (1) 4-Bromobiphenyl was treated with 2 equiv of *tert*-butyllithium and then with dimethyl disulfide to afford 4-(methylthio)biphenyl. (2) The 4-(methylthio)-biphenyl was treated with sodium methanethiolate in DMPU to provide the desired 4-mercaptobiphenyl. All the intermediates as well as the final product were purified by flash chromatography on silica gel. The final product was >99% pure, and it had the following spectral characteristics: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, $J = 8.4$ Hz, 2 H), 7.31 (m, 1 H), 3.47 (s, 1 H). LRMS calcd for $C_{12}H_{10}S$ 185, found 185. The length of this molecular system is approximately 10 Å.

Experimental Setup. The conductivity properties were studied by using field emission[8] from the thiols deposited on Pt field emitters. Pt was used in place of the more common gold substrate because gold field emitters are very unstable even at room temperature and cannot be used for reproducible comparision studies. Pt has similar resistance to oxidation as Au and has been used successfully as a substrate for self-assembled layers of the aromatic molecules.[9] Pure polycrystalline Pt wire was first spot-welded on a W wire heating loop that was in contact with a liquid air reservoir. Sharp Pt field emitters were produced by electrochemical etching in a $CaCl_2$−HCl solution.[10] The tips were studied in an ultrahigh vacuum (UHV) system (base pressure 5×10^{-11} Torr) equipped with a channel plate for imaging the field electron emission microscopy (FEM) and a modified commercial electron energy analyzer with a nominal resolution of 10 meV placed behind a probe hole (see Figure 1b) for field emission electron spectroscopy (FEES). The electron energy analyzer allows measurement of the total energy distributions[8] (TED's) of the emitted electrons. The tip mounting system allowed both mechanical and electrical deflection for immediate changing between FEM or FEES. The FE patterns were filmed by video camera. Freshly etched Pt tips were inserted in the UHV and were then cleaned by a combination of heating, ionic bombardment, and field desorption until clean field emitter patterns were obtained. The *I*/*V* characteristics and FE patterns were recorded after final tip preparation. The general idea was to make quantitative measurements on the *in situ* prepared tips for initial conditions just before exposure to the organic molecules so that quantitative comparisons could be made.

Deposition of the Organic Thiols. The thiols were deposited in a N_2 environment on the cleaned and characterized Pt tips immediately after they were removed from the UHV. The deposition of the molecules was performed by immersing the Pt emitters in solutions of 7 mg of either of the thiols dissolved in 10 mL of dry dichloromethane for roughly 18 h. The tips were lightly rinsed in the pure solvent after the deposition cycles. The tips were immediately reintroduced into the UHV after the rinsing. The vacuum system was only partially baked out after the reintroduction to avoid damaging the molecular films, but pressures of $(2-5) \times 10^{-10}$ Torr were obtained before starting the FEM/FEES studies. Five depositions were made in total: three of 5-mercapto-2,2′-bithiophene (defined as thiol A), one of 4-mercaptobiphenyl (defined as thiol B), and one control immersion in the pure solvent. The emission currents were very unstable at room temperature after exposure to the molecules and solvent due to temperature-induced diffusion, especially assisted by the applied field. To improve the stability, all FEM and FEES measurements reported here were made at liquid-air temperatures (~80 K) with currents well under the nanoampere range. Note that field emission currents and spectra of the clean or molecule-covered tip vary little in the 80−300 K range because the tunneling barriers depend only slightly on temperature. A schematic diagram depicting emission from the tip with the molecules is shown in Figure 1c.

Results

The experimental results consist of three basic measurements: (1) The field emission patterns. These give information on the spatial distribution of the field emission areas with absolute resolution of ~20 Å (see ref 8 for example). (2) The *I*/*V* characteristics. These allow analysis of the modification of the apparent tunneling barrier. They must be correlated with (3). (3) The measurement of the total energy distributions of the emitted electrons. The TED's of the emitted electrons[8] give details on the tunneling barrier, the energy of the emission with respect to the Fermi level, and the local temperature at the emission region.

