The arguments presented above imply that stretched-exponential kinetics, with $\beta \approx 1/2$, should describe a general class of physical processes that are rate-limited by diffusion at a surface. This contrasts with the usual view that surface on-off processes are characteristically rate-limited by the equilibrium energy of adsorption and therefore the desorption-adsorption kinetics should be exponential. The origin of the nonexponential kinetics in our model does not support the common interpretation of a distribution of relaxation times or of predominantly collective motions; they are simply a logical consequence of the experimental geometry. Kinetic processes that fall into this category are expected to be widespread, in fields from tribology to biology.

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Molecular Light Emission Induced by Inelastic Electron Tunneling

Eli Flaxer, Ofer Sneh, Ori Cheshnovsky*

Light emission from molecular layers has been induced by inelastically tunneling electrons in a tunneling junction. The fast quenching of molecular emission on metal surfaces was suppressed by use of the "transparent conductor" indium-tin-oxide for the junction electrodes. The emission measurements have been made in squeezable tunneling junctions as small as 10^{-9} square centimeters, coated with 9-10 dichloro-anthracene layers. At a bias of 2.5 to 3.5 volts, yields of 5000 photons per microcoulomb were observed. Evidence for the molecular origin of the emission is given. This method shows good prospects for use in the imaging of chromophores on surfaces with atomic resolution.

The appearance of the scanning tunneling microscope (STM) inspired the birth of a wide class of scanning probe microscopes (SPMs). In addition to their excellent spatial resolution, SPMs are useful for probing the nature of species on the surface. Impurities or perturbed states on a surface are routinely measured with an STM by scanning with a variable bias (*1*). Spectroscopy of local densities of states can be probed with current voltage curves of the tunneling current (*2*). Images of adsorbed molecules and molecular layers have been viewed on surfaces (*3*). Vibrational spectroscopy of a single molecule adsorbed on a surface has been recorded (*4*) with current voltage spectroscopy. However, spectroscopic mapping of specific molecules on surfaces has not been reported so far.

Optical spectroscopy is a possible probe of adsorbed molecules. However, the spatial resolution of conventional optical spectroscopy is limited by the wavelength of the excitation source. Substantial effort has been directed toward overcoming the intrinsic resolution limits of the light microscope. The most promising solution is probably the near field microscope (*5*), which scans an object close to its surface with a small aperture while monitoring light transmission or fluorescence. In spite of recent progress (*6*), this microscopy is yet in its infancy and is limited to ~100 Å in spatial resolution.

To overcome such limitations, one could excite molecules on surfaces by inelastic tunneling processes in the STM and record their light emission. Such a method would combine the high spatial resolution of the STM for excitation with the specificity of the fluorescence spectroscopy in order to scan and identify with atomic resolution chromophores on surfaces.

Light emission from STM junctions has been previously observed. Gimzewski, Berndt, and co-workers have explored inverse photoemission (*7*), electron hole recombination in semiconductors (*8*), and plasmon emission from solid-state surfaces (*9*). Recently, the same group observed enhanced photon emission from small metallic particles on surfaces (*10*). However, no reports of light emission from molecules adsorbed on surfaces in STM junctions are known.

Two processes are fundamental to molecular light emission in STM junctions: molecular excitation by inelastic tunneling, and the quantum efficiency of light emission. Theoretical estimates of the cross section for the excitation process (*11*) (about 10^{-17} cm^2 for electronic excitations) predict millions of excitations per second for typical tunneling currents (nanoamperes) in the STM. However, the quantum efficiency for light emission of molecules adsorbed on conductive surfaces is very low (*12*) (of the order of 10^{-6}), precluding a measurable emission rate from the excited molecules.

The very low emission efficiency from molecules adjacent to metallic and semiconductor surfaces is caused by the fast deexcitation processes (*13*) governed by energy transfer to nonradiative surface excitations (Auger processes). We replaced

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School of Chemistry, Tel-Aviv University, 69978 Tel-Aviv, Israel.

*To whom correspondence should be addressed.

the conventional conductive STM surface by a "transparent conductor" (*14*) to block these emission-quenching processes. Natural candidates for such surfaces are indium-tin-oxides (ITOs). This family of materials is characterized by a wide optical transparency (up to 4.1-eV photon energy) and maintains a conductivity sufficient for an STM experiment. The band structure of ITOs, responsible for the optical transparency in the visible and near ultraviolet, will also preclude efficient energy transfer processes in this energy range, thus allowing for efficient light emission from molecules excited on the ITO surface.

