Bias dependence of tunneling-electron-induced molecular fluorescence from porphyrin films on noble-metal substrates

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We investigated scanning tunneling microscope (STM)-excited luminescence from porphyrin (PhTPP and H_2TPP) thin films on metal substrate (Au and Ag) under ambient conditions. Molecular fluorescence similar to the corresponding photoluminescence was observed from PhTPP/Au and H_2TPP/Ag at both STM bias polarities. We found that at the same experimental condition and parameters, the STM-induced luminescence intensities of maxima peak are similar for PhTPP and H_2TPP but weaker by a factor of about 4 than that for H_2TBPP which we studied previously, probably due to fluorescence quenching by aggregation. The polarity dependence and the bias voltage dependence of the fluorescence intensity for the PhTPP/Au were similar to that for the respective pristine metal. These facts support our proposal that intense molecular fluorescence from porphyrin film on the noble metals is a result of the enhancement of molecular excitation by substrate surface plasmons.

I. INTRODUCTION

Since light from the junction of a scanning tunneling microscope (STM) was observed in 1988 for the first time,[1] extensive researches of STM-induced luminescence (STML) on metal and semiconductor surfaces have been carried out.[2–12] Studies on the STML of organic molecules have attracted much attention since it enables to investigate the optical properties of those molecules at nanometer scale and provides useful information to develop the organic light emitting diode devices in the future.[13–21] Hoffmann *et al.*[22] observed light emission from single hexa-*tert*-butyl-decacyclene molecules on noble-metal surfaces. They found that the emission spectra are indicative of plasmon-mediated emission of the metal substrate and tip, while the molecule slightly modifies the plasmon emission. Qiu *et al.*[14] reported light emission from individual ZnEtioI molecules adsorbed on Al_2O_3/NiAl(110) and explained that the spectra were due to deexcitation of excited anion states resulting from hot electron injection. Dong *et al.*[15] reported molecular fluorescence (MF) from *meso*-tetrakis (3,5-di-tertiarybutyl-phenyl) porphyrin (H_2TBPP) thin film on Au (100) and found that the spectra were similar to their photoluminescence (PL) spectra. According to them, the MF is generated by the hot electron injection excitation followed by the radiative decay associated with the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) transitions: the mechanism proposed is a double-barrier model with a vacuum barrier on the tip side and a Schottky-type barrier at the molecule-substrate interface and, when the tip is negatively biased, electrons tunnel elastically through the vacuum barrier into the unoccupied molecular orbital while the HOMO is partially emptied simultaneously.
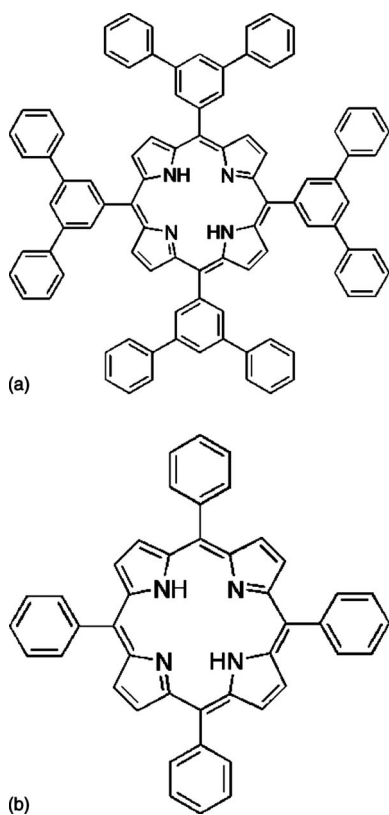
Most recently, we observed strong STML from H_2TBPP film on noble metals comparable to substrate plasmon-mediated light emission and proposed a model for such strong molecular light emission, named surface-plasmon-enhanced molecular fluorescence (SEMF),[18] based on the finding that molecular fluorescence was observed for gold and silver substrates but not for pyrolytic graphite and indium tin oxide ones. We ideally divide the entire optical process into two steps. The first one is that the local surface plasmons of the metal substrate are excited by the tunneling electrons under the local electric field caused by the tip. The second one is the molecular excitation by electrodynamical coupling between the oscillating dipole associated with the molecule and local surface plasmons, and MF associated with HOMO-LUMO transitions in porphyrin film. In this process, MF is well enhanced, so that the MF can be detected in the far-field region. Such an involvement of plasmons in STML from molecules on a metal has been suggested previously.[23]

Porphyrin molecules may exhibit different luminescent characters caused by their conformation and aggregation in film. In this study, we first investigate STML from two porphyrin molecules 5,10,15,20-tetrakis([1,1′:3′,1″-terphenyl]-5′-yl)-21*H*,23*H*-porphyrin (PhTPP) and tetraphenylporphyrin (H_2TPP). The bias dependence of STML was also studied in detail to further understand the mechanism of STML from molecules.

