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## STM fluorescence of porphyrin enhanced by a strong plasmonic field and its nanoscale confinement in an STM cavity

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We have investigated scanning tunneling microscope-induced luminescence (STML) from porphyrin molecules by varying the tip (PtIr, Ag, and Au)/substrate (Pt, Ag, Au, and indium tin oxide) combinations. Strong molecular fluorescence by highest-occupied molecular orbital and lowest-unoccupied molecular orbital transition comparable to plasmon-mediated light is emitted only when both the substrate and the tip are metals but not in other cases. Along with calculations of relative electromagnetic-field powers in the tip-substrate gaps, the enhancement of STML from molecules can be interpreted in terms of the strong plasmon field and its confinement in an STM cavity. We also find rather strong energy-forbidden fluorescence of porphyrin in an Au-tip/porphyrin/Au cavity that occurs under the extremely strong field in the plasmonic nanocavity.

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Enhancement of and novel nonlinearities in the light-emitting process of molecules<sup>1</sup> are topics of great current interest in plasmonics, which promises a new generation of highly miniaturized photonic devices.<sup>2</sup> Nowadays, the plasmon enhancement effect is widely used to increase the light-emission intensity from molecules in Raman scattering,<sup>3–7</sup> second-harmonic generation,<sup>8</sup> near-field microscopy,<sup>9</sup> and fluorescence.<sup>10–14</sup>

Scanning tunneling microscope (STM)-based plasmonic enhancement of molecules would be fundamentally important to the development of organic electrophotonic nanodevices.<sup>15</sup> STM-induced light emission (STML) (Refs. 15–28) is different from the above-mentioned optical techniques because (1) the light emission is excited in an extremely narrow gap (the tunnel junction), while (2) the traditional excitation source, a laser is abandoned and the tunneling electrons are used instead. In the past few years, we have focused on improving the electron-photon conversion efficiency in STML by surface plasmons of novel metal substrates such as Ag and Au. We proposed a model of surface-plasmon-enhanced molecular fluorescence (SEMF) (Ref. 15) based on our experimental results, wherein the STML intensity from molecules on a silver substrate could be enhanced  $\sim 100$  times compared to that on a nonmetal substrate such as highly oriented pyrolytic graphite and indium tin oxide (ITO). Subsequently, this model was verified by showing that the plasmon-mediated light emission from a metal substrate overlapping with the absorption of molecules enhances molecular fluorescence.<sup>28</sup> In this paper, we propose a plasmonic cavity effect on STML from molecules for specific tip-substrate combinations.

Berndt *et al.*<sup>19</sup> investigated the plasmon-mediated light emission for different metallic tip-substrate combinations, including Au, W, and Ag tips with Au and Ag substrates, and explained the spectral shapes and relative intensities in terms of tip-induced plasmon modes, which were found to be sensitive probes of nanocavities between the tips and samples. There are various tip-substrate combinations possible: either

of the tip or substrate is a metal while the other is a nonmetal (case I), both are metals (case II), or both are nonmetals (case III). In this study, in order to get in-depth insights into the cavity effects in STML and the molecular fluorescence process in a nanocavity, we investigated case I above, wherein one of the electrodes is a nonmetallic substrate and case II wherein both electrodes are noble metals with small skin depths. Four different substrates (ITO, Pt, Ag, and Au) and three types of tips (PtIr, Ag, and Au) were used in this experiment. We also found rather strong energy-forbidden molecular fluorescence in a metallic cavity that occurs under the extremely strong electromagnetic field of the nanoscale plasmonic cavity.

The Au, Ag, and Pt substrates were prepared in a vacuum chamber by evaporating Au and Ag and by sputtering Pt onto freshly cleaved mica, respectively. The ITO substrates were obtained from Sanyo Vacuum Industries Co., Ltd. The STM tip was either PtIr (10%) or Ag. The porphyrin H<sub>2</sub>TBPP 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 as-prepared substrates were spun from a 0.81 mM solution of H<sub>2</sub>TBPP in chloroform (CHCl<sub>3</sub>) at a spin velocity of 2000 rpm. The topographies of the films were characterized by STM (DI Nanoscope E). The organic overlayer consists of nanoaggregates of molecules. The films were smooth and uniform in the scan area ( $20 \times 20 \mu\text{m}^2$ ). The overall surface morphologies of the films were similar to those of the underlying substrates.<sup>15</sup>

