# Plasmon-mediated light emission from rubrene/Au(111) induced by scanning tunneling microscopy

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## Introduction

In the cases of organic molecules on metallic substrates, STM-induced light emissions from both molecules and local surface plasmons (LSPs) are observed, and the mechanisms including molecule-substrate interactions have been proposed. In the present study, we measured STM-LE from rubrene molecular layers on Au substrate under experimental conditions where degradation of molecular structures was reduced.

## Experiment

We performed STM measurements in both air and ultra-high vacuum (UHV) with constant-current mode. Emitted photons from tunnel junction were focused onto an entrance edge of an optical fiber using lenses and introduced to a monochromator. A high-sensitive CCD was used for detection. In air, topography measurement and CCD exposure were started and finished simultaneously. STM bias voltage was applied to the samples. We used mechanically cut or electrochemically etched PtIr wires as STM tips. Under UHV condition, the system was cooled by liquid nitrogen or helium. We also developed a wavelength-resolved 2D photon mapping system, for UHV-STM measurement, which consists of a photon detection system synchronized with STM. Signal intensity can be integrated for the specific regions as we like for a deeper analysis.

Rubrene/Au(111) samples were prepared by vacuum deposition. In air, samples were handled in a darkroom to be prevented from degradation and desorption of the molecules prior to measurements.

## Results and discussion

Figure 1 shows a sequential STM-LE spectra from rubrene/ Au(111) measured in air at room temperature. The film thickness was 15 nm. Black and gray dashed lines stand for the energies corresponding to the sample bias voltage (1.8 eV) and the rubrene HOMO-LUMO gap (~2.0 eV) identified by PL, respectively. The observed change in spectra, due to molecular desorption during the measurements, clearly indicates that the prominent peak component in the first spectrum is originated from the electronic transition in the rubrene molecules.

It is intriguing that the signal from rubrene molecules has a higher energy than the applied bias voltage, suggesting the mechanism assisted by the LSPs including a triplet-singlet transition in the molecule. In order to investigate the mechanism in detail, analysis on the spatial distribution of wavelength-resolved 2D photon maps are of great importance, which will be discussed at the colloquium.
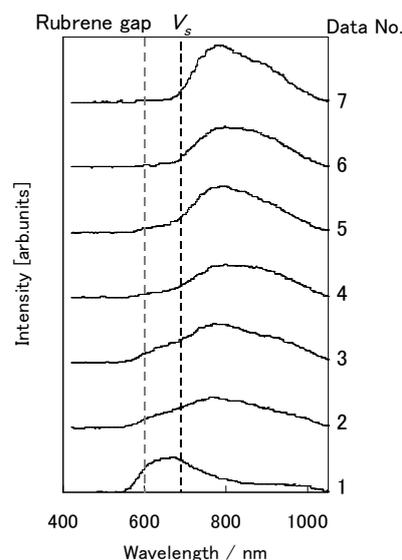


Fig. 1. A sequential STM-LE spectra from rubrene/Au(111), sample where measurements were repeated in air at room temperature ($V_s$ = +1.8 V, $I_t$ = 5 nA, CCD exposure time = 128 sec/ spectrum). Black and gray dashed lines stand for the energies corre- sponding to the sample bias voltages and the rubrene HOMO-LUMO gap identified by PL measurement.