To test this idea, we constructed large-area, squeezable tunnel junctions (*15*). Our apparatus (Fig. 1) allows us to simultaneously control the tunneling current and monitor the emitted light from the junction. One tunneling electrode (#2) is a laser-quality quartz lens (radius of curvature, 50 cm), coated with ITO. This electrode is negatively biased in the range of 0 to 5 V. The other tunneling electrode (#1) is made of a fused silica light guide. One end is optically polished and coated with ITO or a transparent gold surface (~200 Å layer); test molecules were coated onto this surface. The other end of the light guide is coupled to a photomultiplier (#6) with index-matching gel (#7). The spacing between the electrodes is coarsely controlled with a leaf spring (#3) loaded with a micrometer screw (#4). The resolution of the micrometer screw (about 1 μm) is enhanced by the ratio of the spring constants of the leaf spring and the quartz lens (about 1000), leading to a practical coarse-tuning resolution of 10 Å. The fine tuning of the tunneling gap is applied with a solenoid (#5), whose current is controlled by a feedback loop to keep a predetermined tunneling current in the junction. We assume that the junction surface is atomically flat and that the main tunneling current originates from the surfaces that are the closest (within 1 Å) to the counter surface. Such assumptions result in the upper limit of 3×10^{-6} cm^2 for the tunneling junction area.

We recorded light emission from bare tunneling surfaces and from surfaces coated with molecules as a function of the bias voltage in the range of 0 to 5 V. We used 9–10 dichloroanthracene (DCA) and the laser dyes DCM and coumarin, molecules that are known for their high emission quantum yield and their photochemical stability. We applied molecular layers by spreading and drying defined volumes of dye solutions. Depending on the initial concentration, these layers corresponded (on the average) to 0.5 and 0.05 monolayers. However, we have no direct knowledge of the aggregation state of the adsorbed molecules. Typical tunneling currents were 10 to 50 nA.

Our results (Fig. 2) show that the bare ITO surface emits light only at biasing voltages larger than 4.0 V, which corresponds to electron hole excitation over the optical gap of ITO. In contrast, ITO surfaces coated with several chromophore molecules showed enhanced light emission onsetting at a bias voltage that roughly corresponded to the allowed excitations energies in the chromophore. At this bias voltage (~2.6 eV for DCA), the bare ITO surface does not show any photon emission, in accord with its wide optical band gap. Enhanced light emission, attributable to chromophore coating, was observed only when the counter electrode (#2) was negatively biased relative to the coated surface. Such a bias maintains the high energy of the tunneling electrons in the vicinity of the coated molecular layers. Estimating our light collection and detection efficiency to be about 1%, we calculated our total photon yield per tunneling electron (including the unknown efficiency of the inelastic tunneling) to be 10^{-7}. The light emission efficiency scales with the surface coverage (Fig. 2), clearly indicating the molecular origin of the emitted light. The light intensity at bias voltages above 4 V which was observed with the bare ITO electrodes is hardly influenced by the molecular coating. Surfaces coated with DCM and coumarin showed light emission yields comparable to that of DCA, onsetting at about 2.6 to 2.7 V and peaking at about 3.6 V. The corresponding transparent gold surfaces, bare or coated with a chromophore, did not show any discernible emission, probably because of a much lower emission quantum efficiency.

All of the above results indicate that ITO can serve as a "friendly" substrate for the investigation of molecular light emission. We cannot positively conclude that we have detected the emission of isolated molecules without detailed knowledge about their aggregation states. However, we have demonstrated molecular light emission induced by inelastic tunneling electrons.

To test the possibility of using this effect for imaging purposes, we replaced the top lens electrode with a smaller ITO-coated glass tip with a 180-μm radius of curvature. The electrode (Fig. 3) shows a smooth surface area, enabling us to estimate an upper limit of 10^{-9} cm^2 for the tunneling area. Such a small surface area, with an increase of more than three orders of magnitude in current density relative to the previous experiment, still maintained stable electron and photon fluxes over periods of 30 min, indicating prospects of good chemical stability of the continuously excited

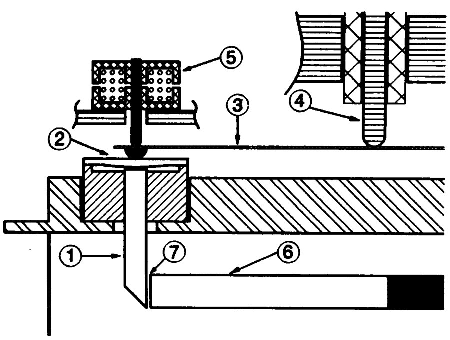

Fig. 1. Schematic view of the squeezable tunnel junction apparatus: (1) Molecular layer ITO-coated electrode and wave guide, (2) negatively biased ITO-coated counter electrode, (3) leaf spring, (4) coarse-approach micrometric screw, (5) fine-tuning feedback solenoid, (6) photomultiplier, and (7) light-coupling gel.

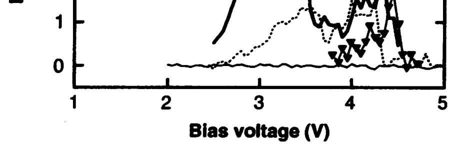

Fig. 2. The bias voltage dependence of light emission from a squeezable tunnel junction [measured by the emission yield in counts per second (cps) per nanoampere]. The full line with triangles represents the emission from bare ITO. The full and the dotted line represent the emission from a DCA-coated ITO surface at 0.5- and 0.05-layer coverage, respectively. Practically no counts were measured for the DCA-coated metal (thin line on the *x* axis). Tunneling current is 50 nA. Spectra were taken at 0.03-V intervals of the bias voltage.

