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Hongwen Liu,[a)] Yutaka Ie, Tatsuo Yoshinobu, Yoshio Aso, and Hiroshi Iwasaki
The Institute of Scientific and Industrial Research, Osaka University, Osaka 567-0047, Japan

Ryusuke Nishitani
Department of Electrical and Electronics Engineering, University of the Ryukyus, Okinawa 903-0213, Japan

Scanning tunneling microscope (STM)-excited molecular fluorescence from H_2TBP porphyrin (H_2TBPP) thin films on Au (111), Ag, highly oriented pyrolytic graphite (HOPG), and indium tin oxide (ITO) surfaces has been investigated in air. Molecular fluorescence was observed from the H_2TBPP films on Au and Ag, but it was extremely weak or undetectable from films on HOPG and ITO. The maximum intensity of molecular fluorescence from H_2TBPP/Ag is at least 100 times stronger than that from $H_2TBPP/HOPG$. Strong enhancement of molecular excitation by substrate surface plasmons is suggested for the STM-excited molecular fluorescence from H_2TBPP only on the noble metal substrates. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2171795]

Light is emitted from the junction of a scanning tunneling microscope (STM) when energetic tunneling electrons or holes induce a radiative process: STM-excited luminescence (STML).[1] Gimzewski *et al.*[2] observed enhanced photon emission (10^{-3}–10^{-4} photons/electron) from the tunnel junction of a STM operating on Ag, Au, and Cu surfaces. Berndt *et al.*[3] explained the measured photon emission in terms of localized, tip-induced plasmon modes which result from the electromagnetic coupling.

Recently, STM-excited molecular fluorescence has been observed from porphyrin thin films on metal substrates. For examples, Ho *et al.*[4] obtained STML from individual ZnEtioI molecules adsorbed on $Al_2O_3/NiAl(110)$, and explained that the spectra were owing to deexcitation of excited anion states resulting from hot electron injection. Mashiko's group reported light emission from *Meso*-tetrakis(3,5-di-teriarybutyl-phenyl) porphyrin (H_2TBPP) on Au (100) (Ref. 5) and ZnTBP porphyrin on Cu(100),[6] whose spectra were found to be similar to their photoluminescence (PL) spectra. They concluded that the entire optical process could be ideally classified into two processes. First, the inelastic tunneling excitation events could lead to plasmon-mediated light emissions associated with the substrate. Second, molecular fluorescence (MF) was 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. How surface plasmons affect the MF, however, has not been studied.[7]

In this study, we have examined STML from H_2TBPP thin films on various substrates including noble metals, highly oriented pyrolytic graphite (HOPG), and indium tin oxide (ITO) glass in order to further understand the mechanism of STM-excited molecular fluorescence. We found that MF could only be observed for the films on the noble metal substrates, which suggests an enhancement of MF by substrate surface plasmons in a STML measurement.

The Au and Ag substrates have been respectively prepared in a vacuum chamber by evaporating gold and silver onto cleaved mica. The deposited Au film was heated at 400 °C to produce atomically flat terraces of Au(111). The H_2TBPP molecule [Fig. 1(a)] was obtained by the condensation of 3,5-di-tert-butyl benzaldehyde and pyrrole in dichloromethane in the presence of trifluoroacetic acid, followed by dehydrogenation with *p*-chloranil. The organic films on Au(111), Ag, HOPG, and ITO substrates were prepared by a simple spin casting from a 0.38 mM solution of H_2TBPP in chloroform ($CHCl_3$) at a spin velocity of 2000 rpm. The topographies of the films were characterized by STM (DI Nanoscope E) and atomic force microscopy (AFM) (DI IIIa).

The STML measurements were performed in air at room temperature by using the STM. STM tip was a commercial Pt–Ir (10%) tip. Photons emitted from the tunneling junction were collected by an optical 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.) in a spectrum range from 300 through 800 nm. The limit of minimum detection is $\sim$3 cps/channel. Every measurement has been done within 3 h after the sample preparation.

The morphological AFM images of H_2TBPP films on as-earlier substrates are shown in Fig. 1. From these pictures, we can know that the films of H_2TBPP are smooth and uniform. The overall surface morphologies of the films are similar to those of the underlying substrates although there are some small vacancies and granular aggregates in organic films. The average thickness of the organic films is evaluated by partially removing the films by using AFM and found to be similarly about 4 nm. All PL spectra of as-prepared four samples exhibit the same two peaks at 650 and 715 nm in wavelength similar to PL of H_2TBPP in solution (curve 5 in Fig. 3).

