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Elucidating the influences of mechanical bending on charge transport at the interfaces of organic light-emitting diodes

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ABSTRACT

In this study, we investigated the effect of mechanical bending on the performance of flexible organic light-emitting diodes (f-OLEDs). External bending was applied to induce tensile stress in the device. The current-voltage-luminescence (*J-V-L*) characteristics of the f-OLED were measured before, during, and after bending. The variation in the f-OLED performance was explained in terms of the changes in the injection barrier measured using ultraviolet photoelectron spectroscopy (UPS). Charge carrier transport was investigated using X-ray photoelectron spectroscopy (XPS). Impedance spectroscopy (IS) was used to analyze the dynamics of the charge carriers. The variations in photoluminescence (PL) peak intensity and position were used to investigate the effects of the inter- and intra-chain distances in the active layer of the f-OLED on the carrier mobility. Based on our analysis, we found that the degradation of the f-OLED after mechanical bending was induced by an increase in the number of charges accumulated at the interface between the emission layer and the electron transfer layer in the f-OLED.

1. Introduction

Flexible organic light-emitting diodes (f-OLEDs) are OLEDs that can endure mechanical deformation without significant degradation in their performance [1,2]. Applications of f-OLEDs in solid-state lighting, displays and even biomedical sensors have received considerable attention because of their excellent characteristics, including wide viewing angles, vivid colors and low power consumption [3–6]. However, the reliability of f-OLEDs under external stress or strain has become a critical issue because of the irreversible failure thus induced in the thin films comprising the devices, such as cracking and buckling in ITO electrode and organic semiconductors [7,8].

Prior to irreversible failure, however, even a small stress or strain can induce significant changes in the functional properties of these thin films and in f-OLED performance. In the case of small-molecule thin films, the charge transport in 6, 13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene) can be tuned by controlling the π-π stacking distance of the conjugated backbone through the solution-shearing method [9]. For metal chelates of the form Mq3 (M = trivalent metal, q = 8-hydroxoyquinoline), a group of well-known small-molecule light-emitting materials, a red shift of the photoluminescence (PL) after compression is caused by the resulting enhancement of intermolecular interaction [10].

In the case of conjugated polymers, the filamentary conduction model explains the formation of high-mobility pathways after mechanical compression in terms of an increase in the degree of conjugation arising from stronger π-electron wave function overlap [11]. Although enormous achievements have been made in investigations of the variations in the functional properties of small-molecule or polymer thin films under mechanical stress, little effort has been devoted to analyzing the performance of devices with multi-layered structures under mechanical stresses. In our previous study, we found that significant degradation of f-OLED performance is induced by the changes in the electronic band structure that occur after the application of compressive stresses [12]. However, the origin of the variation in the band structure was not fully understood.

In this study, the effect of mechanical bending on f-OLED performance was investigated. The variation in the electronic band structure of an f-OLED was measured for each layer comprising the f-OLED using ultraviolet photoelectron spectroscopy (UPS) before and after mechanical bending, and we found that the degradation of the f-OLED was caused by an increase in the charge injection barrier at the interface between the emission layer (EML) and the electron transport layer (ETL). To understand the mechanism of this increase in the charge injection barrier, the behavior of the charge carriers was analyzed using X-ray photoelectron spectroscopy (XPS) and the dynamics of the charge carriers was investigated using impedance spectroscopy (IS). Finally, the change in charge carrier transport behavior after mechanical bending was explained in terms of the inter- and intra-chain distances in the EML based on PL spectra.

2. Experiment procedures

A dc magnetron sputtering system was used to prepare 100 nm thick crystalline indium tin oxide (ITO, In_2O_3:Sn_2O_3 = 90:10 in wt%) as the anode for the f-OLED on a polyethylene terephthalate (PET)

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substrate (188 μm thick). Poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS, Clevios P VP AI4083, Heraeus, Germany) was diluted with 50 wt% isopropyl alcohol (IPA) and spin coated onto the ITO electrode at 1000 rpm. Super Yellow (SY, PDY-132 from Livilux, Merck, Germany) solution (5 mg/mL in toluene) was spin coated onto the PEDOT:PSS-coated substrate inside a nitrogen-filled glove box. Subsequently, 0.5 wt% cesium carbonate (Cs_2CO_3 from Sigma-Aldrich, USA) was dissolved in 2-ethoxyethanol and stirred at 80 °C for more than 12 h.

After the spin coating of the Cs_2CO_3 solution, an Al layer of 100 nm in thickness was deposited via thermal evaporation. The structure of the f-OLED is shown in Fig. 1a, where the number on each layer indicates the thickness of that layer. Fig. 1b shows a cross-sectional image of the f-OLED captured using a transmission electron microscope (TEM, JEM-ARM 200F from JEOL Ltd., Japan). The cross section of the f-OLED was prepared using a focused ion beam (FIB, JIB-4601F from JEOL Ltd., Japan).

The dimensions of the substrate were 15×12 mm^2, and the f-OLED cell of 5×5 mm^2 was located at the center. The electrical contacts were fabricated using wires and silver paste in regions far from the lighting cell. The device was then heated on a hot plate at 60 °C for 1 min to evaporate the solvent from the silver paste. With the f-OLED lit, the current-voltage-luminescence (*J-V-L*) characteristics in the bending state were measured, as shown in Fig. 1c. Mechanical bending was applied to the device using a two-plate bending machine, with two ends of the substrate fixed to the blocks, as shown in Fig. 1c and d. The initial distance between the two blocks was 15 mm, which was identical to the length of the substrate.

