# Anomalous Light Emission from Metal Phthalocyanine Films on Au(111) Activated by Tunneling-Current-Induced Surface Plasmon

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We performed a scanning-tunneling-microscopy-induced light emission (STM-LE) study on Cu- and Zn-phthalocyanine films formed on a Au(111) surface. Optical emission with transition between the highest occupied and lowest unoccupied molecular orbitals (HOMO–LUMO) was observed at bias voltages lower than the energy corresponding to the molecular HOMO–LUMO gap. The voltage and current dependences of STM-LE intensities show an inconsistency for both samples, i.e., although the former shows the existence of onsets below the HOMO–LUMO gap energies, suggesting excitations by a two-electron process via an intermediate state, the latter shows a linear relationship expected from one-electron excitation processes. © 2010 The Japan Society of Applied Physics

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For example, because of their durability and characteristic electronic properties, metal phthalocyanines are widely used as a hole injection layer for electroluminescence devices.[1] Therefore, it is of great importance to clarify the detailed electronic transition processes in the films of these dye materials not only for the understanding their scientific basis but also for determining their applications. A scanning-tunneling-microscopy-induced light emission (STM-LE) technique is one of the methods for studying such processes and for obtaining a localized signal.

In recent studies of STM-LE from molecular layers on metal substrates, such as copper phthalocyanine and porphyrine derivatives on a Au(111) surface, highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) emission was observed despite the fact that the bias voltage for excitation was lower than the HOMO–LUMO gap energies.[2,3] Various mechanisms, such as excitation via an intermediate state[2] and the energy level shift,[3] have been discussed and the effect of surface plasmon is suggested;[2–9] however, their details have not yet been clarified.

To determine the basic mechanism, we investigated the bias voltage and tunneling current dependences of STM-LE intensity using two types of sample, namely, Cu- and Zn-phthalocyanine [CuPc and ZnPc, the molecular structure is shown in Fig. 1(a)] films formed on a Au(111) surface. Despite the fact that the tunneling current dependence provides the basis for determining a certain process, for example, a one- or two-electron process, such an experiment has never been performed, probably owing to the instability of the molecular films at a high tunneling current. In this paper, we present the results of the experiment; a stable measurement over the necessary range of tunnel current intensities was realized with the flow of nitrogen gas.

A custom-made STM-LE system was prepared for the experiment, in which an STM head was set in a metallic shading box. A mechanically cut PtIr tip was used for injecting tunneling current, and the emitted photons were focused onto the entrance edge of an optical fiber (single core, diameter: 600 μm) using two fused-silica lenses, as shown schematically in Fig. 1(b). The focal lengths and spacing of these lenses were carefully selected to minimize chromatic aberration. The emitted photons were introduced into a monochromator with a 150 grooves/mm grating and detected with a Peltier-cooled charge-coupled device (CCD) with a high sensitivity (1024 × 127 pixels). The CCD exposure time was fixed at 128 s. STM topographic and spectroscopic measurements were started and finished simultaneously. A median filter was applied to remove spike noises of the CCD. The scan area was $1 \times 1\,\mu m^2$. When the measurements were performed in air, the obtained signal was not stable and rapidly decreased in intensity during the measurements. The dry $N_2$ gas flow around the STM tip enabled stable measurements, probably by preventing the sample from being damaged by oxidation. We repeated the measurements several times over the same area to verify the stability of the signal under the measurement conditions. Samples were prepared by the vacuum deposition of ~200-nm-thick CuPc and ZnPc films on Au(111)/mica substrates.

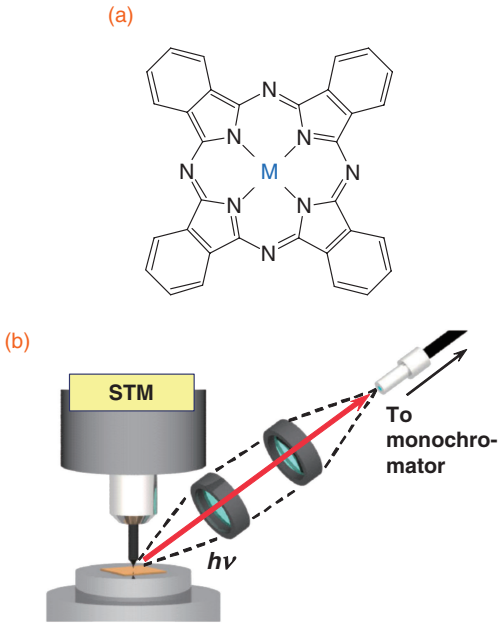


Fig. 1. (a) Molecular structure of metal phthalocyanine (in this study, M stands for Zn and Cu); (b) Schematic drawing of STM-LE light collection system.

