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Electrically controlled photoluminescence efficiency of organic rubrene microplates

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ABSTRACT

Semiconducting organic rubrene (5,6,11,12-tetraphenyltetracene) microplates (MPs) were fabricated using physical vapor transport to study tunable photoluminescence (PL) characteristics through an applied electric field. The nanoscale PL intensities of a rubrene MP, which were measured via high-resolution laser confocal microscopy (LCM), clearly depended on the applied electric field intensity. The LCM PL intensity of the rubrene MP sinusoidally varied with the periodic change of the electric field. We also observed the aging effect on the LCM PL intensity of rubrene MPs. Control of the charge dissociation rate of photoinduced excitons by the external electric field can be the cause of the tunable PL efficiency of the MP.

1. Introduction

Organic small molecules with π-conjugated structures can be self-assembled to form single crystals [1,2] and nanostructures [3,4] through π–π intermolecular stacking. The π-conjugated organic semiconducting crystals and nanostructures show both high mobility with *p*-type characteristics and luminescent efficiency owing to the molecule-based crystalline structures [5,6]. Therefore, these crystals and nanostructures have been utilized for organic light emitting diodes (OLEDs) [7–9], organic field effect transistors (OFETs) [10–12], and organic photovoltaic cells (OPVCs) [13,14].

Organic rubrene molecules are representative π-conjugated systems, which can be self-assembled leading to single crystalline or nanostructure formations. OFETs that use rubrene single crystals as an active layer show excellent hole carrier mobilities of 10–40 $\mathrm{cm^2/V\,s}$ due to the ordered π–π stacking. Moreover, rubrene crystals show highly anisotropic and efficient luminescence characteristics [4,15–19]. Therefore, rubrene molecules and their crystalline nanostructures have been intensively studied for organic-based optoelectronics and nano-devices [4,10,15–19]. OLEDs can work through electrically driven electron and hole pairs (i.e., excitons) and their radiative decay process. OLEDs employing a rubrene-based mixed molecular layer were previously reported [20,21], in which rubrene used as an assisting emission dopant. For the OPVCs, the charge dissociation of photoinduced excitons contributes to the generation of the electric current. The power conversion efficiency (PCE) of OPVCs has been enhanced through the maximized short-circuit current which is controlled with the amount of rubrene molecules [13]. Furthermore, the doping effect of rubrene molecules in OPVCs was studied in terms of photoinduced exciton generation [14]. The rubrene layer in OPVCs played a role in the charge transport between the donors and acceptors, resulting in a PCE enhancement. In particular, the intrinsic variation of optical properties such as the photoluminescence (PL) efficiency of semiconducting organic crystals and nanostructures via the applied bias is important for fundamental studies involving the dissociation of photoinduced excitons and applications of electrically controlled optical devices.

In this study, we observed that the PL intensity of a rubrene micoplate (MP), which was measured via laser confocal microscopy (LCM), depends on the applied electric field. By increasing the electric field from 0 to 30 kV/cm, the LCM PL intensity of the MP gradually decreased, and it was recovered after decreasing the electric field back from 30 to 0 kV/cm. Despite the aging effect occurring during LCM PL measurements, we could control the PL efficiency of the rubrene MP via an applied bias. The results can be analyzed in terms of the control of the exciton dissociation rate by means of the applied electric field.

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2. Experimental

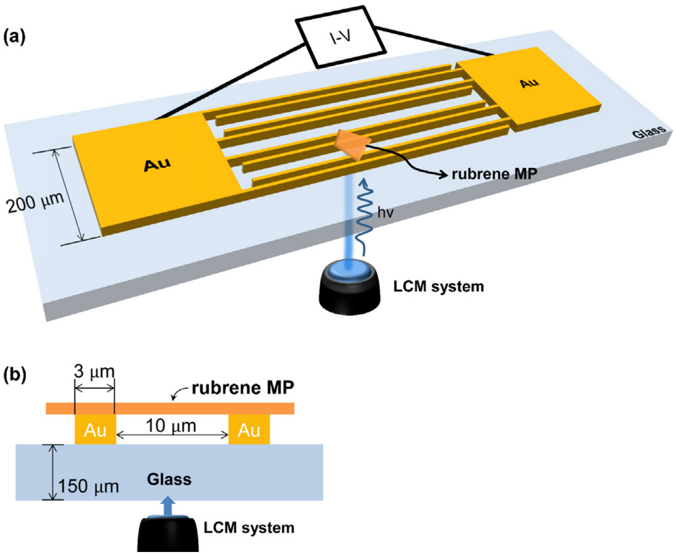
2.1. Sample preparation

Rubrene powder was purchased from Sigma–Aldrich Co. and used without further purification. The rubrene MPs were fabricated in a home-made furnace, via physical vapor transport (PVT) [22]. The gold (Au) nanoparticles that were used as seeds for MP growth were placed on a SiO_2 substrate, which was placed at the end of the heating zone of the furnace. The ground rubrene powder located on an alumina (Al) boat was placed in the middle of a furnace with a source temperature of about 310–320 °C. While heating the furnace for 200 min, N_2 gas flowed into the furnace with a flow rate of 50–100 cm^3/min in order to prevent oxidation. The rubrene MPs were grown on SiO_2 substrates.

