



Plasmonic excitation of light emission and absorption by porphyrine molecules in a scanning tunneling microscope

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Light emission from a scanning tunneling microscope is investigated from Ag(111) surfaces using tips with a clean metallic apex and a molecule-covered shaft. The measurements are conducted such that no molecules are located in the tunneling gap. Nevertheless, spectra of the emission exhibit absorption and emission features of the tetraphenyl-H₂-porphyrine molecules used. The experimental data show that molecules in the vicinity of the tunneling gap are excited through tip-induced plasmons and their radiative decay. The excitation of plasmons is due to inelastic tunneling and does not involve an external light source.

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The scanning tunneling microscope (STM) may be used to locally excite the emission of light from surfaces covered with molecules. Molecular and submolecular resolution have been achieved.¹⁻⁴ Fluorescence spectra, which exhibit features due to molecular transitions, have been reported from molecules on ultrathin insulating films and from molecular multilayers.³⁻¹² A detailed interpretation of the mechanisms involved in exciting the molecules and in their radiative decay has been difficult because an intriguing mixture of physical effects is involved. In the tunneling junction, a molecule may be electronically excited by the injection of electrons or holes from the electrodes. However, it also electromagnetically interacts with the nanoscale junction. The close proximity of the electrodes to the molecule significantly changes its radiative and nonradiative lifetimes.¹³⁻¹⁸ Nonradiative energy transfer to the metallic substrate may quench fluorescence. At the same time, in the case of noble metals, strong plasmon resonances of the tip-sample cavity occur, which have been suggested to increase the light emission from molecules, which are excited by electron tunneling.^{8-10,12} In addition to their effect on the molecular emission, localized plasmon modes emit light themselves, even in the absence of fluorescent molecules when they are excited by the shot noise of the tunneling current.¹⁹ Furthermore, molecules may be excited by surface plasmon resonances, which is utilized in surface-plasmon fluorescence spectroscopy.^{20,21} Recently, a similar plasmon-mediated excitation was proposed for molecules confined in a STM junction.²² In this scenario, plasmons resonantly excite a molecule and thus induce fluorescence. Tian *et al.* used this mechanism to explain some spectral features from Ref. 6. It has also been invoked to interpret light emission observed when tunneling to porphyrine multilayers on graphite.²³

Here we present direct experimental evidence that molecules in a STM may be excited by plasmons rather than by tunneling-induced electronic excitations. Specifically, we prepared tips with a molecule-covered shaft and a clean metallic apex. We thus make sure that, in contrast to prior work, no electron tunneling to molecules takes place. Spectra of the light emission from these tips tunneling to a clean metal surface nevertheless exhibit clear molecular features, which are interpreted in terms of molecular emission and absorption lines. These data show that plasmon-mediated

excitation occurs in the absence of electron current through the molecules.

Experimental details. Experiments were performed with an STM in ultrahigh vacuum (UHV) at low temperature (5.8 K). Light emitted from the STM was collected with a lens and guided to a grating spectrometer and a liquid nitrogen cooled CCD camera via an optical fiber. Light emission spectra are not corrected for the detection efficiency of the optical setup, which was reported in Ref. 24. The spectrometer was operated at a resolution of 8 nm.

Ag(111) surfaces and electrochemically etched Ag tips were cleaned in UHV by Ar⁺ bombardment and annealing. Tetraphenyl-H₂-porphyrine (TPP, from Sigma-Aldrich) was sublimated from a Ta crucible onto the tips at room temperature. After the deposition, the entire front part of the tip is covered with molecules as verified from its blue-purple color. The molecular film at the tip apex prevented stable tunneling and imaging of the Ag(111) surface. In order to remove molecules from the apex, the tips were repeatedly approached toward clean surface areas at a sample voltage $V = 100$ mV, which lead to the transfer of clusters of molecules to the sample. This procedure was repeated until the transfer of molecules stopped and single Ag atoms were deposited instead. Figure 1(a) shows a Ag adatom (protrusion) deposited in this way along with an impurity (depression). In addition, the tip resolves electron standing waves around these features as expected. The imaging properties of the tip are inconsistent with the presence of a molecule at the tip apex.^{25,26} As a further test of the cleanliness of the tip apex the conductance of the junction was measured while approaching the tip from the tunneling range to contact with a single deposited atom [Fig. 1(b)]. The conductance at the point of contact formation is very close to the conductance quantum $G_0 = 2e^2/h$ as expected for a Ag atom²⁷ and exceeding typical molecular conductances. The results clearly show that no molecules are present at the apex of the tip. However, the thick layer of TPP on the remainder of the tip is still present. While the fluorescence of molecules directly at the tip surface may be quenched, TPP molecules in higher layers are expected to be partially decoupled from the metal. For simplicity we call such tips “*m*-tips” below.

