Modulation of local plasmon mediated emission through molecular manipulation

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We use single molecular manipulation to investigate the modulation effect of adsorbed molecules on local plasmon mediated emission (LPME) from the Au surface. Tunneling electron excited luminescence spectra indicate an overall suppression of LPME when an intact or excised CoOEP molecule is inserted into the junction. However, the LPME for the excised molecule is found to be stronger than that of the intact molecule, somewhat unexpected for a slightly larger molecule-substrate separation. We attribute such enhancement to a competing result of three different kinds of roles an adsorbed molecule can play in LPME: a geometric dielectric spacer, an energy dissipater, and a dynamic dipole oscillator.

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I. INTRODUCTION

Photon emission in the scanning tunneling microscope (STM) was reported from Ta and Si(111) by Gimzewski *et al.* in 1988.[1] From then on, STM-induced photon emission has drawn a lot of attention because it offers an opportunity to explore optical properties of various surfaces and nanostructures. Extensive research of STM-induced luminescence has been reported on metal surfaces,[2,3] semiconductors,[4,5] and molecules.[6–8] Early studies of STM-induced luminescence from C_{60} molecules adsorbed on Au(111) suggested that photon emission was from molecules.[6] Only until 2002, Hoffmann *et al.*[9] demonstrated that the adsorbed molecules in the first monolayer (ML) act merely as spacers to modify plasmon mediated emission from the metal surface. In order to generate fluorescence from molecules, a decoupling layer such as a thin dielectric layer or molecular layers has been used to avoid the quenching effect from the metal substrate.[10–13] Luminescent properties from molecular tunnel junctions offer fundamental information on how tunneling electrons are coupled with molecular states and local plasmon fields. However, because of the competing effect of fluorescence quenching and metal enhanced fluorescence, it remains debated about the role of molecules in STM-induced luminescence: does the adsorbed molecule enhance the plasmon mediated emission[9,14] or suppress it?[6,15]

On the other hand, molecular manipulation offers various promises for nanoresearch. Aiming for structure modification and function modulation, scientists have used various methods to manipulate single molecules, e.g., via push-pull,[16,17] high-voltage pulses,[18,19] or simply touching.[20] Our group demonstrated previously that an adsorbed CoPc molecular conformation could be changed by applying high-voltage pulses above its lobes to modulate its magnetism.

In this paper, we investigate the influence of a single CoOEP molecule on local plasmon mediated emission (LPME) from Au(111) through molecular manipulation. CoOEP is a very weak fluorescent molecule with quantum efficiency of less than 10^{-4} and nearly featureless broad spectra according to Gouterman's work,[21] and it is thus used in the present work as a spacer molecule that can be manipulated, allowing us to focus on how CoOEP molecules modulate the spectral shape and intensity of plasmon mediated emission from the Au surface.

II. EXPERIMENT

The experiments were performed by a low-temperature STM (Omicron). The base pressure of the system is about 5×10^{-11} mbar and all the measurements were acquired at 5 K. A piece of 200-nm-thick Au film on mica was cleaned with ion sputtering and used as the substrate.[22] The CoOEP molecules were thermally evaporated onto Au(111) at room temperature, and then the sample was transferred into the STM cryostat and cooled down to 5 K. Electrochemically etched tungsten tips and silver tips were used for imaging and photon emission.[22,23] The tips were cleaned by argon-ion sputtering at 1 kV for about 5 min. STM images were acquired in the constant-current mode.

As shown in Fig. 1, photons emitted from the tunnel junction are collected by a lens placed near the tip-sample region, transmitted through a viewport, and then refocused into an optical fiber using another lens located outside ultrahigh vacuum. The fiber cable is connected to either a microchannel plate-photomultiplier tube (MCP-PMT, Hamamatsu-

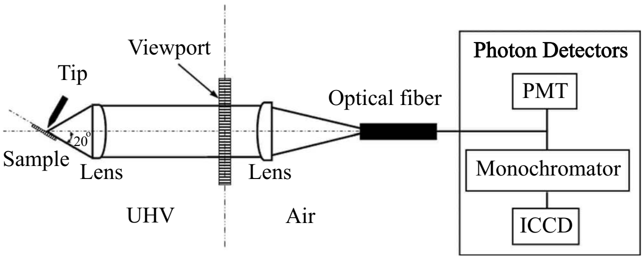

FIG. 1. Schematic diagram of the optical collection system. Photons are generated in the tunneling junction, collected by two lenses, and detected in PMT and ICCD.