After reducing the distance between the two blocks by 2 mm, an 8 mm bending radius ($R = 8$ mm) could be achieved. As R was further decreased, irreversible mechanical failures (cracks and lateral buckles) were observed in the ITO. In terms of moisture from ambient air, the performance of the OLED in the ambient air was compared right after fabrication and 3 min after fabrication which was comparable to the time needed to conduct the bending experiment. We found that the performance of the OLED maintained at the same level. Hence, the effect of moisture was eliminated.

Fig. 1d shows an image of the lit f-OLED in flex. Because the Al layer was opaque, the light emitted through the substrate was measured. The total thickness of the f-OLED, except for the substrate, was approximately 300 nm. Compared with the 188 μm thick PET substrate, the f-OLED was sufficiently thin that the tensile stress induced by the external bending could be assumed to be constant throughout the film thickness. Because the f-OLED consisted of multiple layers, the rule of mixture could be used to estimate the effective Young's modulus (E_{eff}) of the device [12],

$$\frac{1}{E_{eff}} = \frac{\nu_I}{E_I} + \frac{\nu_P}{E_P} + \frac{\nu_S}{E_S} + \frac{\nu_C}{E_C} + \frac{\nu_A}{E_A} \quad (1)$$

where the ν_is and E_is are the thickness ratios and Young's moduli, respectively, of each component layer. The subscript i corresponds to the first letter of each material comprising the f-OLED, as shown in Fig. 1a. The values of E_I, E_P, E_S, and E_A were approximately 116 [13], 2 [14], 6.79 [15], and 75 GPa [16], respectively. Because the Cs_2CO_3 layer was too thin to affect the mechanical properties of the device as a whole, it was excluded from the calculation. Using Eq. (1), E_{eff} was calculated to be 5.34 GPa. Hence, the strain (ε_b) and stress (σ_b) induced by bending were estimated using the following equations [17],

$$\varepsilon_b = \frac{t_f + t_s}{2R\text{-}(t_f + t_s)} \quad (2)$$

$$\sigma_b = E_{eff} \times \varepsilon_b \quad (3)$$

where t_f and t_s are the thicknesses of the f-OLED and the substrate, respectively. Based on Eqs. (2) and (3), the magnitudes of ε_b and σ_b (at $R =$ 8 mm) were calculated to be 1.19% and 0.064 GPa, respectively.

The *J-V-L* characteristics of the f-OLED were measured in the bending state with $R = 8$ mm using a Keithley 2400 SourceMeter and a Konica Minolta CS-200 Chroma Meter. The changes in the electronic band

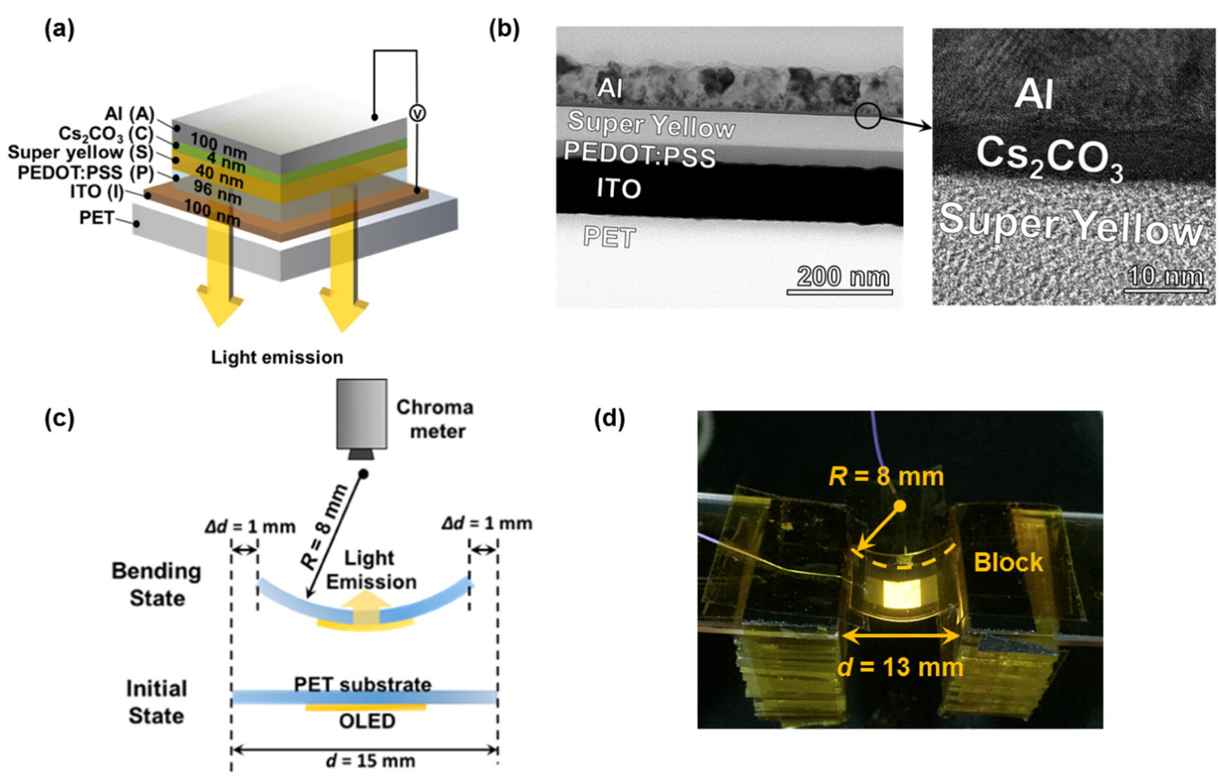

Fig. 1. (a) Schematic image of the f-OLED structure, (b) TEM cross-sectional image of the f-OLED, (c) schematic illustration of the f-OLED bending experiment, and (d) image of the lit f-OLED in flex.

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