As shown in Fig. 1(a), rubrene MP thicknesses were measured using atomic force microscopy (AFM; Nano-Focus Ltd., Albatross), and determined to be approximately 1 μm. The surface areas of rubrene MPs, which were determined from images obtained with a field-emission scanning electron microscope (FE-SEM; Hitachi S-4300), turned out to be approximately hundreds of μm^2 (for example, the surface area of the MP displayed in Fig. 1(b) is approximately 20 μm × 30 μm).

2.2. Measurements

For the electrode pattern, Ti/Au electrodes with a thickness of 110 nm were thermally evaporated on glass wafers, after which their backsides were polished to a thickness of 150 μm as shown in Scheme 1 (a). The distance between electrodes was about 10–20 μm, and the lateral size of each pad was 200 μm (Scheme 1(a)–(b)). A rubrene MP was placed on the electrodes and the electrode pattern was connected to a Keithley 2450 source-measurement unit in order to measure current–voltage (*I*–*V*) characteristics. By applying an electrical bias, the nanoscale PL characteristics of a rubrene MP were measured using an LCM PL mapping system with a scan stage (PSIA E-120). The scan size of the LCM PL measurement was about 20–30 μm and a single line-scan contained 64 data points. The excitation wavelength (λ_{ex}) of the laser was 405 nm, while the size of the focused laser spot was about 200 nm. The power of the laser varied between 15 and 50 μW for each measurement and the acquisition time of each spectrum was 47.5 ms. In the LCM mapping system, two types of objective lenses were used, one being an oil immersion lens and the other a conventional air gap lens, both with a magnification of 100× and numerical apertures (NAs) given by 1.40 and 0.95, respectively. More details on the experimental methods for the LCM PL mapping were reported in a previous study [23]. Scheme 1 depicts the experimental setup of the electrically controlled PL-efficiency measurements for rubrene MP using the LCM PL mapping system with the designed electrode pattern.



Scheme 1. (a) Experimental setup schematics for electrically controlled PL characteristics measurements, using an LCM system and Au electrodes. (b) Schematic cross-sectional illustration of the electrically controlled PL device.

3. Results and discussion

3.1. LCM PL characteristics

Fig. 2 shows the results of the steady-state LCM PL characteristics of a rubrene MP without an applied bias. For this LCM PL measurement, the oil gap lens was used, while the excitation wavelength and power of the focused laser equaled 405 nm and 15 μW, respectively. The red line in Fig. 2(a) indicates the line-scan for the LCM PL mapping. Fig. 2(b) shows the corresponding LCM PL mapping image, obtained from 64 repetitive line-scans. The color-based scale bar at the bottom represents the CCD counts, i.e., the PL intensity. In this regard, a color change from violet to red

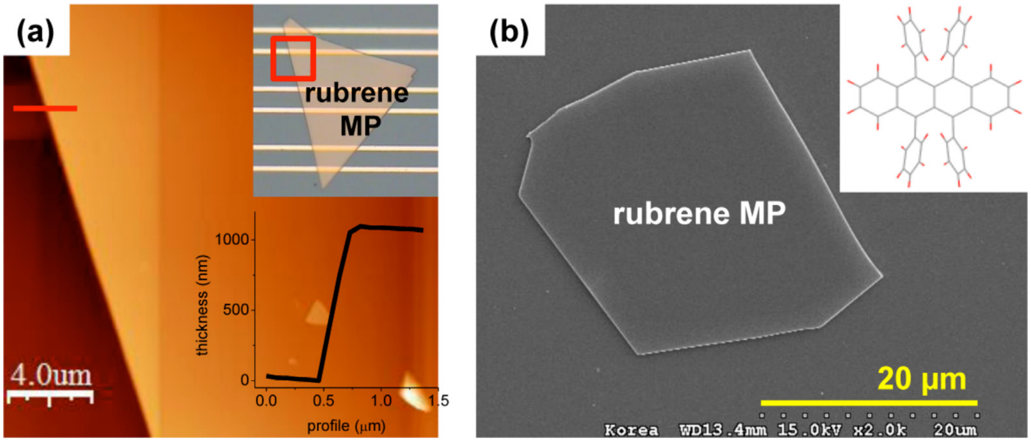


Fig. 1. (a) AFM image of a part of a rubrene MP. Top inset: optical microscope image of rubrene MP placed on the Au electrodes. The red rectangular area represents the AFM scanning area. Bottom inset: AFM scanning profile of the rubrene MP. (b) SEM image of a rubrene MP. Inset: schematic illustration of the chemical structure of a rubrene molecule. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)