

Tunneling-current-induced light emission from PTCDI-C7 thin films on the graphite and the Au(111) surfaces

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We have investigated the emission properties of N,N'-diheptyl-3,4,9,10-perylenebiscarboximide (PTCDI-C7) thin films on the highly oriented pyrolytic graphite (HOPG) and the Au(111) surfaces using tunneling electrons from a scanning tunneling microscope (STM). The STM-induced light emission (STM-LE) analysis is a useful tool for characterizing the optical and electrical properties of nanoscale materials such as not only metal and semiconductor nanostructures but also organic single molecules. It involves, however, analytical difficulties of extremely weak signal. The combination of STM-LE analysis and plasmon enhancement effects is quite promising for overcoming the difficulties. Surface plasmons in the interface between a metallic and a dielectric medium generate an intense electromagnetic field on the metal surface, which provides an efficient enhancement field for some optical processes, such as fluorescence/phosphorescence emission and optical absorption of organic molecules on the metal surface. Indeed, we have first observed metal enhanced fluorescence of Cu phthalocyanine with the assistance of enhancement effect utilizing tip-induced plasmon (TIP) [1]. Liu et al. [2] reported that they observed molecular fluorescence from porphyrin thin films on the Au and Ag substrates but not on the HOPG and indium tin oxide substrates. In this work, we prepared PTCDI-C7 films on conducting substrates using a simple spin-casting method, and studied by STM-LE in air and at room temperature. To examine effects of surface plasmons on the substrates, we employed HOPG and Au(111) as the substrates. We observed molecular fluorescence from PTCDI-C7 on Au(111) in company with plasmon-mediated light emission from the Au substrate. We also observed a significant intensity of fluorescence from PTCDI-C7 on the HOPG substrate in contrast to the previous reports.

The HOPG and the Au(111) substrates show different surface plasmon modes, therefore, plasmon-mediated fluorescence resulting from the TIP excitation could be observed only on the Au(111) in our previous studies[1,3]. We prepared the Au(111) substrate by an evaporation of Au onto a cleaved mica substrate heated at 300 degrees centigrade to produce atomically flat terraces of Au(111). The PTCDI-C7 (Fig.1) thin films on HOPG and on Au(111) were prepared by spin-casting method with 2 mg/5 ml solution of PTCDI-C7 in 1-tetradecene at a spin velocity 1000 rpm under ambient condition. The STM-LE measurements were performed in air and at room temperature by using a commercial STM (Nanoscope IIIa of Digital Instrument). Mechanically sharpened Pt/Ir tip was used as an STM tip in all measurements. A schematic drawing of whole STM-LE system is shown in Fig. 2. By using this system we obtained a photon integration mapping (photon counting signals synchronized with every pixel of an STM topographic image) with a photon counting detector and emission spectra with a CCD spectrometer.

The light emission was observed from PTCDI-C7 thin films both on HOPG and Au(111). The reason which we could observe the molecular fluorescence on HOPG substrate in contrast to the previous reports[1,2] is seemed to a large quantum yield of fluorescence emission of PTCDI-C7 and/or crystal characteristics less subject to quenching effect from the substrate than those of phthalocyanine and porphyrin cases. Figure 3 shows (a) an STM topographic image, (b) a photon integration map and (c) optical spectra at four bias voltages from 1.0 to 2.2 V obtained from PTCDI-C7 thin films on the HOPG substrate. A photon mapping image (Fig. 3(b)) showed that the homogeneous emission was obtained from whole

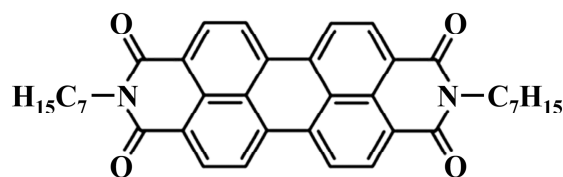


Figure 1. Molecular structure of PTCDI-C7.

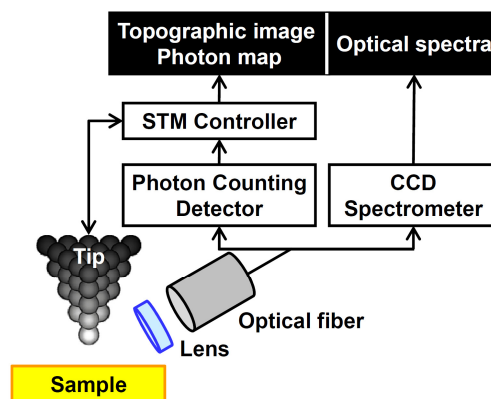


Figure 2. Schematic diagram of the photon detection system equipped with an STM working in ambient condition.

scan area. Note that the STM tip contacted with the thin films under our current condition, that is, the tunneling electrons pass through the thin film to the substrate. In the emission spectra (Fig. 3(c)), one can see peaks at ~ 660 nm, ~ 750 nm and ~ 890 nm. As no emission was observed from a bare HOPG surface and the peak positions didn't shift by changing the bias voltages, these peaks were originated from PTCDI-C7. Compared with the absorption spectra, these peaks are attributed to the fluorescence from PTCDI-C7 with its vibronic progression with large Stokes shift [4]. Figure 4 shows the results of STM-LE obtained from PTCDI-C7 thin films on the Au(111) substrate. A photon mapping image was similar to that on the HOPG substrate. In the emission spectra (Fig.4 (c)), three kinds of emission peaks at ~ 750 nm, ~ 880 nm and ~ 960 nm were observed and the peak intensity of PTCDI-C7 films on Au(111) was ~ 5 fold larger than that on HOPG. This is due to the plasmon enhancement effect in which molecular emission originated from PTCDI-C7 could be observed in company with plasmon-mediated light emission on the Au substrate. Peak-positions on the Au(111) substrate seemed to coincide with those on the HOPG substrate, where the peaks at ~ 750 nm, ~ 880 nm and ~ 960 nm were effectively enhanced by the TIP, on the other hand, the peak at ~ 660 nm observed on HOPG was not well resonated with TIP.