Influence of the Solvent. To study the behavior of the pure solvent on the FE, the same sequence of deposition was followed but without the organic thiols. In Figure 2 we show photographs of field emission patterns and *I*/*V* characteristics of a Pt field emitter after UHV treatment and after immersion of the tip in the pure solvent. The pattern of the clean tip and after exposure to the solvent shows the 4-fold symmetry of the tip-ending (100) single crystal with the low work function (100) plane in the center. The pattern of the tip after exposure to the solvent consisted of many unstable bright spots. This is the normal state of a tip that has just been introduced to the vacuum. In Figure 2c the corresponding Fowler−Nordheim plots are given which show no appreciable differences in the overall FE behavior.

Influence of the Organic Thiols. The field emission patterns and *I*/*V* characteristics after deposition of the thiol A and after

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[7] For the original preparations of thiol B, see: (a) Kharasch, N.; Swidler, R. *J. Org. Chem.* **1954**, *19*, 1704. (b) Klemm, L. H.; Karchesy, J. J. *J. Heterocycl. Chem.* **1978**, *15*, 281 & 561.

[8] For examples, see: Gomer, R. *Field Emission and Field Ionization*; Harvard University Press: Cambridge, MA, 1961. Gadzuk, W. *Rev. Mod. Phys.* **1973**, *45*, 487−548.

[9] Soriaga, M. P.; Hubbard, A. T. *J. Am. Chem. Soc.* **1982**, *104*, 3937−3945 and references therein.

[10] Nieuwenhuys, B. E.; Sachtler, W. M. H. *Surf. Sci.* **1973**, *34*, 317−336.

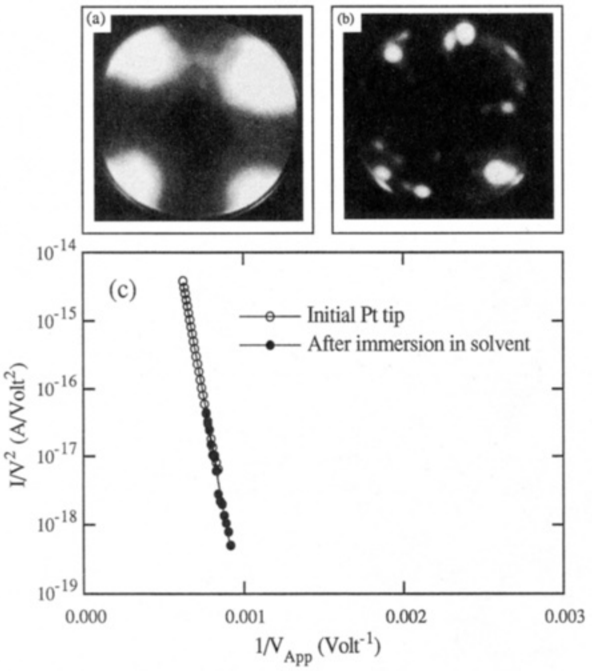

Figure 2. Field emission patterns from (a) Pt (100) (1500 V) and (b) Pt (100) after being immersed in the dichloromethane for 18 h and then reinserted in the UHV (1400 V). (c) Fowler–Nordheim plots for the emission from the cleaned Pt (100) and after immersion in the solvent.

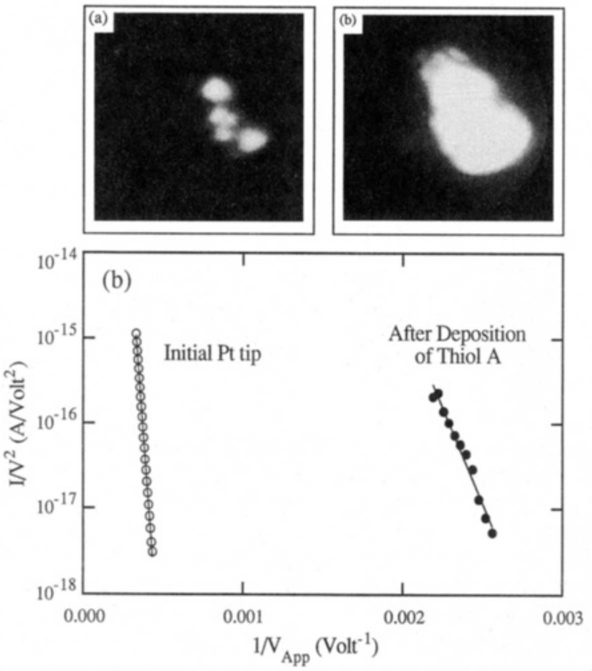

Figure 3. (a, b) Field emission patterns from a Pt (100) after deposition of thiol A (400, 500 V). The voltages were increased from (a) to (b) to show that a relatively large area of the tip has been affected by exposure to the organics. (c) Fowler–Nordheim plots for the emission from the cleaned Pt (100) and after immersion in the thiol A.

