Low Operating Voltage Bilayer Organic Light Emitting Diodes Using Electrochemically Synthesized and *p*-Doped Starburst-Polymer as Hole Transport Layer

Yoshihito Kunugi, Yoshie Niwa, Lihua Zhu, Yutaka Harima, and Kazuo Yamashita*
Faculty of Integrated Arts and Sciences, Hiroshima University, 1-7-1 Kagamiyama, Higashi-Hiroshima 739-8521

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Bilayer organic light emitting diodes based on electrochemically synthesized and *p*-doped PTPA hole transport layer have been investigated. When a thin *p*-doped PTPA layer is inserted between the anode (ITO) and Alq_3, the operating voltage of the devices has been clearly decreased while the current density and luminance increased.

Recently, organic light emitting diodes (OLEDs) are receiving much attention because of their potential application to full color flat panel displays and organic laser diodes.[1] Typical OLEDs are based on bilayer configuration and composed of a hole transport layer (HTL) and an emissive electron transport layer.[2] In bilayer OLEDs the hole transport layer is very important to decrease the operating voltage and to improve the electroluminescent (EL) efficiency.

We have recently found that a starburst-polymer, poly{tris[4-(2-thienyl)phenyl]amine} (PTPA) synthesized by electrochemically oxidative polymerization can be used as HTL of bilayer OLEDs[3] and also as an emissive polymer layer of single layer OLEDs.[4] PTPA consists of triphenylamine and bithienylene units which are electrochemically active. Hence, subsequently to the electrochemical polymerization PTPA can be electrochemically *p*-doped.

In this work, we demonstrate that low operating voltage bilayer OLEDs can be achieved by use of an electrochemically synthesized and *p*-doped PTPA as a hole transporting material.

Tris[4-(2-thienyl)phenyl]amine (TPA) was synthesized by Pd(II)-catalyzed coupling of 2-thienylmagnesium bromide with tris(4-bromophenyl)amine as described elsewhere.[5] A PTPA film was electrochemically prepared on commercial indium-tin-oxide (ITO) coated glass electrode by cycling the electrode potential between –0.3 and 0.9 V vs Ag/0.1 M $AgClO_4$ (Ag/Ag^+) in 0.1 M tetraethylammonium perchlorate (Et_4NClO_4) acetonitrile (CH_3CN) solution saturated with TPA. The resulting film was rinsed thoroughly with CH_3CN, and then dedoped at –0.3 V in TPA-free solution for over 10 min until a current density reduced to 0.1 μA cm^{-2} or below. Subsequently the dedoped PTPA film was doped at desired potentials or doping levels if necessary. The bilayer OLEDs are prepared in a vacuum chamber at a pressure of 5×10^{-6} Torr. The emissive tris(8-quinolinolato)aluminum (III) (Alq_3) (60 nm thick) was sublimed onto the pre-deposited PTPA (20 nm) on ITO substrate and successively Mg:Ag (10 : 1) alloy (100 nm) was vacuum deposited. The light emitting area of the OLED was 0.1 cm^2. The device structure of the bilayer OLED and the chemical structures of Alq_3 and PTPA are shown in Figure 1. The EL characteristics were measured by using a regulated dc power supply with a calibrated photodiode. Doping level of the PTPA film is defined as the number of charges per 5,5'-diphenylene-2,2'-bithienylene unit, and can be calculated from the doping charge and conductivity obtained for the PTPA film. The conductivities were measured by in situ two prove method as described previously.[6] All the measurements were conducted at room temperature.

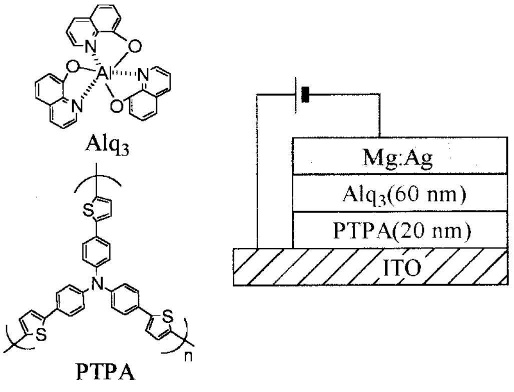

Figure 1. Chemical structures of organic materials used and the device structure of the OLED.

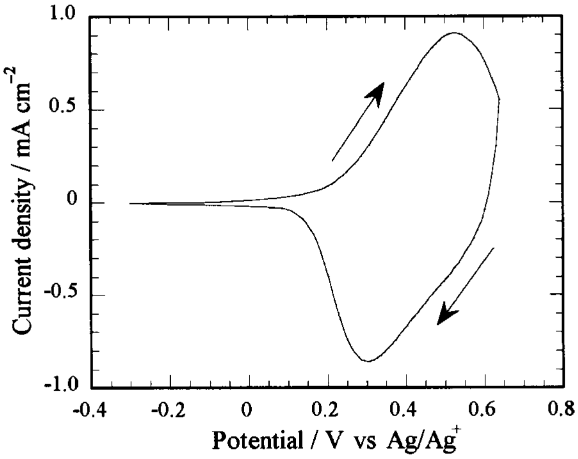

Figure 2. Cyclic voltammogram of the PTPA film electrochemically deposited on an ITO electrode in CH_3CN/0.1M Et_4NClO_4. Potential sweep rate is 100 mV s^{-1} and arrows denote the sweep direction.