Figure 2 shows STML for Ag substrate before and after the deposition of H_2TBPP thin film on it. The STML spectrum from the pristine Ag surface shows a broad single-peak feature at around 685 nm (curve 1). However, two additional

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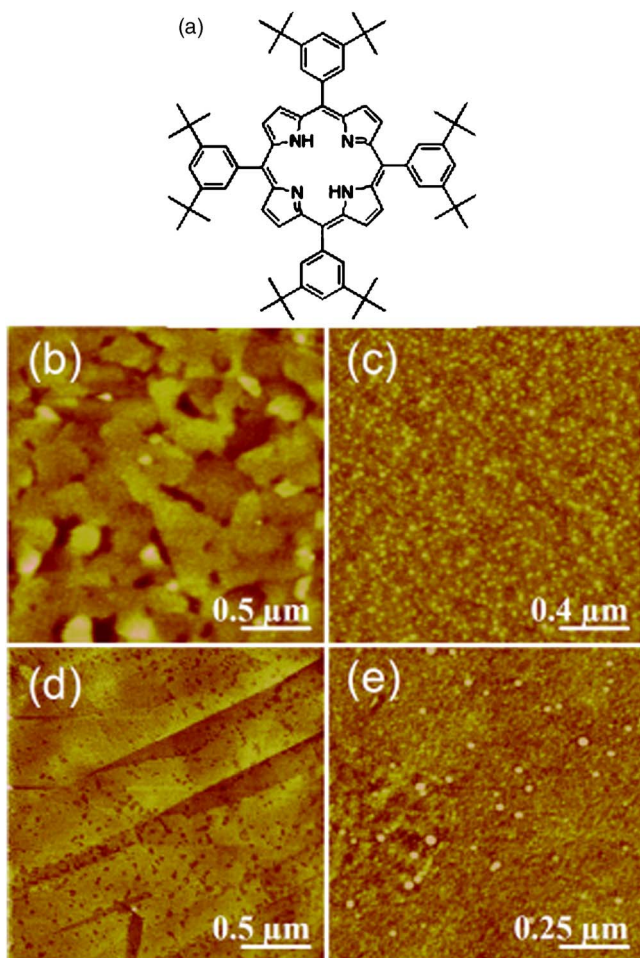[a)]Author to whom correspondence should be addressed; electronic mail: hwliu31@sanken.osaka-u.ac.jp

FIG. 1. (Color online) (a) The molecular structure of H_2TBPP. The topographies of H_2TBPP film on (b) Au(111), (c) Ag, (d) HOPG, and (e) ITO by AFM in tapping mode.

peaks appear at 662 and 715 nm from H_2TBPP-covered Ag substrate (curves 2 and 3) which are well matched with those in the PL from H_2TBPP films and the molecules in $CHCl_3$. This result reveals the contributions of luminescence from H_2TBPP molecules themselves to the STML.[5] The luminescence is emitted from H_2TBPP/Ag (Ref. 8) at both polarities
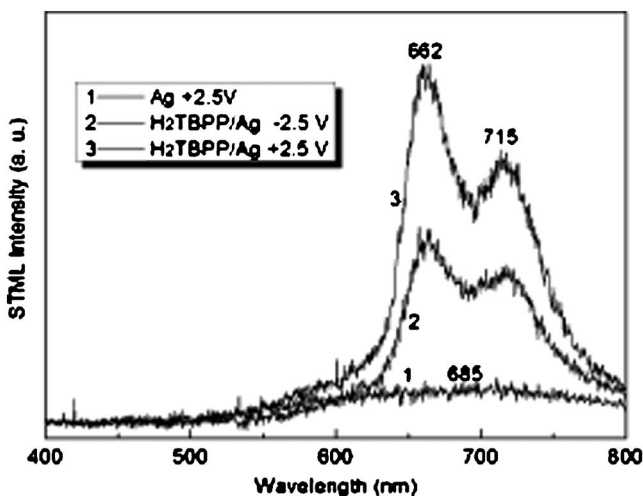