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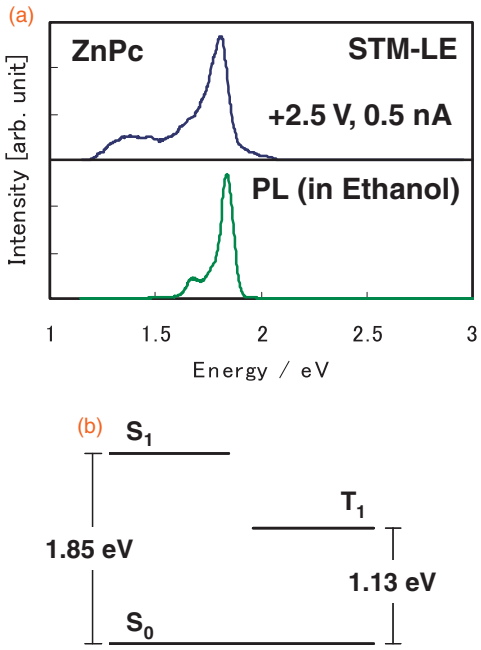


**Fig. 2.** (a) Typical STM-LE and photoluminescence spectra from ZnPc/Au(111) system. The STM spectrum consists of tip-induced plasmon and molecular electronic transition components. (b) Energy diagram around ground and first excited states of ZnPc.[10)]

Figure 2(a) shows typical spectra obtained by observing the STM-LE (+2.5 V and 0.5 nA) from a ZnPc/Au film (upper spectrum) and by the photoluminescence (PL) measurement of ZnPc solution with excitation using a 405 nm CW laser (lower spectrum). Figure 2(b) shows electronic levels around the first excited state.[10)] The emission components at 1.81 eV in the STM-LE spectrum and at 1.84 eV in the PL spectrum are in good agreement and are attributed to the emission induced by the HOMO–LUMO transition of ZnPc [$S_1 \rightarrow S_0$ in Fig. 2(b)]. The low-energy component appearing in the STM-LE spectrum (dominant below 1.5 eV here) originates from the localized tip-induced surface plasmon.

Figure 3(a) shows STM-LE spectra from CuPc/Au(111) obtained at a bias voltage of +1.6 V for various tunneling currents (0.5 nA step, shown with a certain offset). Despite the fact that the bias voltage is lower than the HOMO–LUMO gap energy of the molecule, the spectra have a component corresponding to the HOMO–LUMO gap energy, similar to the previous case.[2)] Spectral intensity increases with the intensity of tunneling current used for excitation. For further analysis, signal intensity was integrated over the blue and red areas in Fig. 3(a) to give the intensity due to the HOMO–LUMO transition, $A_M$, and that due to the tip-induced Plasmon process, $A_P$, respectively. The overlapping component of the plasmon-related emission on the HOMO–LUMO signal was removed by assuming a linear background.

Figure 3(b) shows the bias voltage dependences of $A_M$ and $A_P$. As shown in Fig. 3(b), $A_M$ rapidly increases with $V_s$ from approximately the voltage corresponding to the HOMO–LUMO gap energy of the molecule (1.77 eV, indicated by a purple dashed line): however, we can clearly observe that the signal appears at a voltage lower than the HOMO–LUMO gap energy. The onset is approximately +1.2 V, as shown in the inset, which is close to that obtained in the previous study (+1.1 V).[2)] The threshold energies are