Results. Figure 2 shows light emission spectra acquired with an *m*-tip on clean Ag(111). A number of positive sample

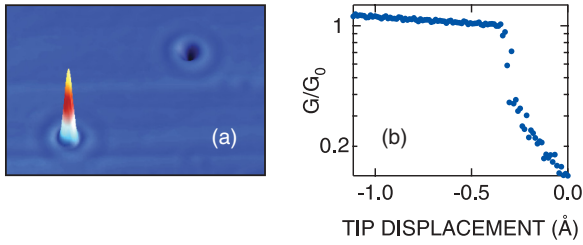


FIG. 1. (Color online) (a) Pseudo three-dimensional image of a single Ag adatom (left) and an impurity (right) on a Ag(111) surface imaged with a metallic tip with a molecule-covered shaft (“*m*-tip”, tunneling current $I = 100$ pA, sample voltage $V = 100$ mV). (b) Conductance (in units of the conductance quantum $G_0 = 2e^2/h$) acquired during the approach of the *m*-tip of (a) from tunneling to contact with the single Ag atom ($V = 100$ mV).

voltages V as indicated at each spectrum was used. The overall shape of the spectra is similar to spectra recorded with ordinary metallic tips on Ag.¹⁹ Not surprisingly, the plasmon modes that are typical of the tip-sample geometry appear to dictate the emission intensities. In addition, several maxima, which are marked by vertical lines, may be discerned. In the investigated range of voltages their wavelengths are independent of the bias voltage and polarity. At $V = 2.4$ V, emission at short wavelengths $\lambda < eV/hc$ is suppressed. While the spectral features and intensities are very reproducible for a given tip changes of the tip shape, which were effectuated by touching the sample surface with the tip, have a strong influence on the overall shape of the spectra.^{28–30} Figures 3(a)–3(c) show data recorded with three different *m*-tips. The center wavelength of the emission shifts to the red from Tip 1 to Tip 3. Despite the drastic change of the global spectral shape several sharp peaks and minima in the range 600–680 nm are observed in all spectra. For example, the distinct combination of a valley and a peak at ≈ 654 and ≈ 658 nm sticks out in all spectra. Their wavelengths are essentially independent of the tip used. From Tip 3, which particularly enhances the emission at long wavelengths, additional features are observed at long wavelengths (700 and 720 nm). Tip 1 intensifies the peaks at short wavelengths (546 and 563 nm). The wavelengths of the

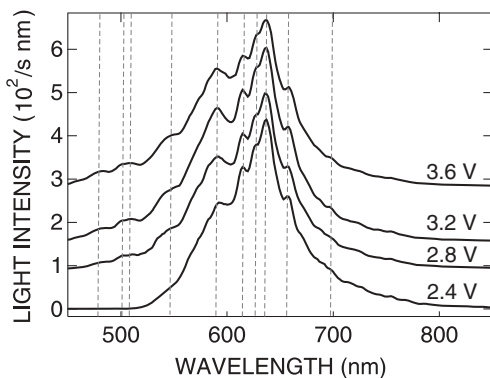


FIG. 2. Light emission spectra acquired with an *m*-tip at a current $I = 1$ nA and sample voltages 2.4, 2.8, 3.2, and 3.6 V over clean Ag(111) surface. The spectra are shifted vertically for clarity. Vertical dashed lines designate peak positions.

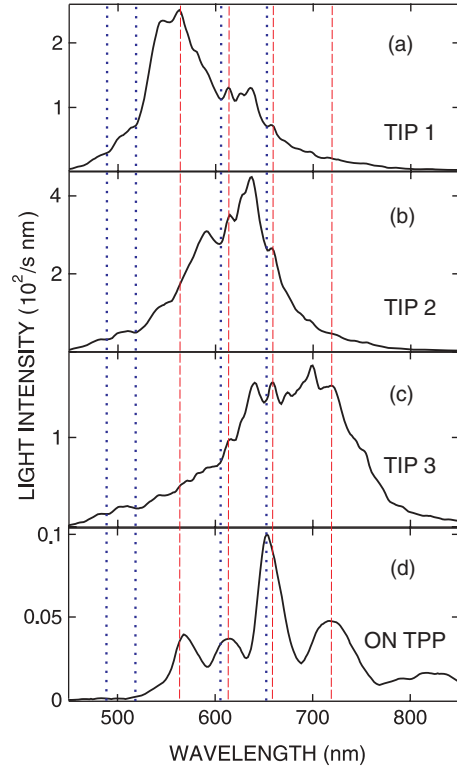


FIG. 3. (Color online) (a–c) Luminescence spectra acquired with different *m*-tips over a clean Ag(111) surface ($V = 3.2$ V, $I = 1$ nA). (d) Spectrum from a TPP multilayer on Ag(111) probed with a clean Ag tip ($V = 3.4$ V, $I = 20$ nA). The absorption and emission wavelengths of TBPP and TPP from Refs. 5, 22, and 31 are indicated by blue dotted and red dashed lines, respectively.

various peaks and dips in the spectra of Figs. 3(a)–3(c) are summarized in Table I.

For comparison the luminescence recorded from a thick layer of TPP molecules on Ag(111) using a clean Ag tip is shown in Fig. 3(d).