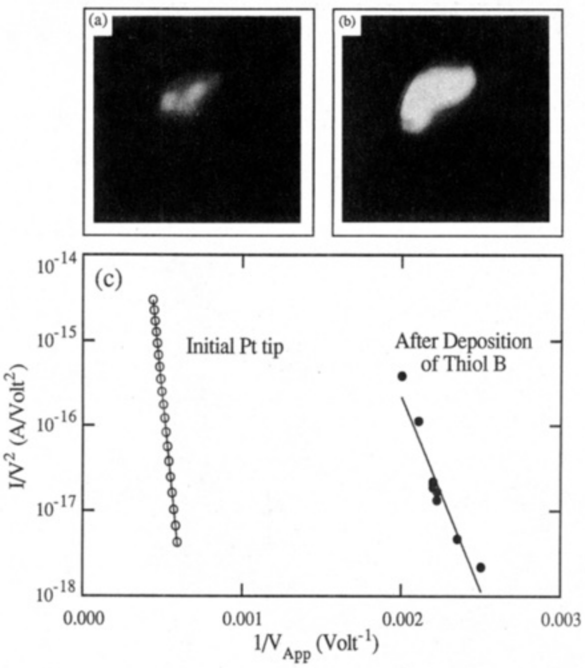

Figure 4. (a, b) Field emission patterns from a Pt (100) after deposition of thiol B (550, 600 V). (c) Fowler–Nordheim plots for the emission from the cleaned Pt (100) and after immersion in thiol B.

deposition of thiol B are shown in Figures 3 and 4, respectively. In contrast to the above cases, the emission patterns from the tips after deposition of the organics showed emission from localized areas at voltages of 3–5 times lower than the initial Pt tips. The emissions were not obviously related to the crystal symmetry of the apex. More areas of emission at somewhat higher voltages can be seen by oversaturating the lowest emission areas (see photos in Figures 3a,b and 4a,b). The emissions were relatively more stable than in the case of the pure solvent, and the features tended to be broader or less punctual, indicative of emission from a more continuous layer rather than very localized sites. Similar emission properties were found for all four depositions of the organic molecules. These results establish that successful deposition of the organic thiols on the Pt tips was achieved. The main result from FE was that the presence of the thiols caused a very large reduction of the effective tunneling barrier. This large reduction for the molecules is difficult to analyze at this time because of the gross uncertainties of the work function and the electric field at the vacuum side of the molecule. However, two factors that reduce the barrier are (1) the reduction of the physical length of the tunneling barrier by the molecule and (2) the fact that the field will tend to be enhanced at the molecules due to their reduced size and protruding geometry.[11]

TED's of the emitted electrons for a clean Pt tip at two voltages are shown in Figure 5a. As is generally the case for metal emitters, the spectrum consists of a single peak pinned at the Fermi energy (E_F) reflecting a continuous, broad distribution of the electron density. The high-energy side of the spectrum is controlled by the temperature through the Fermi–Dirac distribution. The low-energy side is controlled by the shape of the tunneling barrier which favors higher energy electrons. It widens with applied voltage because the increase in the slope of the tunneling barrier allows proportionally more electrons to be emitted from lower in the conduction band.

The TED's for the organic molecules show different, specific characteristics, an example of which is shown in Figure 5b for thiol A. The TED shown consists of a single peak roughly 0.2 eV wide. This peak is not fixed at E_F, but shifts linearly with applied voltage. Also the peak shape does not change with applied voltage. As we discuss below this means that the electrons are emitted from a localized narrow band and not from a wide conduction band. The results were similar for all three depositions of thiol A and the deposition of thiol B. The positions of the peak and their shifting with field varied for the different bright emitting areas, but their spectra almost always

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[11] Atlan, D.; Gardet, G.; Vu Thien Binh; Garcia, N.; Saenz, J. J. *Ultramicroscopy* **1992**, *42–44*, 154–162.