II. EXPERIMENT

The Au and Ag substrates have been respectively prepared in a vacuum chamber by evaporating gold or silver onto cleaved mica. The PhTPP [Fig. 1(a)] and H_2TPP [Fig. 1(b)] molecules were obtained by the condensation of 3,5-diphenylbenzaldehyde or benzaldehyde with pyrrole in the presence of boron trifluoride-diethyl etherate in dichloromethane, followed by oxidation with *p*-chloranil. The organic films on Au and Ag substrates were prepared by spin casting from a 0.81 mM solution PhTPP and H_2TPP in chloroform ($CHCl_3$) at a spin velocity of 2000 rpm. The topog-

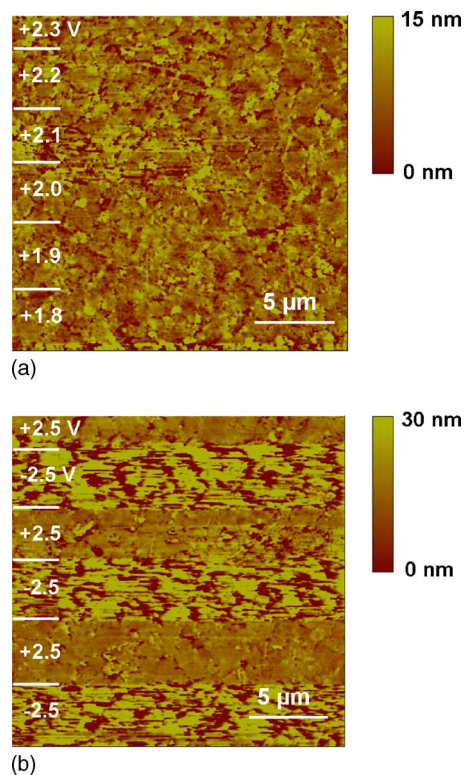FIG. 1. (a) PhTPP and (b) H$_2$TPP molecular structures.

FIG. 2. (Color online) Typical STM topographies of PhTPP film on Au. Tunneling current, 1.2 nA; bias voltage, from +1.8 V to +2.5 V in (a), and alternately, ±2.5 V in (b).

raphies of the films were characterized by STM (DI Nanoscope E).

The STML measurements were performed by using the STM under ambient conditions. The system setup has been described elsewhere.[18] The STM tip was a commercial Pt-Ir (10%) tip. Photons emitted from the tunneling gap were collected by a fiber near the tip-sample gap region, and then guided into a spectrograph (HoloSpec f/2.0, Kaiser Optical Systems, Inc.) and recorded with an intensified charge-coupled device (PI-MAX camera and ST-133A Controller, Princeton Instruments, Inc; spectrum range between 385 and 800 nm, dark current <3 counts/s at −33 °C). Every measurement has been done within 3 h after sample preparation.

III. RESULTS AND DISCUSSION

To prevent the film from being destroyed by the energetic electrons, a large scan area of 20×20 μm^2 was selected for one scan: a total of six STML spectra are obtained for scanning an image from the bottom to the top. Typical STM images are shown in Figs. 2(a) and 2(b). The organic film formed patches with more than micrometer size during spin casting and uniformly overcovered the poly-Au substrate. The underlying Au substrate can be seen from the patch boundaries, which consists of small Au clusters. The thickness of the organic films is estimated to be 8 nm. Slightly increasing the bias voltage from 1.8 to 2.5 V at sample positive bias would not affect the topographies too much. However, the topographies at two bias polarities are rather different [Fig. 2(b)] because of the STM tip being closer to the

surface at negative sample bias. In the measurements, the tunneling condition is stable. After several ten times of scanning, little uppermost molecules are dragged by the STM tip.