FIG. 2. STML from the pristine Ag (curve 1: 0.8 nA, 2.5 V), and polarity dependence of STML from H_2TBPP/Ag (curve 2: 0.8 nA, −2.5 V; curve 3: 0.8 nA, 2.5 V).
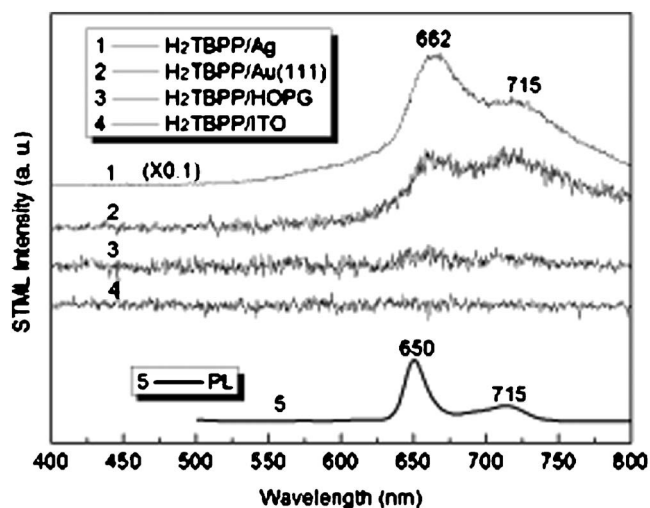

FIG. 3. STML spectra from H_2TBPP/Ag (curve 1: 0.8 nA, 2.5 V), $H_2TBPP/Au(111)$ (curve 2: 2 nA, 2.8 V), $H_2TBPP/HOPG$ (curve 3: 1.5 nA, 2.5 V), H_2TBPP/ITO (curve 4: 8 nA, 2.5 V), and PL spectrum from H_2TBPP in $CHCl_2$ solvent using a He–Cd laser at 425 nm (curve 5).

of the applied voltage, and the intensity at negative bias voltage (curve 2) is weaker than that at positive voltage (curve 3) as described in Ref. 5. Here the positive bias voltage means that the sample is positively biased relative to the tip. The luminescence spectra from H_2TBPP/Ag seem to consist of two components: the molecular fluorescence similar to PL and the plasmon-mediated light emission from the Ag substrate.[4]

Similarly, we can observe two obvious peaks at 662 and 715 nm in STML spectrum from $H_2TBPP/Au(111)$. However, in contrast to noble metal substrates, it is much difficult to observe molecular fluorescence from H_2TBPP on HOPG and ITO. Even after varying a large number of the scanning parameters, we have obtained only few curves repeatedly showing intensity from $H_2TBPP/HOPG$ with peaks at 662 and 715 nm, which are extremely weak and only two times stronger than the experimental accuracy, i.e., 3 cps/channel, as shown in Fig. 3. We did not observe any light emitted from H_2TBPP/ITO in all the experiments. The maximum intensity of MF from H_2TBPP/Ag is at least 100 times stronger than that from $H_2TBPP/HOPG$ under the same experimental conditions in our measurements.

From our experimental results, we can further point out that once MF occurs, its intensity also depends on the kind of substrate. The intensity of MF from H_2TBPP on Ag is ten times greater than that on Au. Two possibilities can be accounted for it. One is that the Ag surface is rougher than Au(111) surface, which will affect the enhancement of STML. The other one is that the coupling of energies between electron-hole pairs in molecular film and the metal surface plasmons is stronger for Ag than that for Au. Recently, Uehara *et al.*[9] observed molecular fluorescence from a single molecule of rhodamine 6G on HOPG by STML but the light intensity seemed to be very weak. It should be mentioned that from our results and previous reports, the strong molecular fluorescence could have been observed only on metal substrates which showed strong plasmon-mediated light emission.[4–6,10,11]

Hence, we propose a mechanism tentatively called surface plasmon-enhanced molecular fluorescence (SEMF). 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 nonlocal electric field caused by the tip. The second one is the molecular excitation and MF associated with HOMO-LUMO transitions in H_2TBPP film. In this process, MF is well enhanced by electrodynamical coupling between the oscillating dipole associated with the molecule and local surface plasmons, so that the MF can be detected in the far field region. This electrodynamical coupling is crucial for observing MF in STML, i.e., if surface plasmons from its substrate like HOPG or ITO are absent or weak, then the MF excited by STM becomes extremely weak. We note that the Pt–Ir tip did not work to produce plasmon mediated lights for these systems in our measurements.