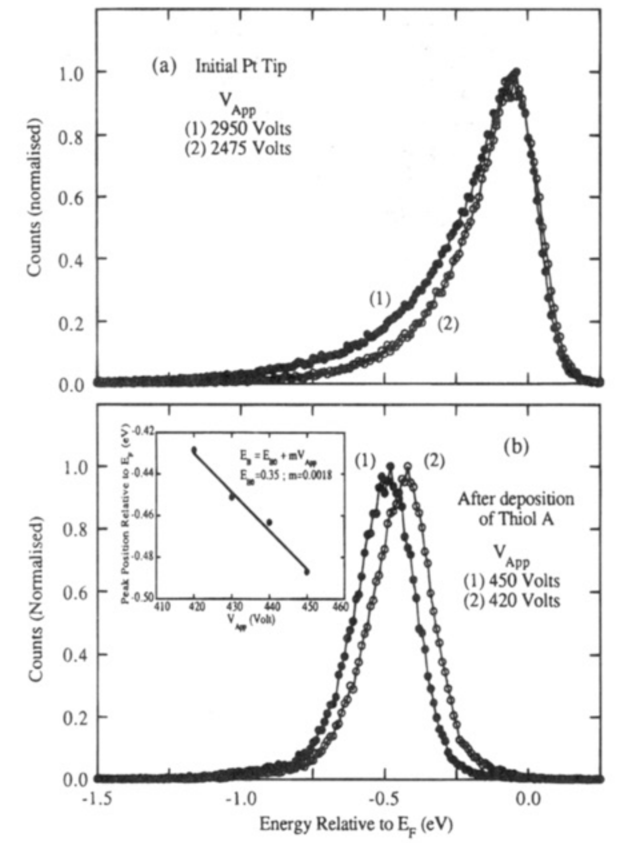

Figure 5. Typical TED's for emission from (a) the initial Pt tip and (b) after the deposition of thiol A on Pt. Inset: shift of the TED with the applied electric field.

consisted of one peak whose extrapolated zero-field value was above E_F. Similar results have been observed for the emission through various organic molecules adsorbed on W and Mo emitters in UHV[12] and more recently on high metallic protrusions formed on W field emitters.[13]

During the measurements it was very apparent that currents even in the subnanoampere range considerably increased the instability of the emitted current. We interpret these instabilities as an increase in the temperature during FE. We have made a quantitative measurement of this in the case of thiol A by measuring the effect of the current on the emission spectra. As for emission from a metal emitter, the slope of the high-energy edge of the spectra decreases with increasing temperature. By fitting the spectra to the known function for field emission,[8] the relative temperature change ΔT due to the field emission current at the emission area can be found.[14] In Figure 6 we plot ΔT as a function of current. In this example, ΔT is ~75 K with the base tip cooled to 80 K for only 0.3 nA current. Therefore, to have FE without heating effects, one has to go to subpicoampere currents.

Discussion

The experiments have revealed two features that have a direct bearing on the conductivity of the molecules: (1) The FEES spectra showed that the emission comes from a narrow band which is not pinned at the Fermi level. (2) There were substantial heating effects in the molecules for very moderate currents.

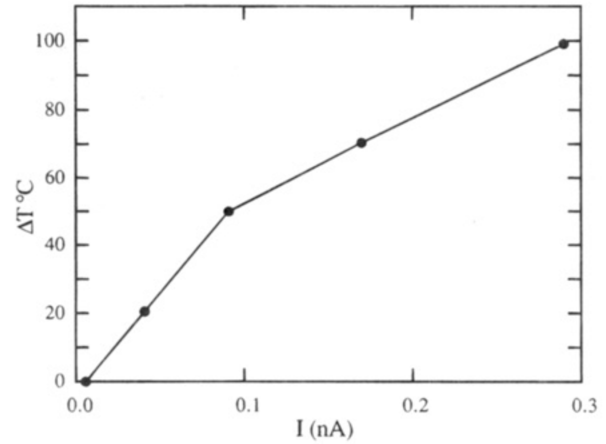

Figure 6. An example of current-induced temperature increases during field emission from thiol A as measured from the high-energy side of the TED's.