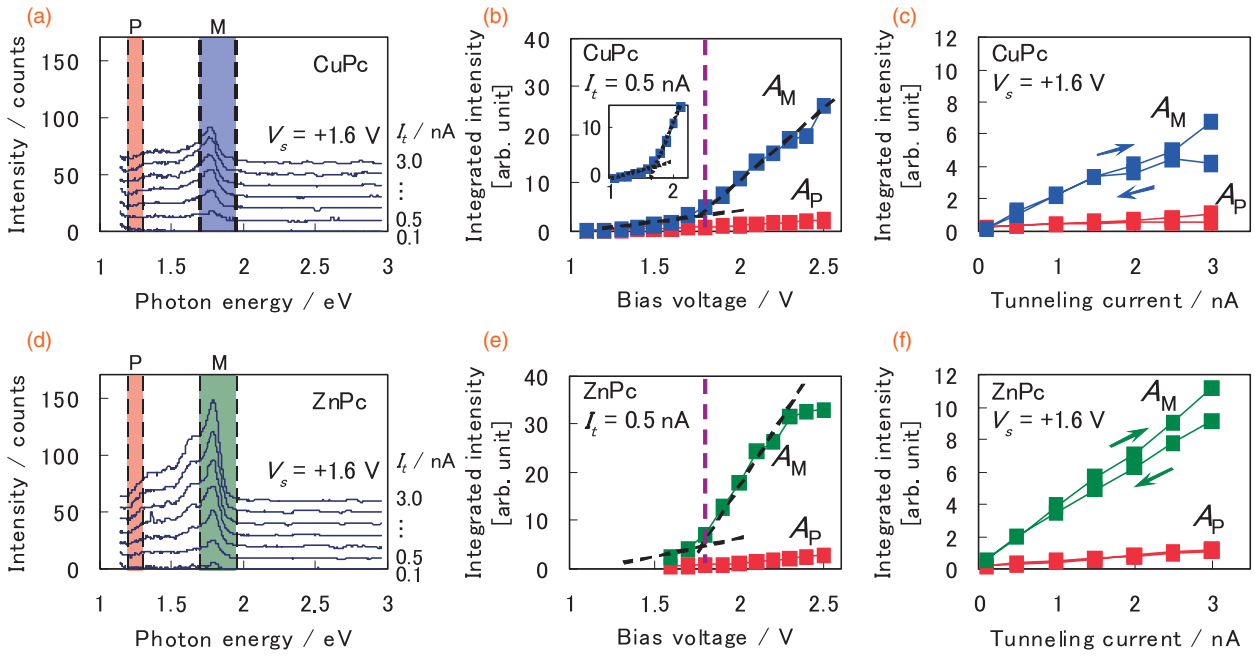


**Fig. 3.** (a) Some STM-induced light emission spectra from CuPc/Au(111) obtained at different tunneling currents. (b,c) Changes in integrated spectral intensities of molecular transition and decay of plasmon of CuPc/Au(111) with bias voltage and tunneling current. The inset of (b) shows a detail from 1 to 2 eV. (d) Some emission spectra from ZnPc/Au(111) at different tunneling currents. (e,f) Changes in integrated spectral intensities of molecular transition and decay of plasmon of ZnPc/Au(111) with bias voltage and tunneling current. Blue, green, and red squares indicate the integrated areas of the hatched regions with the same colors as in (a) and (d). All the data of dependences on the tunneling current are obtained at lower bias voltages than the molecular HOMO–LUMO energy gaps. Black dashed lines in (b) and (e) serve as visual guides, having intersection points close to the HOMO–LUMO gap of each molecule.

close to the triplet state of CuPc, suggesting an excitation process via a triplet state as an intermediate state for a two-electron excitation process, similar to that in the triplet–triplet annihilation process.[2)] However, in consideration of the tunnel current intensity used for the excitation, the STM-LE signal intensity is extremely high for the excitation process including a triplet state.[3)]

To investigate the excitation process in detail, we, for the first time, examined tunnel current dependence of the STM-LE signal intensity using $A_M$ and $A_P$. For the measurement of the current dependence of the STM-LE signal intensity, the bias voltage should be selected below the threshold of the direct HOMO–LUMO transition. On the other hand, it was difficult to obtain a stable signal at a bias voltage lower than 1.6 V when the current was increased, probably owing to sample damage. Therefore, we set the voltage at 1.6 V, which is lower than the threshold as shown in Fig. 3(b). If the excitation is via an intermediate state, i.e., the mechanism is a two-electron process, the emission intensity is expected to have a quadratic dependence on the tunnel current. As shown in Fig. 3(c), however, $A_M$ has a linear current dependence, which is generally observed for a one-electron process, in contrast to the $V_s$ dependence of the emission intensity, i.e., the appearance of the signal with the bias voltage lower than the HOMO–LUMO gap energy that results in a two-electron excitation process.

To confirm the anomalous results obtained for the CuPc/Au sample in this experiment, we performed similar experiments on the ZnPc/Au sample. The obtained results are shown in Figs. 2(d)–2(f). Signal intensity was integrated over the green and red areas in Fig. 3(d) in the same manner as in the case of CuPc. The STM tip came into contact with the sample at a bias voltage lower than +1.5 V in the case of ZnPc. The saturation of $A_M$ observed for bias voltages higher than +2.4 V [Fig. 3(e)] was reproducible, suggesting that such saturation is not due to the damage of the sample surface. The properties of a plasmon, such as electromagnetic decoupling for high-frequency components, may induce the saturation to some extent.[11,12)] As shown in Figs. 2(e) and 2(f), the characteristic properties observed for the ZnPc/Au sample are similar to those observed for the CuPc/Au sample. The voltage and current dependences of STM-LE intensities seem to show an inconsistency for both samples, i.e., the former shows the existence of onsets below the HOMO–LUMO gap energies, suggesting excitations by a two-electron process via an intermediate state, while the latter shows a linear relationship expected from one-electron excitation processes.

Note that when a highly oriented pyrolytic graphite (HOPG) was used as a substrate, no emissions were observed, which is similar to the results of other studies,[2,6)] indicating that the molecular excitation is not due to a simple mechanism, such as the tunneling of electrons from the Fermi level of the tip to unoccupied molecular states[3,13)] or the direct excitation of electrons from HOMO to LUMO states by tunneling electrons. Namely, the process includes energy transfer from a plasmon. Excitation through a plasmon may play an important role in modifying the excitation processes, for example, via the triplet state as an intermediate state. Enhancement by a localized surface plasmon and the immediate saturation of the intermediate triplet state may result in the observed one-electron-like tunneling current dependence. In the development of organic EL devices, improvement in emission efficiency by energy transfer using triplet states has been attracting interests,[14)] and it is of great importance to study the basic processes in more detail.

As has been clarified, unique characteristics exist in the process of STM-induced light emission from metal phthalocyanine films formed on a metal surface. To obtain a comprehensive understanding of the mechanism, further theoretical analysis on the phenomena, such as the coupling of the surface plasmon with the excitation process including a triplet state, is urgently required.


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