The fact that the luminescence is observed from H_2TBPP/Ag and H_2TBPP/Au at both polarities may support our SEMF model because local surface plasmons of a metal substrate could be excited at both polarities.

Now, we consider rate equations for SEMF. We consider the simplest case that the organic molecule has two states: the ground and the excited states. The number of the excited molecules N_2 will increase by

$$dN_2/dt = N_1\gamma_e I_t + (N_1 - N_2)W_p B - N_2(\Gamma + k_{NR}), \quad (1)$$

where N_1 is the number of the ground state molecule, γ_e is the direct excitation probability per unit tunneling current, I_t is the tunneling current, W_p is the energy density of the plasmon-mediated light at the HOMO-LUMO transition energy, B is the rate of transition induced by the plasmon-mediated light, Γ is the radiative decay rate, and k_{NR} is the nonradiative decay rate. The first, second, and third terms of the right-hand side of Eq. (1) represent direct molecular excitation by the tunneling current, the radiation induced process, and the spontaneous deexcitation process, respectively.

We assume that the energy density of the plasmon-mediated light W_p is solely determined by the tunneling current. As $dN_2/dt=0$ in equilibrium and $N_1+N_2=N$, where N is the total number of the organic molecule, N_2 is given by

$$N_2 = N(\gamma_e I_t + W_p B)/(\gamma_e I_t + 2W_p B + \Gamma + k_{NR}). \quad (2)$$

Then the intensity of the molecular fluorescence for a metal substrate, $I_{MF\ metal}$ is given by

$$I_{MF\ metal} = N_2(\Gamma + W_p B) = (\Gamma + W_p B)(\gamma_e I_t + W_p B)N/(\gamma_e I_t$$
$$+ 2W_p B + \Gamma + k_{NR}). \quad (3)$$

For a nonmetal substrate, as W_p is negligibly small, the intensity of the molecular fluorescence for a metal substrate, $I_{MF\ nonmetal}$ is given by

$$I_{MF\ nonmetal} = N_2\Gamma = \Gamma\gamma_e I_t N/(\gamma_e I_t + \Gamma + k_{NR}). \quad (4)$$

For $W_p B \gg \Gamma$, $k_{NR} \gg \gamma_e I_t$, the enhancement factor by surface plasmon is given by

$$I_{MF\ metal}/I_{MF\ nonmetal} = (W_p B/2\gamma_e I_t)(\Gamma + k_{NR}/\Gamma) \gg 1. \quad (5)$$

Thus the enhancement factor could be very large when the direct excitation of organic molecules by tunneling electron is very small compared with the excitation by plasmon field $W_p B$.

Surface plasmon enhancement is not a quite unacquainted concept. We have met it before in other techniques of light detection such as PL[12,13] and Raman scattering.[14,15] Some decades ago, Fleischmann[14] and then Van Duyne *et al.*[15] sequentially reported huge Raman intensities observed under certain conditions. Van Duyne concluded that the signal arose due to a tremendous enhancement of the Raman cross section for the adsorbed molecules by surface plasmons. Today, it is commonly accepted that it arises mainly due to electromagnetic enhancement. For such an enhancement, a suitable choice of the metal (copper, silver, and gold being the most used) and a roughening of the surface turned out to be the key factors. These considerations are in good agreement with our experimental results.

Our success to observe MF from organic molecules at atmospheric conditions suggests the possibility of STML for biological samples in the nearest future.

In summary, we have studied luminescent properties of spin-coated H_2TBPP films on solid substrates Au(111), Ag, HOPG, and ITO by means of STM in air at room temperature. We have observed STM-excited molecular fluorescence associated with the HOMO-LUMO transitions for the $H_2TBPP/Au(111)$ and H_2TBPP/Ag, which are in agreement with their PL spectra, however, we did not obtain signal for $H_2TBPP/HOPG$ and H_2TBPP/ITO while we observed PL peaks for all the samples. We propose a new mechanism as SEMF, suggesting that the electrodynamical coupling between molecular excitation and surface plasmons is crucial for observing molecular fluorescence in STML.

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