

# Molecular Light Emission Induced by Inelastic Electron Tunneling

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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  $\sim 100$  Å in spatial resolution.

To overcome such limitations, one could excite molecules on surfaces by in-

elastic 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<sup>2</sup> 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.

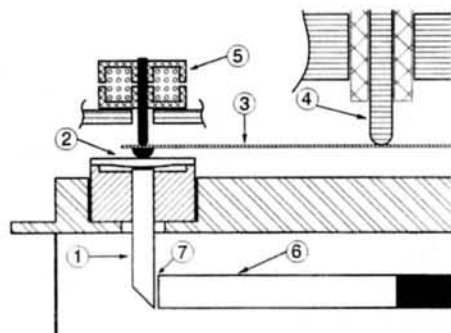
The very low emission efficiency from molecules adjacent to metallic and semiconductor surfaces is caused by the fast deexcitation processes (13) governed by energy transfer to nonradiative surface excitations (Auger processes). We replaced

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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 ( $\sim 200$  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  $\mu\text{m}$ ) 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

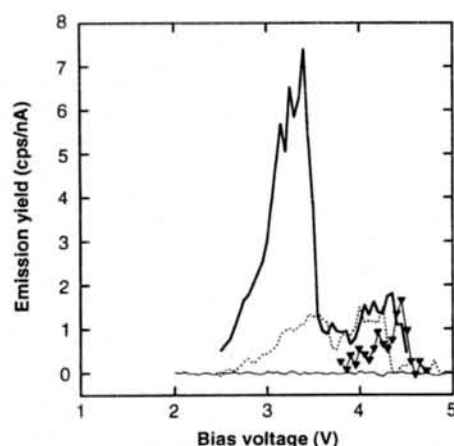


**Fig. 1.** Schematic view of the squeezable tunnel junction apparatus: (1) Molecular layer ITO-coated electrode and wave guide, (2) negatively biased ITO-coated counter electrode, (3) leaf spring, (4) coarse-approach micrometric screw, (5) fine-tuning feedback solenoid, (6) photomultiplier, and (7)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

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  $3 \times 10^{-6}$  cm<sup>2</sup> 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 on setting at a bias voltage that roughly corresponded to the allowed excitations energies in the chromophore. At this bias voltage ( $\sim 2.6$  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

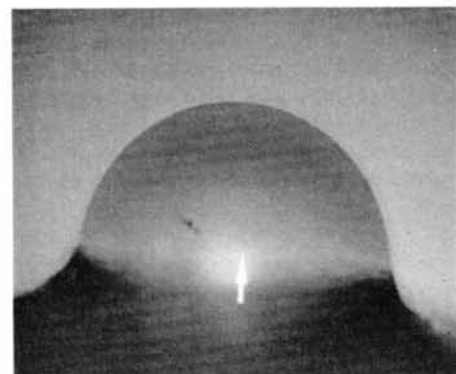


**Fig. 2.** The bias voltage dependence of light emission from a squeezable tunnel junction [measured by the emission yield in counts per second (cps) per nanoampere]. The full line with triangles represents the emission from a DCA-coated ITO surface at 0.5- and 0.05-layer coverage, respectively. Practically 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.

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, on setting 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- $\mu\text{m}$  radius of curvature. The electrode (Fig. 3) shows a smooth surface area, enabling us to estimate an upper limit of  $10^{-9}$  cm<sup>2</sup> 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. 3.** Tunneling electrode made of fire-rounded Pyrex glass coated with ITO. Radius of curvature is 180  $\mu\text{m}$ .

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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