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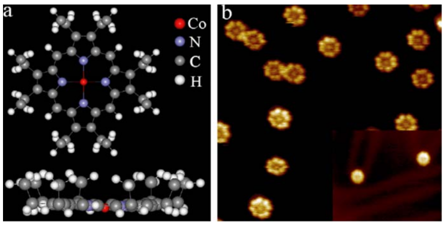

FIG. 2. (Color online) (a) Top and side views of the conformation of the CoOEP molecule adsorbed on Au surface. (b) STM image of a 0.1 ML coverage of CoOEP molecules adsorbed on Au(111). The CoOEP molecules show the eight-lobe feature (−0.9 V, 0.5 nA, 17×17 nm^2). The inset is an image with very low coverage of molecules (~0.01 ML, −0.9 V, 0.5 nA, 16 ×14 nm^2).

R3809U-50, dark counts < 10 counts/s at −20 °C, 160–850 nm) or a spectrophotometer (Hamamatsu PMA-100). The spectrometer includes a grating monochromator (C5094) and an intensified charge-coupled-device (ICCD) with Peltier-cooled multialkali (S-20) and multichannel plates. The ICCD operates in the pulse counting mode at a dark count rate of ~1 count/s at −15 °C for the wavelength range of 350–850 nm. The estimated collection efficiency is about 5% (hemisphere). Typical quantum efficiencies measured on the Au substrate were ~10^{-5} photons per electron for tungsten tips and ~10^{-4} photons per electron for silver tips. All the statistically significant spectra presented in the paper are not corrected for the wavelength dependent sensitivity of photon detection systems. In order to rule out the possibility that the observed spectral change was caused by the change in the tip condition, we alternately measured the spectra over the bare Au surface and above single CoEOP molecules and used the spectra on the bare Au surface as references.

III. RESULTS AND DISCUSSION

The molecular structure of 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine cobalt(II) (CoOEP) is shown in Fig. 2(a). It reveals the top and side views of the conformation of the CoOEP molecule absorbed on Au(111). Theoretical simulations[24] indicate that all the eight ethyl groups of CoOEP buckle up in the same direction. Figure 2(b) is a STM image of CoOEP molecules absorbed on Au(111) with a coverage of about 0.1 ML. The eight-lobe feature is clearly distinguishable with the length diagonally across about 2 nm, consistent with previous studies.[25] The inset shows a surface with a much lower coverage of molecules (about 0.01 ML), which was used for the manipulation and STM-induced luminescence experiments in order to ensure the studied molecules being well isolated from each other. The slightly brighter feature for the upper lobes of Fig. 3(a) is due to the adsorption of these lobes to the protruded herringbone structure, as shown in the inset.

According to theoretical simulations, the porphyrin core plane of CoOEP is found to attach directly to the Au surface,[24] which is different from the core-plane suspended situation in tetraphenyl porphyrin (TPP) and mesotetrakis(3,5–di-tertiarybutyphenyl)porphyrin (TBPP)molecules.[14]