The STML measurements were performed under ambient conditions. The accumulation time for each spectrum was 60 s or 180 s. Photons emitted from the tunneling gap are collected by a glass fiber of 1 mm diameter, placed 1 mm from 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 [(ICCD) PI-MAX camera and ST-133A Controller, Princeton Instruments, Inc., spectrum range between 385 and 800 nm, and

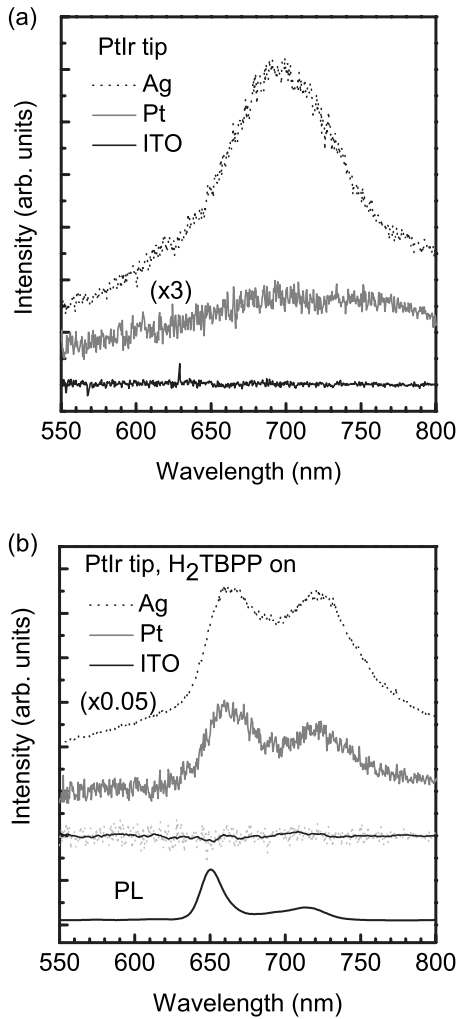


FIG. 1. (a) STML spectra of Ag, Pt, and ITO. (b) STML spectra of porphyrin on the above-mentioned substrates and PL spectrum of porphyrin in  $\text{CHCl}_3$  solvent using a xenon lamp at 518 nm. A PtIr tip was used in the STML experiments (bias voltage = +2.2 V; tunneling current = 1.0 nA).

dark current < 3 counts/s at  $-33^\circ\text{C}$ ]. The estimated solid angle of light detection is about 0.16 str in the present experiments.

In Fig. 1, we show the STML spectra of the pristine substrates [Fig. 1(a)] and those with porphyrin overlayers [Fig. 1(b)] using the PtIr tip at a sample bias of 2.2 V and tunneling current of 1.0 nA. Figure 2 shows the STML spectra of the pristine substrates [Fig. 2(a)] and those with porphyrin overlayers [Fig. 2(b)] with an Ag tip at a sample bias of 2.2 V and tunneling current of 1.0 nA, except for pristine ITO for which the sample bias was increased to 2.6 V to obtain a stronger intensity. The integrated intensities of the distributions under the spectra in Figs. 1 and 2, including the two vibronic peaks in Figs. 1(b) and 2(b), are given in Table I(a) for comparison. For the pristine substrates, we find that the STML intensities are  $I_{\text{Ag}} > I_{\text{Pt}} \gg I_{\text{ITO}}$  for both the PtIr and Ag tips. For the same substrate, the STML intensity with an Ag tip is much stronger than that with a PtIr tip. STM light emission from the metallic cavities has been realized to be extremely strong with excitation yield of one photon in the