Porphyrin molecule has strong interaction with photons including absorption and fluorescence, as it has a core π plane inside, where the luminescence originates through Franck-Condon π-π^* transitions.[15,20] Three kinds of porphyrin (PhTPP, H$_2$TPP, and H$_2$TBPP) in CHCl$_3$ solvent exhibit the same maxima peaks in their PLs and UV-visible absorptions when they exist in a relatively free state. A set of STML, PL, and absorption spectra for PhTPP are given in Fig. 3. Typical STML of the films of the three organic materials show clear vibronic peaks (662 and 715 nm), well in agreement with the spectra (650 and 715 nm) of porphyrin solution but with a redshift about 10 nm. UV-visible absorption measurements in Fig. 3 indicate a Q-band energy of 1.9–2.4 eV (518–650 nm) and a Soret-band energy of 3.0 eV (418 nm). Although the huge Soret-band absorption can excite much stronger PL intensity than Q band, for example, the emission intensity of PL excited by 418 nm is ten times stronger than that by 518 nm. We also noticed that there are weak absorption bands from 1.90 to 2.4 eV. The "turn on" voltage to excite the plasmon-mediated light of Au substrate is ~1.65 V.[4] Thus we suppose that molecular fluorescence of porphyrin can be emitted at low bias voltages corresponding to these low-energy absorption bands: electron excites the plasmon-mediated light of Au substrate and it excites PhTPP via absorption at the low-energy absorption bands for film. One of the experimental evidences of this idea is that we can see the vibronic peaks of porphyrin at bias
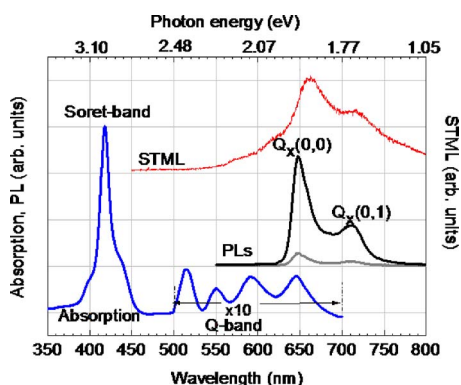
FIG. 3. (Color online) STML of PhTPP film on Au together with UV-visible adsorption (the intensity in the range of 500–700 nm magnified ten times) and PL spectra of PhTPP in $CHCl_3$ solvent using a xenon lamp at 518 nm (gray one) and 418 nm (black one) for comparison.

voltages above the critical voltage of 2.0 V for PhTPP and H_2TPP as well as for H_2TBPP,[21] which corresponds to the minimum energy of the low-energy absorption bands of the films.

Typical bias and polarity dependences of STML of PhTPP/Au are shown in Fig. 4. We can see that with increasing bias voltage, the photon intensity tends to increase in this energy range, and the STML intensity of PhTPP at positive bias is stronger than that at negative one. Similarly, the bias dependence [Fig. 5(a)] and the polarity dependence [Fig. 5(b)] were obtained from H_2TPP film on Ag substrate. The two peaks of molecular fluorescence from H_2TPP on Ag at the bias voltage of 2.5 V became ten times stronger than those from H_2TPP on Au probably due to a stronger surface plasmon field of Ag compared to Au.[18,21]