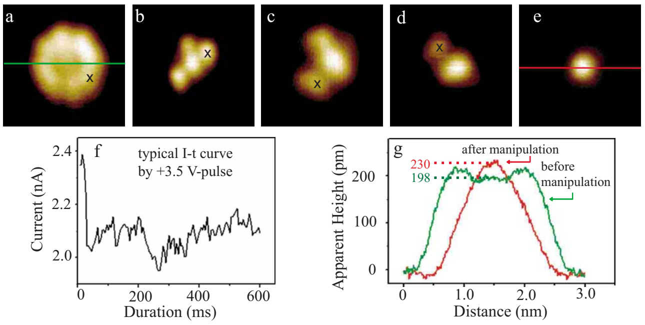

FIG. 3. (Color online) (a)–(e) show the manipulation process by +3.5 V pulses. The mark "×" indicates the position where we applied +3.5 V pulses.(−0.9 V, 0.5 nA, about 3×3 nm^2) (f) Typical *I-t* curve using +3.5 V pulses with an abrupt current reduction typically within 50 ms. (g) Apparent heights of molecules of (a) and (e) in constant-current line scans.

The coupling between the molecule and the substrate is quite strong, probably involving substantial hybridization of the metal states with molecular orbitals. In order to reduce the coupling, we changed the molecular geometry through molecular manipulation.

The manipulation process was carried out by applying voltage pulses, typically at +3.5 V, as shown in Figs. 3(a)–3(e). Theoretical simulations suggest that the "CH_3" terminals of the ethyl groups are most likely to be cut off during the process.[24] Figure 3(f) is a typical *I-t* curve when applying +3.5 V pulses. This curve shows that the demethyl incidents happened very soon after a +3.5 V pulse was applied, with an abrupt current reduction typically within 50 ms. (The excised methyl group is referred as a lobe in the text.) It is possible to have the lobes cut off by a lower voltage pulse such as +3.0 V. But, sometimes, +3.0 V pulses just made the lobes rotating. We adopted +3.5 V pulses in the present work, which appeared to give high probabilities for cutting off the lobes. Nevertheless, it is worth mentioning that it is extremely difficult to cut off the lobes one by one. Often, three or four lobes were cut off at the same time. After all the lobes were excised, we got an excised d-CoOEP molecule, as shown in Fig. 2(e).

Figure 3(g) shows different apparent heights for an intact CoOEP and an excised d-CoOEP molecule. The molecular conformation was changed from a flat-lying geometry to an arch geometry with the center of the molecule raised up by about 0.3 Å. The center of an excised d-CoOEP molecule is also higher than the border of an intact one, though only by about 0.15 Å. It is worth noting that these apparent heights may vary, depending on different tip conditions, and may thus yield different increments in the apparent heights of the center ranged from 0.3 to 0.8 Å.[18]

Figure 4(a) shows STM-induced luminescent spectra on single intact CoOEP and excised d-CoOEP molecules. The emission spectrum on the bare Au surface is also plotted as a reference, with the characteristic plasmon mediated emission band around 620 nm.[11,26] The primary feature is the suppressed intensity of plasmon mediated emission above molecules in comparison with that on the bare metal surface, regardless the molecule is intact or excised. The second fea-

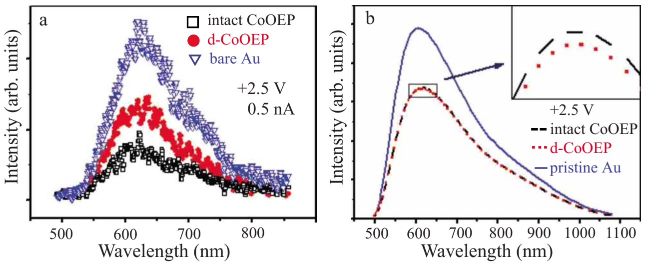

FIG. 4. (Color online) (a) Photon emission spectra from an intact CoOEP (□), an excised d-CoOEP (●), and bare Au surface (■) by a W tip. All the optical spectra were acquired at the same bias (+2.5 V) and the same tunneling current (0.5 nA). (b) Calculated emission spectra from the Au surface for different situations, (–) corresponds to an intact CoOEP, (•••) corresponds to an excised d-CoOEP, and (—) corresponds to the pristine Au surface. The excitation voltage is +2.5 V. Both the measured and calculated spectra are scaled according to counts/s per electron.

ture, somewhat unexpected, is that the emission intensity above the excised d-CoOEP molecule is higher than that above the intact CoOEP. No obvious peak shifts of plasmon mediated emission were observed within the spectral resolution $(\sim 8$ nm) used for the measurements.