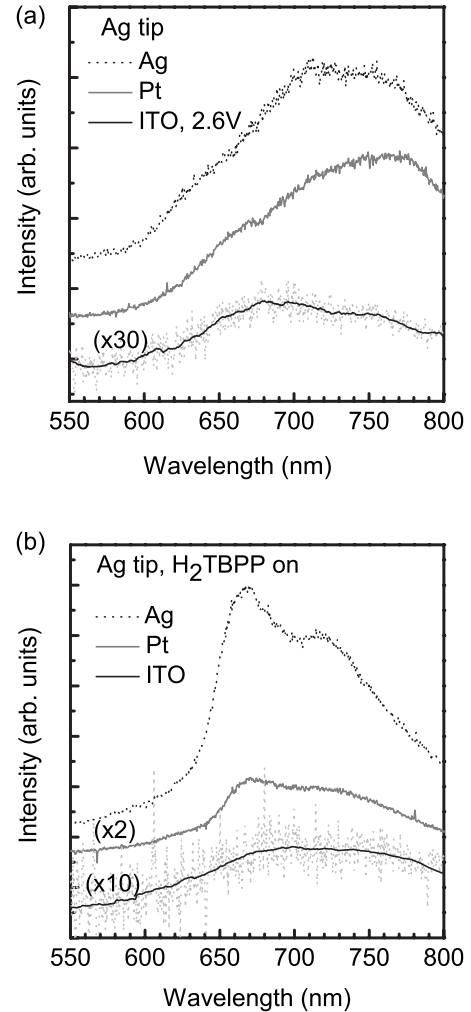


FIG. 2. (a) STML spectra of Ag, Pt, and ITO. (b) STML spectra of porphyrin on the above-mentioned substrates. An Ag tip was used in the STML experiments (bias voltage = +2.6 V for pristine ITO and +2.2 V for others; tunneling current = 1.0 nA).

visible range per  $10^4$  tunneling electrons for an Ir-tip/Ag-substrate system and considered to be mediated by tip-induced plasmons at the tunneling junction.<sup>20</sup> For the samples with porphyrin overlayers [Figs. 1(b) and 2(b)], the light-emission spectra change from a plasmon-mediated one to molecular fluorescence and substrate plasmon-mediated one, wherein the molecular fluorescence is the main component.

The porphyrin molecular luminescence is similar to the photoluminescence spectrum [Fig. 1(b) bottom], and thus it arises from radiative transitions between the highest-occupied molecular orbital and lowest-unoccupied molecular orbital (HOMO-LUMO) in neutral molecules. The peak of STML at  $\sim 660$  nm can be assigned to the  $Q_x(0,0)$  fluorescence while the  $\sim 723$  nm peak to the vibronic overtone  $Q_x(0,1)$ .<sup>24</sup> The intensities of the molecular fluorescence are comparable to those of the plasmon-mediated light emission for the corresponding pristine substrates. That is, the molecular fluorescence depends on the substrate and the tip materials in a similar manner as plasmon-mediated light emission from the pristine substrate. These results support, in a more

TABLE I. (a) The integrated intensities of the distributions under the spectra in Figs. 1 and 2 by various tip/substrate combinations with and without molecules (unit: counts/s). Sample bias voltage: 2.2 V; tunneling current: 1.0 nA (\* 0 counts/s at 2.2 V and 34 counts/s at 2.6 V). (b) Calculated relative electromagnetic-field powers in the tip-substrate gaps to those in free space (gap=1 nm; bias voltage=2.2 V).

	PtIr tip	Ag tip
(a)		
ITO		34*
Pt	460	4223
Ag	3600	6018
H <sub>2</sub> TBPP on ITO		102
H <sub>2</sub> TBPP on Pt	300	2910
H <sub>2</sub> TBPP on Ag	8543	14551
(b)		
ITO	51.0	67.8
Pt	1356	3242
Ag	2727	6955

detailed manner, our previous proposal of SEMF (Ref. 15) for tunneling-electron-induced molecular fluorescence from an organic film in the STM, which is as intense as the plasmon-mediated light emission from the corresponding pristine substrate, is significantly enhanced by surface plasmons of the substrate and the tip.

Strong plasmon-mediated light emission and molecular fluorescence are observed for both cases of Ag-tip/Pt-substrate and PtIr-tip/Ag-substrate [Table I(b)]. This result is in accordance with the optical properties of Ag for which an intense localized surface-plasmon resonance can be excited in the visible or near-infrared (IR) region. One may expect that by using an Ag tip, strong molecular fluorescence can be observed even for an ITO substrate, since molecular fluorescence is enhanced by strong local surface plasmons on the Ag tip. Plasmon-mediated light emission and molecular fluorescence of porphyrin are indeed stronger for the Ag-tip/ITO cavity than for the PtIr-tip/ITO cavity. However, the STML intensities for the Ag-tip/ITO cavity do not exceed those for the PtIr-tip/Pt cavity. We consider that this result shows how an electromagnetic field is confined in a cavity. For a metal/metal cavity, the electromagnetic field is confined within the tip/substrate gap as the field penetrates into the metal electrodes only by a thin skin depth (around 10 nm). For a metal/nonmetal cavity, the electromagnetic field is not confined within the tip/substrate geometrical gap, as the field penetrates into the nonmetal electrode. The skin depth is estimated by the calculation shown below to be around 1000 nm for ITO and is much thicker than the value of 12.5 nm for Pt which is in the visible range. Thus, the effective volume of the STM-substrate cavity for metal/metal combinations is much smaller than that for metal/nonmetal combinations.