Fig. 3. Tunneling electrode made of fire-rounded Pyrex glass coated with ITO. Radius of curvature is 180 μm.

layers. We reproduced the bias voltage dependence of light emission with a substantially lesser signal-to-noise ratio, yet with a comparable photon yield per tunneling electron. This light-emitting junction, even at its current incarnation, has an imaging area that is notably smaller than that of the best optical microscope, comparable to that of near field microscopes. Our main goal, however, is to image individual adsorbed chromophore molecules by monitoring their light emission images in STM. Unlike transmission electron microscopy or x-ray diffraction, our method could be performed in the natural (that is, aqueous) environment, "highlighting" specific chemical groups.

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Fabrication of Conducting Polymer Interconnects

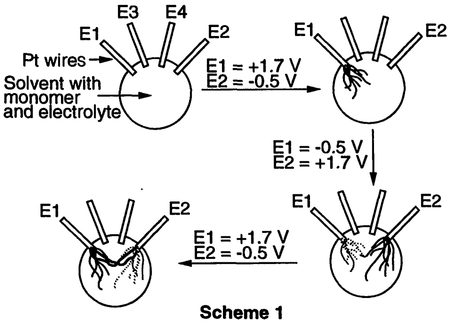
Corrine L. Curtis, Jason E. Ritchie, Michael J. Sailor*

A nonmechanical approach to the construction of complex three-dimensional interconnect arrays has been developed with the use of conducting polymer dendrites. Electrically independent connections between pairs of wires in an array were successfully grown through alternating-current electrochemical polymerization of poly(3-methylthiophene), without mechanical or optical masking steps. The electrically active links were insulated by subsequent electropolymerization of 4-vinylpyridine or 2-methylthiophene or by the dip-coating of the connections in a polystyrene solution.

A major obstacle in the development of nanoscale fabrication techniques lies in the increasing difficulty of manipulating three-dimensional (3D) structures as their sizes decrease. For molecular electronics or artificial neural networks, the number and size of the interconnects required makes the fabrication of structures with >100 nodes difficult (*1–6*). A structure as complicated as the human brain, which contains $\sim 10^{12}$ nodes (neurons) and a thousand times that many interconnecting links (*7*), would be virtually impossible to fabricate with conventional mechanical or photolithographic techniques (*8*). The use of chemical procedures to direct the linking of "molecular wires" such as conducting organic polymer strands has been recognized as a potentially viable approach for some time, and progress has been made in this direction (*9–16*). However, a general technique for connecting a large number of such molecular wires independent of each other has not been discovered.

In this report, we demonstrate an electrochemical polymerization technique that allows for the interconnection of many individual Pt nodes in three dimensions. The technique takes advantage of the ability of conductive polymers such as poly(3-methylthiophene) (P3MT) to be electrochemically switched between electronically conducting and nonconducting states. These polymers only grow when they are in their conducting form. We show that a pair of selected Pt wires can be electrically linked with polymer dendrites by the passing of an alternating current between them. The polymer dendrites alternate between conducting and nonconducting states until they come into contact with each other. When an actively polymerizing strand electrically contacts a nonconductive strand, the nonconductive strand switches into its conductive state in the region close to the connection. Further polymerization then occurs in the contacted region to reinforce the connection. The process requires no external mechanical manipulation or lithographic patterning. By the use of a separate insulation step, sets of nodes can be prepared that are electrically independent of each other.

A square array of four Pt wires was mounted in epoxy, each equidistant (~2 mm) from the others. These four "nodes" served as the working electrodes, and a fifth Pt wire coated with doped P3MT was used as a reference electrode. A counter electrode (Pt strip, 1-cm^2 area) was mounted in a compartment separated from the Pt wire array by a sintered glass filter. The polymerization solutions consisted of 3-methylthiophene (0.17 M) and tetrabutylammonium tetrafluoroborate (between 0.1 and 0.025 M) in dry, deoxygenated acetonitrile (*17*). Two of the four Pt nodes were connected to a bipotentiostat setup as independent working electrodes, with a common reference electrode (*18*). The potentials at the two nodes were scanned (triangular waveform, 100 mV/s) from −0.5 to +1.7 V relative to the reference electrode potential. The triangular waveform at one electrode was inverted with respect to the other, so that when either node was at −0.5 V the other was at +1.7.



Scheme 1

The rationale for the conducting polymer connection technique is outlined in Scheme 1. The accepted mechanism for electropolymerization of 3-alkylthiophenes involves the oxidative coupling of thiophene rings primarily at the 2 position (*19*). Concomitant with the polymerization reaction is the partial oxidation of the polymer chain, which dopes the polymer into an electronically conducting state. Thus, when the potential on one of the Pt leads (E1 in Scheme 1) is +1.7 V, polymerization and chain growth occurs. Under the conditions of the present experiments, the growth morphology is dendritic, and so fibers of P3MT propagate into solution (Fig. 1). The potential at the original Pt node (E1 in Scheme 1) is then scanned in the negative direction as the potential of a second Pt node (E2) is scanned positive, relative to the reference electrode. The polymer dendrites attached to the first node

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Department of Chemistry, University of California, San Diego, La Jolla, CA 92093–0358.

*To whom correspondence should be addressed.