In order to understand the physical mechanism behind the observed spectral difference, we calculate optical spectra of plasmon mediated emission in the framework of electrodynamics using a hyperbolic tip geometry and boundary charge method.[27,28] In our calculations, the molecular layer serves as a pure dielectric spacer (with an approximate dielectric constant $\varepsilon \approx 3.1$ used for TPP porphyrins[29]); the dynamic dipole moment of molecules is not taken into account. Figure 4(b) shows the calculated light-emission spectra for the pristine Au (solid curve), intact CoOEP (dashed curve), and d-CoOEP (dotted curve). In agreement with the experimental observation, the calculated light intensity is also decreased when the metal surface is covered with either an intact CoOEP or an excised d-COEP molecular layer. Such suppression can be rationalized as follows: the insertion of a molecular layer into the STM junction increases the separation distance between the tip and metal substrate, leading to reduced local-field enhancement and thus suppressed light emission. It should be noted that both the measured and calculated spectra are scaled according to counts/s per electron.

According to the argument above, the calculated intensity for excised d-CoOEP is slightly weaker than that for intact CoOEP molecules, as expected for a slightly larger gap distance. However, such theoretical prediction is in contradiction with the observed emission enhancement from intact CoOEP to excised d-CoOEP molecules. The conflict raised here implies that the excised molecules play additional roles beyond pure dielectric spacers.

In order to clarify what kind of role the adsorbed molecule may play, we designed an experiment below as an effort to exclude the geometric influence (Fig. 5). A silver tip was used in this experiment instead of W tips because on one hand, we want to show our observation is a general phenomenon independent of tip materials, and on the other hand, the use of Ag tips could facilitate spectral acquisition since plasmon mediated emission by a Ag tip is about three to four times stronger than that by a W tip in the present work.

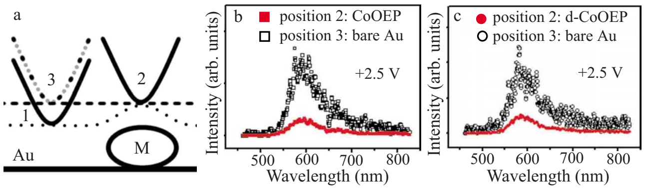

FIG. 5. (Color online) Comparison of spectra acquired at the same tip-substrate distance. (a) A schematic diagram of tip movements when scanning above a molecule adsorbed on Au. (b) Optical emission spectra from an intact CoOEP molecule (■, +2.5 V, 500 pA) and the bare Au surface (□, +2.5 V, 50 pA). (c) Optical emission spectra from an excised d-CoOEP molecule (●, +2.5 V, 500 pA) and the bare Au surface (○, +2.5 V, 33 pA). All measured spectra are normalized according to counts/s per electron. Optical measurements were performed by a Ag tip.

The distance between the STM tip and the Au surface may increase when scanning above a molecule under the same tunneling current and bias voltage, as illustrated in Fig. 5(a) from tip position 1 to position 2. In order to exclude the geometric influence of different tip-substrate distances on STM-induced luminescence, we do the following experiment to obtain spectra for the *same* gap distance but with or without molecules underneath the tip. First, we acquired a STM image of an intact CoOEP (or excised d-CoOEP) molecule, measured its apparent height, and collected the light-emission spectra from the molecule in position 2 [solid curves at bottom of Figs. 5(b) and 5(c)]; then, we moved the tip to a bare Au surface, reduced the current to retract the tip to position 3 that has the same height as in position 2, and collected the photon emission spectra from the bare Au surface [upper curves in Figs. 5(b) and 5(c)]. Comparisons of spectral intensity normalized according to injected charge (i.e., per electron) indicate that both intact CoOEP and excised d-CoOEP molecules suppress the tip induced plasmon emission from the Au surface for the same tip height, suggesting the presence of additional nonradiative decay channels via molecules during tunneling. Consistent with the height difference in Fig. 3(g) using a W tip, the gap distance for position 2 for the excised d-CoOEP is again about 0.3–0.8 Å larger than that for the intact CoOEP molecule. However, the emission intensity for the excised d-CoOEP is found to be stronger than that of the intact CoOEP molecule by only about 30%, not as strong as the nearly doubled intensity in Fig. 4(a) using a W tip. The origin of this difference in the enhancement effect is still not clear but might be related to the different plasmon field strengths between the tip materials; the Ag tip is about three to four times stronger than the W tip in the present work. If we assume that an excised molecule itself contributes about the same enhancement for either Ag tips or W tips, then, the enhancement proportion to the total plasmon mediated emission would be smaller for a Ag tip than for a W tip.