The intense broad peaks at ≈ 567 , 614, 652, and 719 nm match those observed previously from multilayers of *meso-tetrakis* (3,5-di-tertiarybutylphenyl) porphyrin (TBPP)⁵ and TPP.^{6,22,23} TBPP differs from TPP only by butyl groups at the phenyl rings at the sides of the molecule which are expected to have a minor influence on the emission and absorption spectra. The emission peaks have been attributed to transitions between the lowest unoccupied molecular orbital (LUMO, S_1) and the highest occupied molecular orbital (HOMO, S_0). In particular, the peaks at 726 and 658 nm are due to inelastic tunneling from the vibrational ground state of the LUMO ($S_1(0)$) to the vibrational ground state and the first excited state of the HOMO [$S_0(0), S_0(1)$]. The peaks at 566 and 614 nm are due to the transitions $S_1(2) \rightarrow S_0(0)$ and $S_1(1) \rightarrow S_0(0)$, respectively.^{6,22}

Discussion. Below, we argue that the emission from *m*-tips is due to a combination of plasmonic light emission from the metallic junction and molecular fluorescence and absorption. The emission is not excited by electron injection into TPP. Rather plasmons, which themselves are generated by inelastic tunneling, transfer energy to the molecules. This energy transfer may partially be radiationless. However, there is also indication of processes involving light.

TABLE I. Wavelengths (in nm) of peaks and dips in spectra acquired with the tips of Figs. 3(a)–3(c) compared with absorption and emission wavelengths of TBPP and TPP from Refs. 5,22,31 (indicated by indices 1, 2, and 3, respectively).³² The positions of peaks in the emission from a multilayer [Fig. 3(d)] are indicated by the index 4.

Peaks	Emission	Dips	Absorption
480		490	480 ⁽³⁾
505		521	525 ⁽¹⁾
546		554	554 ⁽¹⁾
563	563 ⁽²⁾ ,567 ⁽⁴⁾		
590		603	603 ⁽¹⁾
614	610 ⁽²⁾ ,614 ⁽⁴⁾	620	
627		630	
636		654	654 ⁽¹⁾
658	658 ⁽¹⁾ ,652 ⁽⁴⁾		
674			
700		708	
720	723 ⁽¹⁾ ,719 ⁽⁴⁾		

The metallic tip-sample junction is known to emit plasmonic light. Neglecting detailed features the overall shape of the spectra of Figs. 2 and 3 is compatible with this sort of emission. The wealth of additional spectral features in Figs. 3(a)–3(c), which are more numerous than typically observed from metallic systems, indicates an involvement of TPP molecules in the emission. The fact that fluorescence peaks observed from TPP multilayers (Fig. 3, red dashed lines at 723, 658, 610, and 563 nm) match the maxima in these spectra well clearly shows that TPP fluorescence is excited at the *m*-tips, too. However, owing to the particular preparation of the tips, the injection of electrons to the molecules can be excluded—there are no molecules in the tunneling junction.

An alternative pathway of excitation, which has recently been proposed,^{22,23} is the electron-induced generation of plasmons, which subsequently couple to TPP. The coupling of tunneling electrons to localized tip-induced plasmon modes

(TIP-modes) is indeed rather efficient. Order-of-magnitude estimates of the efficiency have been made for a model that successfully describes the intensities of STM-induced light emission from metal surfaces.³³ For Ag, up to approximately 1 out of 100 tunneling electrons excites a local plasmon. Once excited, several decay channels are accessible. With a high probability the localized plasmon may decay into electron-hole pairs, which are unlikely to excite TPP. Electronic excitation of TPP may occur via energy transfer directly from the localized modes. Delocalized plasmons are also created, which may lead to the excitation of molecules at significant distances from the tip apex.

The fluorescence spectra to be expected from these channels of excitation are similar to those observed via electron injection [Fig. 3(d)]. However, Figs. 3(a)–3(c) exhibit several additional reproducible details and, in particular, sharp intensity dips close to the fluorescence lines. A natural explanation of these dips is that some of the plasmonic emission from the metallic tip apex is absorbed by the molecular film at the tip. Indeed, several of the observed minima (at ≈ 490 , 521, 554, 603, and 654 nm) match reported values of molecular absorption lines (blue dotted lines in Fig. 3).

While fluorescence and absorption together explain many of the spectral features some maxima and minima do not directly match published transitions. We tentatively attribute these deviations to two factors. Trivially, two adjacent maxima are separated by a minimum that does not necessarily reflect an absorption line. Second, the uncontrolled structure of the molecular film, where various relative orientations and distances of TPP molecules are present. The electromagnetic interaction between molecules is affected by these parameters and may lead to shifts of the emission and absorption wavelength of the order of several nanometers.^{34,35}

Conclusion. The light emission properties of a metallic tunneling junction can be strongly influenced by molecules close to it. Although no current is passed through the molecules, molecular fluorescence lines are observed. The role of the tip-induced plasmon mode is twofold. First, photons can be emitted directly by radiative decay. Next, energy may be transferred to a nearby molecule resulting in absorption and molecular fluorescence. The excitation of tip-induced plasmons is achieved by inelastic tunneling and does not involve an external light source.

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