Figure 2 illustrates a typical cyclic voltammogram of the PTPA film (ca. 100 nm) on an ITO electrode in CH_3CN containing 0.1 M Et_4NClO_4. Anodic and cathodic peaks are observed at around 0.53 V and 0.3 V vs Ag/Ag^+, respectively, corresponding to *p*-doping and dedoping. The PTPA film was very stable for the electrochemical doping and dedoping. After 70 times potential cycling between –0.3 and 0.65 V at 100 mV s^{-1}, the decrease of the anodic peak current was only 4.5%.

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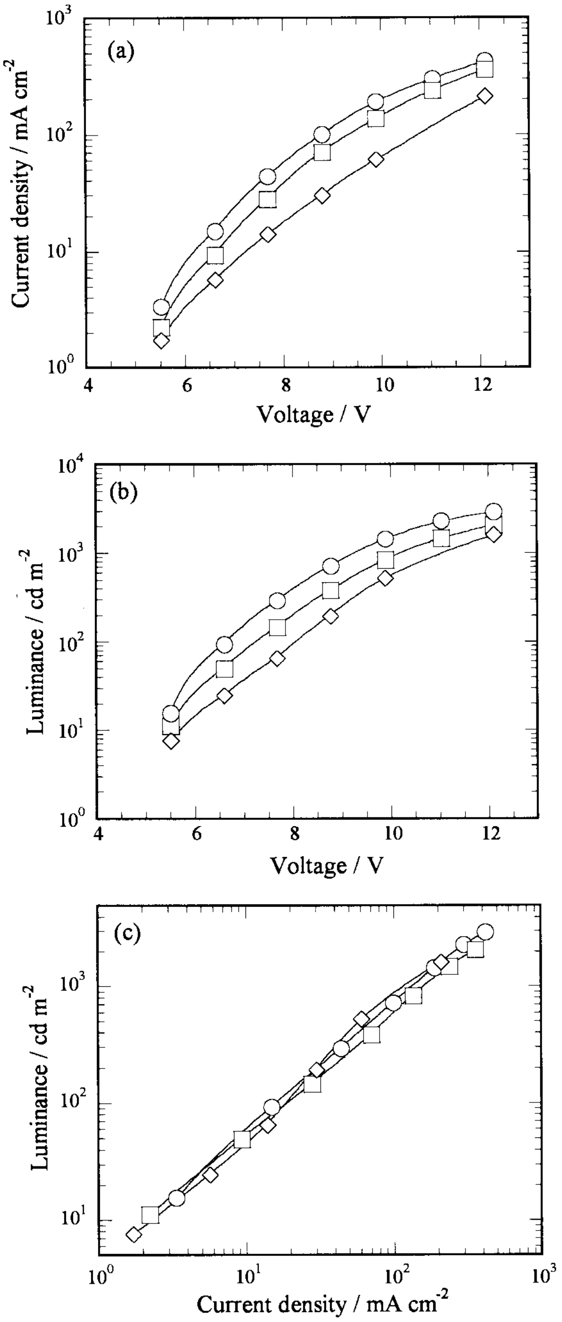

Figure 3. (a) *J-V*, (b) *L-V* and (c) *L-J* characteristics for the OLEDs with PTPA films doped at different doping levels; (◇) dedoped (□) 5.5% and (○) 65%.

The current density–voltage (*J–V*) and luminance–voltage (*L–V*) characteristics for the ITO/PTPA/Alq_3/Mg:Ag devices are depicted in Figures 3(a) and (b). The EL spectra of all devices are identical with the photoluminescence of Alq_3 films, independing on the doping levels. This suggests that the luminance of the OLEDs originates from the Alq_3. The devices with doped PTPA generate large current density and luminance at the same forward drive voltage in comparison with the undoped devices. The highest doped PTPA (65%) shows the highest current density and conductivity (1.2×10^{-1} S cm^{-1}). The OLEDs with 65% and 5.5% doped and dedoped PTPA exhibit operating voltages of 6.6, 7.2 and 8.0 V for obtaining 100 cd m^{-2}, respectively. Thus the doping strikingly decreases the operating voltage. These results clearly show that hole injection is enhanced by doping, whereas the electron injection from the cathode is independent of doping under forward bias conditions.

Figure 3(c) shows the *L–J* characteristics of the devices. The devices with the PTPA films doped at 5.5 and 65% show similar EL efficiencies, which are comparable with that of the dedoped PTPA device, though the luminance at a given drive voltage is increased with the increase of the doping level.

In conclusion, we fabricated bilayer OLEDs with electrochemically synthesized and *p*-doped PTPA hole transporting layers. The doping leads to a lower operating voltage and increasing the luminance.

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