For the metallic cavities, the experimental results [Table I(a)] are in accordance with the expectation that the stronger surface-plasmon field of Ag, as compared to Pt, leads to fur-

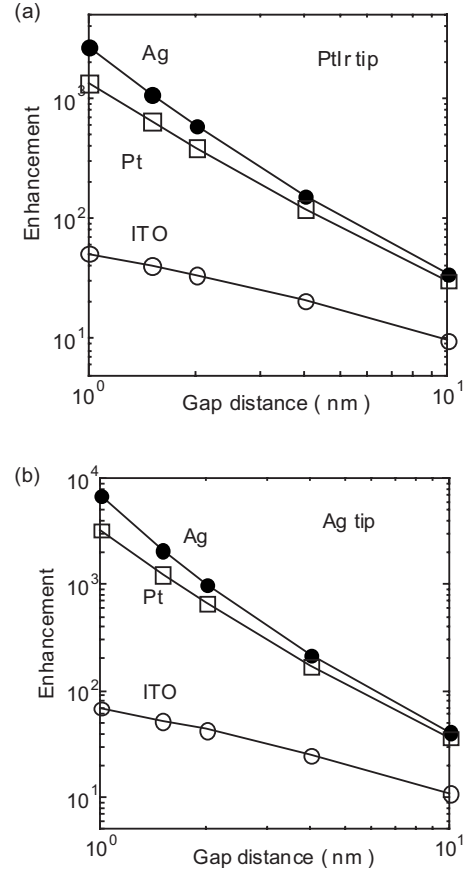


FIG. 3. Using a PtIr-tip (a) and an Ag tip (b) calculated electromagnetic-field power enhancement inside the STM nanocavity as a function of the tip-substrate gap for various substrates (Ag, Pt, and ITO) (tip radius=40 nm, bias voltage=2.2 V, and photon energy=1.85 eV).

ther enhancement of plasmon-mediated light emission and light emission from the porphyrin molecule. The enhancement of light intensity for the metal cavity depends on plasmon damping in metals. The plasmon field in a metal is strong for weak damping. At optical frequencies, surface plasmons exhibit the greatest intensity in Ag and Au due to their weak damping ( $\epsilon_2 \ll |\epsilon_1|$  where  $\epsilon_1$  and  $\epsilon_2$  are real and imaginary parts of the dielectric function, respectively). At a photon energy of 2 eV, the dielectric function is  $\epsilon = -3.53 + 0.192i$  for ITO,  $-10.39 + 17.48i$  for Pt,  $-15.46 + 0.409i$  for Ag, and  $-8.72 + 1.60i$  for Au.<sup>29-33</sup> For Pt, the imaginary dielectric constant is large and thus, the resonance is rather broad and the surface plasmons are not intense. The plasma frequency for dielectric ITO occurs in the near-IR region, causing this material to be reflective in the mid-IR region and transparent in the visible region.

In order to examine the cavity material dependence and gap size dependence of plasmon-mediated light emission, we calculate the electromagnetic-field power enhancement inside a STM nanocavity as a function of the tip-substrate gap size  $d$  for substrate materials (Ag, Pt, and ITO) with a PtIr tip [Fig. 3(a)] and an Ag tip [Fig. 3(b)]. The STM cavity is approximated by a flat substrate and a spherical metal tip of 40 nm radius. The field power inside the STM cavity  $P_c$  is

calculated according to the scheme described by Rendell and the others<sup>34–37</sup> for a sample bias of 2.2 V and at a photon energy of 1.85 eV ( $\sim 660$  nm), which corresponds to the peak energy of STM light emission from porphyrin molecules. The complex dielectric constants for the substrate and the tip are obtained from Refs. 29–33. The dipole is produced by the tunneling of an electron from the tip to the sample. The field power of this dipole placed in free space  $P_{\text{free}}$  is given by

$$P_{\text{free}} = \frac{\omega^4 p^2}{4\pi\epsilon_0 3c^3},$$

where  $\omega$  is the angular frequency of the photon, and  $p$  is the electric dipole and is assumed to be  $e \times d$ . The electromagnetic-field power enhancement is defined as the ratio of the plasmon field power  $P_c$  to the field power  $P_{\text{free}}$  after the work of Johansson *et al.*,<sup>38</sup>