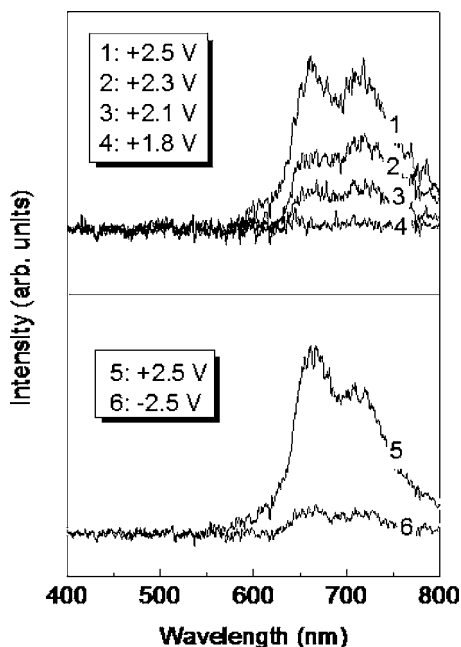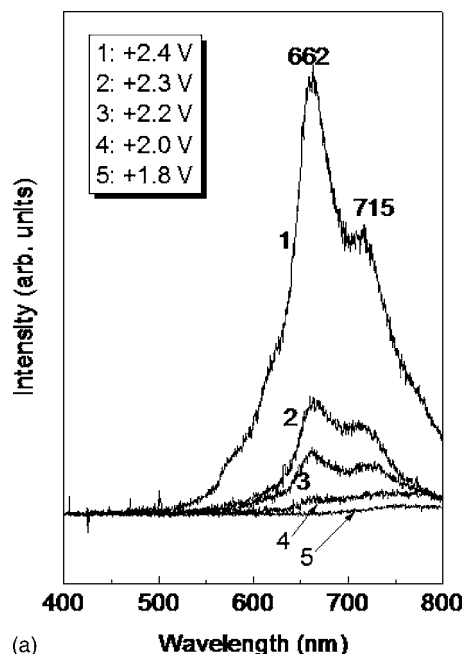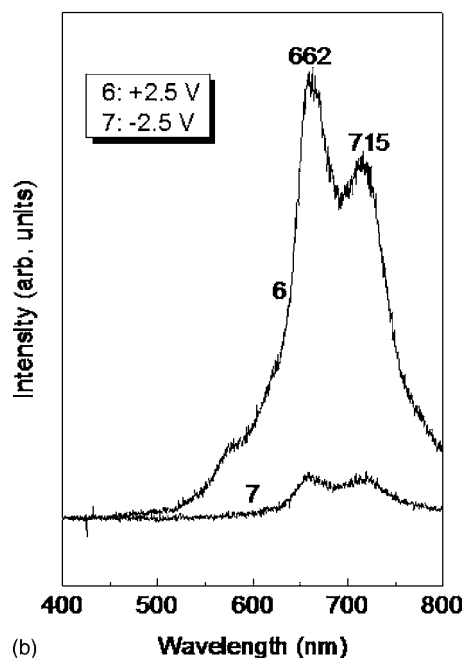Combining the present study with the previous one,[21] we found that at the same experimental condition and param-

FIG. 4. Bias and polarity dependences of STML of PhTPP film on Au, corresponding to Figs. 2(a) and 2(b), respectively.

FIG. 5. (a) Bias dependence and (b) polarity dependence of STML of H_2TPP on Ag. Tunneling current: 0.8 nA.

eters, the STML intensity of maxima peak of H_2TBPP on Ag is up to four times stronger than those of PhTPP on Ag and H_2TPP on Ag. The difference between the three molecules, H_2TBPP, PhTPP, and H_2TPP, is the substituents at the terminal position that the porphyrin molecules have. Among them, H_2TPP is the one without substituent. The sequence which prevents stacking of core π-planes is as follows: nonplanar $H_2TBPP >$ planar PhTPP and H_2TPP. Kobayashi and co-worker have observed the J aggregation formed in porphyrin[24] and other organic films[25] during spin casting: small aggregates randomly oriented are obtained in a sample film, in addition to large J aggregates well oriented along the
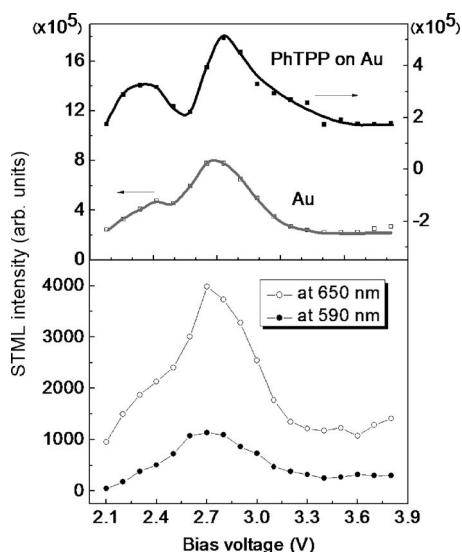
FIG. 6. Bias dependences of STM-induced total excited photons from PhTPP film on Au and pristine Au substrate. The lower ones are the excitation intensities from pristine Au at absorption energy (Q band, 590 and 650 nm). Tunneling current: 1.0 nA.

direction of solvent flow.[25] We suggest that core π-planes of PhTPP and H_2TPP molecules are stacked in about 3/4 of the films and the unstacked 1/4 contributes to the molecular fluorescence with the two peaks. More details will be described elsewhere.