Such enhancement of LPME from an intact CoOEP to an excised d-CoOEP may be related to the change in branching ratio of nonradiative decay channels to radiative channels when a molecule is better decoupled. To be more specific, once an adsorbed molecule is excited by inelastic tunneling electrons, the associated dynamic dipole oscillation may excite local plasmon modes defined by the tip-molecule-substrate cavity.[30] The excited state may dissipate its energy to the substrate nonradiatively via two routes: charge transfer through orbital hybridization and energy transfer through dipole-dipole interaction.[13] The quenching rate depends strongly on the strength of interaction between the molecule and substrate. The porphyrin core plane of an excised d-CoOEP is lifted up slightly relative to that of an intact CoOEP [Fig. 3(g)], leading to weaker coupling between the core plane of the excised d-CoOEP molecule and the Au substrate. As a result, the quenching rate for both charge transfer and dipole-dipole energy transfer is reduced for the excited excised d-CoOEP molecule.

On the other hand, the radiative rate for a dynamic dipole (i.e., the dipole oscillation probability) also depends on the strength of the molecule-substrate hybridization. The dynamic dipole will be driven harder for the excised d-CoOEP molecule because of the slightly larger molecule-substrate distance and resultant weaker interaction. Therefore, both the decrease in the quenching rate and increase in the dipole oscillation probability suggest that the LPME will be enhanced for the excised d-CoOEP molecule in comparison with the intact CoOEP, as observed experimentally. Another factor that may contribute to the enhancement of LPME is the arch geometry of the excised d-CoOEP molecule, which may give more perpendicular dipole component as compared with the horizontally lying dipole for the intact CoOEP.[30] When the porphyrin core plane and the metal substrate are further separated by bulky legs such as tertiary-butyl groups in hexa-tert-butyl-decacyclene (HBDC) (Ref. 9) and TBPP,[14] the electronic decoupling becomes more efficient, and thus the resonance enhancement could be so large that the intensity of LPME from the adsorbed molecule is stronger than that from the bare metal surface.

IV. CONCLUSIONS

In summary, we have investigated the effect of a single adsorbed molecule on LPME through manipulating a single CoOEP molecule. While the presence of adsorbed molecules suppresses the intensity of LPME overall, a somewhat unexpected emission enhancement was observed for the excised molecule with respect to the intact molecule. We attribute the influence of an adsorbed molecule on LPME to three main aspects. First, the molecule acts as *a geometric dielectric spacer*, which leads to increased molecule-substrate separation and resultantly decreased local-field enhancement and suppressed LPME. Second, the molecule acts as *an energy dissipater*, providing additional nonradiative decay channels via charge transfer and dipole-dipole energy transfer. Third, the molecule acts as *a dynamic dipole oscillator*, offering resonance enhancement to the LPME. The last two factors play an opposite role to the first factor in the modulation of LPME as a function of the gap distance. The emission enhancement from an intact CoOEP to an excised d-CoOEP is a result of the decrease in the quenching rate and increase in the dipole oscillation probability due to a slightly increased molecule-substrate separation. Further increase in the electronic decoupling may offer greatly enhanced plasmon emission and even molecular specific fluorescence from the STM nanocavity.

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