$$\text{enhancement} = \frac{P_c}{P_{\text{free}}}.$$

The intensity of STM light emission is proportional to the squared oscillating dipole at the STM junction with the tip and substrate present.<sup>18</sup> The enhancement is given by the relative ratio between the squared dipole with the tip and substrate present and that without the tip and substrate. Figures 3(a) and 3(b) show that the enhancement factor of the electromagnetic-field power is sensitively dependent on the materials; the factors at  $d=1$  nm are  $\sim 50$ , 1400, and 2700 for ITO, Pt, and Ag, respectively for a Pt tip and  $\sim 70$ , 3200, and 7000, respectively, for the Ag tip.<sup>39</sup> The material dependence of the experimentally observed light-emission intensities for pristine substrates is qualitatively reproduced by this simple calculation using the dielectric functions given above. These results are in good agreement with previous theoretical work by Mills<sup>18</sup> wherein surface-plasmon-induced field enhancements in the STM environment are much stronger for a Ag substrate than for a Cu substrate.

The calculated relative electromagnetic-field powers in the tip-substrate gaps are shown in Table I(b). The calculated ratios of the electromagnetic-field power for different combinations of STM tips and substrates are  $P_{\text{tip-Ag}_{\text{sample}}}/P_{\text{tip-Pt}_{\text{sample}}}=2.0$ ;  $\text{Ag-Ag}/\text{Ag-Pt}=2.1$ ; and  $\text{Ag-Ag}/\text{Pt-Ag}=2.6$ , at a bias of 2.2 V, photon energy of 1.85 eV, and gap of 1 nm. The corresponding experimental data are 6.5, 1.4, and 2.0 at 2.2 V. The big difference between the calculations and experiments for  $P_{\text{tip-Ag}_{\text{sample}}}/P_{\text{tip-Pt}_{\text{sample}}}$  may be caused by the different Ag and Pt film topographies. Further experiments in a UHV system and theoretical studies are needed to understand these results.

Figures 3(a) and 3(b) show that the electromagnetic-field power is strongly enhanced with decreasing gap size  $d$ . This indicates that the enhancement is a result of the cavity effect.<sup>19</sup> As the gap separation decreases, the gap mode is confined to a narrower gap and the electric field energy density in the gap increases. As can be seen from Figs. 3(a) and 3(b), the electromagnetic-field power is roughly in proportion to  $d^{-x}$  where  $x$  is—using a PtIr (Ag) tip—0.7 (0.8) for ITO, 1.7 (1.9) for Pt, and 2.0 (2.2) for Ag. According to the