In conclusion, we investigated the STM-LE of PTCDI-C7 thin films on HOPG and Au(111). Both STM-LE of the fluorescence with its vibronic progression from PTCDI-C7 on the HOPG and on the Au(111) substrate including large Stokes shifts. It was interesting that we could observe a significant intensity of fluorescence on the HOPG substrate. Obtained results indicated that the light emission from PTCDI-C7 in this case was due not to the isolated molecular condition but to the thin-film structure although the highly localized TIP enabled STM-LE analysis to evaluate a single molecular level interaction, which was in contrast to our previous study [1].

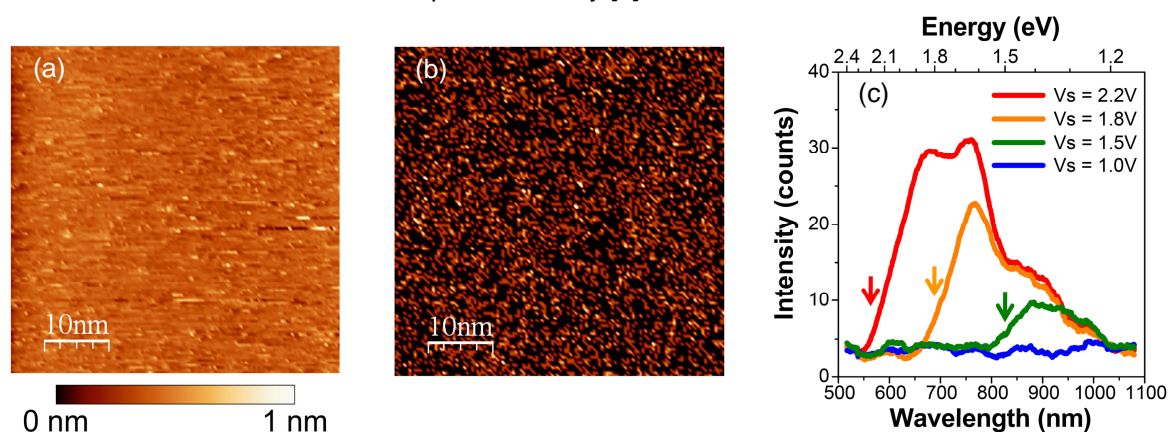


Figure 3. (a) Topographic image, (b) photon map, and (c) emission spectra of PTCDI-C7 thin film on HOPG. Tunneling current, 20 nA; bias voltage, 2.2 V in (a) and (b), and at 1.0 V \sim 2.2 V for 15 min in (c).

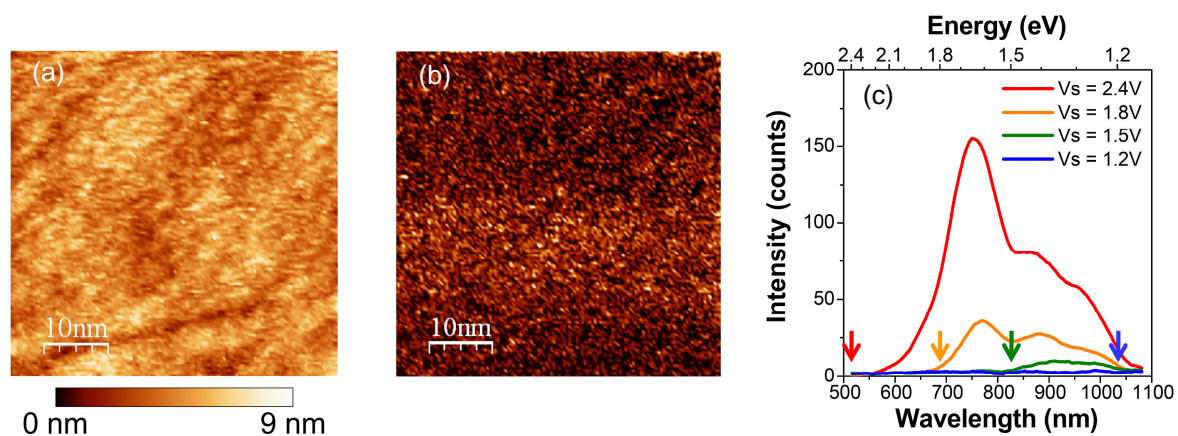


Figure 4. (a) Topographic image, (b) photon map and (c) emission spectra of PTCDI-C7 thin film on Au(111). Tunneling current, 20 nA; bias voltage, 2.2 V in (a) and (b), and at 1.2 V \sim 2.4 V for 15 min in (c).

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