The bias dependences of the total intensities of STM-induced light emission of PhTP/Au and pristine Au are given in the upper frame of Fig. 6. During the measurements, a $20 \times 20~\mu m^2$ area of PhTPP/Au and Au substrate was continuously scanned. The measurement was performed starting from a lower bias voltage of +2.1 to +3.8 V. The initial trend of increase in STML intensity for PhTPP with increase of the bias voltage can be seen in Fig. 4. In Fig. 6, the initial trend of increase and the final trend of decrease for PhTPP are well according to those for pristine Au film. The result shows that the STM-excited molecular fluorescence of the organic film is most enhanced where the plasmon-mediated light of the Au substrate is stronger. The lower curves in Fig. 6 show the plasmon-mediated light intensity from pristine Au at absorption energies (Q band, 590 and 650 nm). There is no big difference between the two and the total intensity. As the peak of the curves is roughly the same as that of the peak of the PhTPP/Au curve, the excitation of PhTPP via substrate plasmon-mediated light may be due to excitations at various absorption energies. Figures 4 and 6 were obtained from two measurements. The trends of initial increase and final decrease in STML intensity for PhTPP/Au in two measurements are the same. The dip at 2.5 V in STML intensity for PhTPP/Au shown in Fig. 6 is not reproducible and is absent in Fig. 4.

With regard to the appearance of the peak in emission intensity vs bias characteristics for the metal film, our result is in agreement with the previous report by Berndt and Gimzewski:[26] they observed a maximum in light intensity for sample bias voltage V_s between 3 and 4 V for Cu, Ag, and

Au surfaces. The initial increase in intensity with bias voltage is attributed to the growing number of channels that can contribute to photon emission.[27] The decrease in intensity with bias voltage is attributed to the increase of the tip-sample distance: it results in a decrease of the field enhancement below the tip and in a decrease in light emission.[26–28]

A weaker but measurable molecular fluorescence was observed for negative bias voltages, too [see Figs. 4 and 5(b)]. As the weaker but measurable plasmon-mediated light is also emitted from the metal substrates for the negative bias voltages, the occurrence of molecular fluorescence for negative biases is a natural consequence of the surface-plasmon-enhanced molecular fluorescence model. Dong *et al.* observed STM-excited molecular fluorescence for H_2TBPP/Au for both positive and negative bias voltages.[15] As they considered that the molecular fluorescence is via electron-hole injection, it is invoked that the energy levels of emitting molecules are not pinned to the substrate but shift with applied bias to ensure the electron-hole injection for the negative sample biases.

The finding that the polarity dependence and the bias voltage dependence of the fluorescence intensity for the PhTPP/Au were similar to that for respective pristine metal supports our SEMF proposal[18,7,29] that the plasmons of the metal substrate are excited by the tunneling electrons under the electric field caused by the tip, and then the molecular excitation and molecular fluorescence associated with HOMO-LUMO transitions in porphyrin film is well enhanced by electrodynamical coupling between the oscillating dipole associated with the molecule and local surface plasmons.

IV. SUMMARY

We first investigated STMLs from porphyrin PhTPP and H_2TPP thin films on metal substrate under ambient conditions. Intense molecular fluorescence similar to the corresponding PLs was observed from the PhTPP/Au and H_2TPP/Ag at both polarities of STM bias. We found that, at the same experimental condition and parameters, the STML intensity of maxima peak is similar for PhTPP and H_2TPP but weaker by a factor of about 4 than that for H_2TBPP, since the sequence which prevents stacking of core π-planes is as follows: nonplanar H_2TBPP > planar PhTPP and H_2TPP. The polarity dependence and the bias voltage dependence of the fluorescence intensity for the PhTPP/Au were similar to that for respective pristine Au substrate. These facts support our proposal that intense molecular fluorescence from porphyrin film on the noble metals is a result of enhancement of molecular excitation by substrate surface plasmons.

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