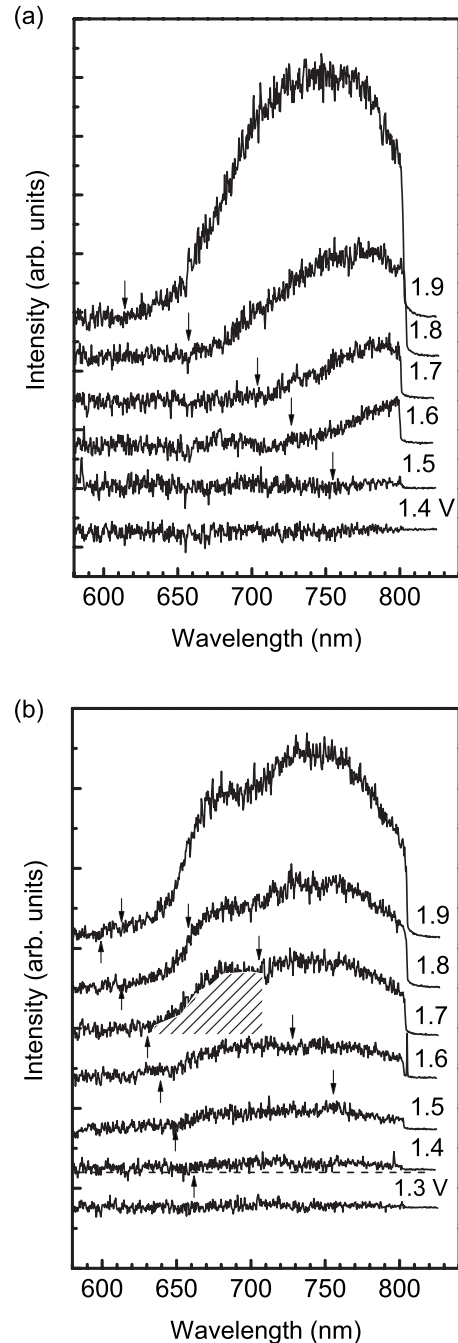


FIG. 4. STML spectra from (a) Au-tip/pristine-Au (plasmon-mediated light emission) and (b) Au-tip/porphyrin/Au (mainly molecular fluorescence) systems at different biases (1.3–1.9 V at intervals of 0.1 V). The tunneling current is 1.0 nA for all measurements. The cut-off energy of molecular fluorescence (up arrows) is much larger than that of plasmon-mediated emission (down arrows), showing strong energy-forbidden light emission of molecules. The dashed line is a base line of the spectrum at 1.4 V as a guide for the eyes.

calculated material and gap size dependences of plasmon-mediated light emission, we attribute the experimentally observed huge plasmon-mediated light emission and molecular fluorescence of porphyrin in the plasmonic cavities to the extremely strong electromagnetic-field power arising from



the nanocavity plasmon modes. The present STML study may be relevant to a surface enhanced Raman scattering (SERS) theory, where enhancement is analyzed via the interaction between a molecule and an electromagnetic mode in the cavity formed by the junction between two closely spaced metal nanoparticles.<sup>3,6,40</sup>

In addition to the enhancement in luminescence due to a high field in the STM cavity, we observed strong “energy forbidden” light emissions in STML of molecules. We measured the STML spectra from the Au-tip/pristine-Au [Fig. 4(a)] and Au-tip/porphyrin/Au [Fig. 4(b)] systems. In principle, the plasmon-mediated emission from the metallic sample satisfies the quantum cut-off condition. In Fig. 4(b), we can see that the cut-off energy of molecular fluorescence of Au-tip/porphyrin/Au (up arrows) is much larger than that of plasmon-mediated emission of Au-tip/pristine-Au (down arrows), showing strong “energy forbidden” light emissions in the STML of the molecule. The threshold of sample bias voltage for molecular fluorescence is 1.4 V. The mechanism of energy forbidden transitions is still not clear. Hoffmann *et al.*<sup>41</sup> observed forbidden transitions for Na overlayers on Cu(111) at high currents and attributed this to a two-electron excitation mechanism. Fourkas and co-workers<sup>42</sup> reported that the multiphoton photoluminescence from Au nanoparticles can be generated efficiently via near-infrared excitation due to field-enhancement effects. However, the two-photon excitation mechanism is probably unlikely in the present study because the excitation source is tunneling electrons and the forbidden transitions were observed at very low currents. A possible cause of this may be related to the extremely strong field of the plasmonic nanocavity-assisted excitation of the “heating” porphyrin layer. More experimental

and theoretical studies are needed. Studies of such nonlinear optical phenomena at nanocavities are very important as nonlinear effects may be used to provide new elements for local-plasmon-based photonics at the nanometer scale.

To conclude, we investigated STML from porphyrin H<sub>2</sub>TBPP thin films on various substrates (Pt, Ag, Au, and ITO) using a PtIr, Ag, or Au tip. The porphyrin-originating fluorescence intensities are strong and comparable to plasmon-mediated light emissions from corresponding pristine substrates. The plasmon-mediated light emission and porphyrin fluorescence for the Ag-tip/ITO (metal/nonmetal) cavity are weaker than for the PtIr-tip/Pt-substrate (metal/metal) one. We ascribe this to higher electromagnetic-field confinement for the latter metallic cavity. Furthermore, for metal/metal cavities, STM light emission is much stronger when at least one of the electrodes is Ag, since an extremely strong electromagnetic field of the gap plasmon mode could be established. We calculated the electromagnetic-field powers in the tip-substrate gaps and found that a simple calculation using the dielectric constants can explain the observed material dependency of the plasmon-mediated light emission quite well. According to these results, our previous proposal of surface-plasmon-enhanced molecular fluorescence<sup>15</sup> is extended to the case for enhancement by a strong cavity plasmon mode. We also find rather strong energy-forbidden fluorescence of porphyrin which occurs only under an extremely strong field in the plasmonic nanocavity. This understanding will provide a pathway to obtain strong light emission from molecules excited by electrons, which will enable fabrication of nano-organic light-emitting devices.

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