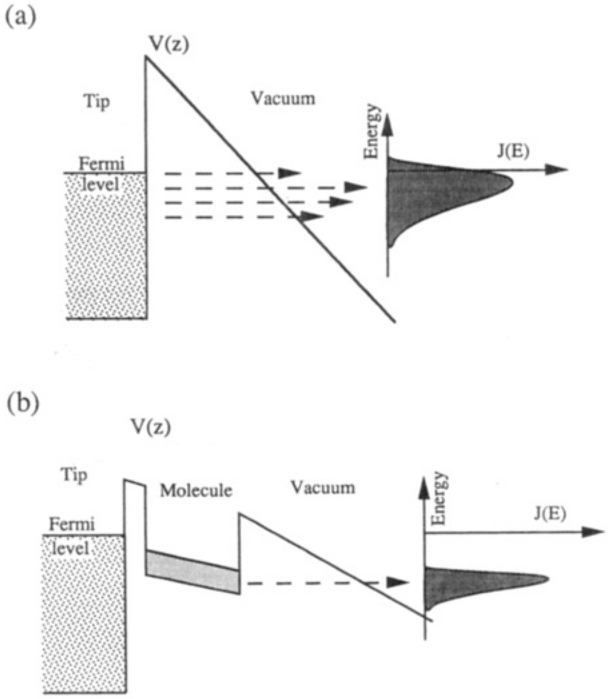

Figure 7. Schematic potential diagrams for field emission from (a) a metal emitter and (b) a metal emitter with an adsorbed species on its surface.

The emission through polyatomic molecules has been a subject of research in the field emission community in the past (see ref 12 for examples). Various models have been used to explain the results. The simplest is that the tunneling occurs through an additional potential well due to the molecule. Potential diagrams for emissions from bare and molecule-covered metal tips are shown schematically in parts a and b, respectively, of Figure 7. For the bare tip the electrons pass through the tunneling barrier of ~15 Å directly from the Fermi sea. For the case of the molecules, the basic idea is that local electron levels will exist in the molecule due to its reduced dimension and that tunneling occurs mainly through or from these levels. The validity of this picture is supported by the narrowness of the peak and the independence of its shape on the applied field. The shifting of the peak to lower energy with the electric field is a consequence of the molecule not containing sufficient free electrons to provide complete electrical screening. This implies field penetration into the molecule, a signature of insulating behavior. In the presented example the molecule

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(12) Swanson, L. W.; Crouser, L. C. *Surf. Sci.* **1970**, *23*, 1–29. Schutt, W.; Koster, H.; Zuther, G. *Surf. Sci.* **1974**, *45*, 163–188.

(13) Vu Thien Binh; Purcell, S. T.; Garcia, N.; Doglioni, J. *Phys. Rev. Lett.* **1992**, *69*, 2527–2530.

(14) Vu Thien Binh; Purcell, S. T.; Gardet, G.; Garcia, N. *Surf. Sci.* **1992**, *279*, L197–201.

blocks all direct tunneling from the Fermi sea of the Pt tip. Similar results were also found in earlier studies on polyatomic molecules,[12] though the reduction in emission voltages and reduction of the emission at the Fermi level were generally less marked than for these relatively longer thiol molecules.

Conclusions

These field emission studies have demonstrated that the thiol molecules in contact with Pt surfaces do not pass electrons directly from the Fermi sea of the metal and that important temperature rises occur even for currents well under the nanoampere range. The molecules have possibilities as interconnecting wires without heating effects for currents in the subpicoampere range. These points should be considered in the possible use of these molecules as interconnecting wires in proposed nanoscale electronics. Finally, the experiments on these particular molecular wires open the door for continuing to study other wires that may have more free or extended electrons.

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Note Added in Proof. Subsequent to the completion of the FE studies, we deposited two similar thiols on evaporated Pt films. Thicknesses equivalent to 1/3 to 1/2 of a molecular layer were found by ellipsometry measurements. This is in general agreement with the FE studies presented here.