Electroluminescent properties of color/luminance tunable organic light emitting diodes and their lifetime enhancement with encapsulation

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ABSTRACT

In this work, color/luminance tunable organic light emitting diodes (OLEDs) (ITO glass/naphthyl phenyl benzidine (NPB; 80 nm)/4,4′-bis(diphenylvinylenyl)-biphenyl (ADS082BE; 35 nm)/1,3-bis[2-(2,2′-bipyridine-6-yl)-1,3,4-oxadiazo-5-yl]benzene (Bpy-OXD; 20 nm)/tris-[8-hydroxy-quinoline]aluminum (Alq_3; 50 nm)/lithium fluoride (LiF; 3 nm)/aluminum (Al, 80 nm)) with low turn-on voltage (3 V) and high luminance (4850 cd/m^2 at 9 V) have been successfully manufactured. The experimental results reveal that their electroluminescent properties (e.g. hue, luminescent intensity, etc.) can be modulated by the manipulation for the layer thickness of NPB/ADS082BE/Bpy-OXD and the applied voltages. In addition, we have also demonstrated lab-made UV-curable silicone-acrylate encapsulating resin exhibits excellent gas barrier capability so that the half-lifetimes of OLEDs reach 98 h whereas those without encapsulation are only 9 h.

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1. Introduction

Organic light emitting diodes (OLEDs) possess the advantages of high contrast ratio, large view angle, less power consumption, fast response time as well as self-luminescence and are extensively applied for illumination and flat panel displays (FPDs) [1–3]. However, most studies focus on the synthesis of electroluminescent materials as well as the fabrication of light-emitting devices and the literatures about the manipulation of electroluminescent (EL) colors of OLEDs with the experimental conditions are less reported.

In recent years, the lifetime improvement has been a vital factor for commercialization of OLEDs since oxygen and moisture in the air erode the organic layers and metal electrodes, dramatically diminishing the lifetimes [4,5]. Without the block of moisture and oxygen in the air into the devices, their lifetimes are so short that they cannot be applied practically.

In this work, color/luminance tunable OLEDs have been successfully fabricated by vacuum evaporation, lighted up with different operational parameters, and packaged by ultraviolet (UV)-curable encapsulating adhesives. The experimental results manifest that the emitting hues and luminance of OLEDs can be ingeniously modulated with not only the thickness of organic layers but also applied voltages and the encapsulation dramatically prolongs the lifetimes of devices.

2. Experimental

2.1. Materials and instruments

Naphthyl phenyl benzidine (NPB; hole transport material), 4,4′-bis(diphenylvinylenyl)-biphenyl (ADS082BE; blue-color emitting material), 1,3-bis[2-(2,2′-bipyridine-6-yl)-1,3,4-oxadiazo-5-yl]benzene (Bpy-OXD; electron blocking material), tris-[8-hydroxyquinoline]aluminum (Alq_3; green-color emitting material), lithium fluoride (LiF; electron injection material), and alumina (<20 nm; filler) were obtained from Aldrich Co., 3-(trimethoxysilyl)propyl methacrylate (silicone-acrylate monomer of encapsulation resin) and the photoinitiators (Irgacure 651, Darocur 1173, and Irgacure 819) were purchased from UCB Co. and Ciba Co., respectively. The chemical structures of these two ingredients are depicted in Fig. 1. All materials were utilized without further purification. The ITO glass was supplied by Merck Co.

We measured the molecular weight, viscosity, and gas permeation rate with a Waters Alliance GPC V200, a Viscolite 700, and

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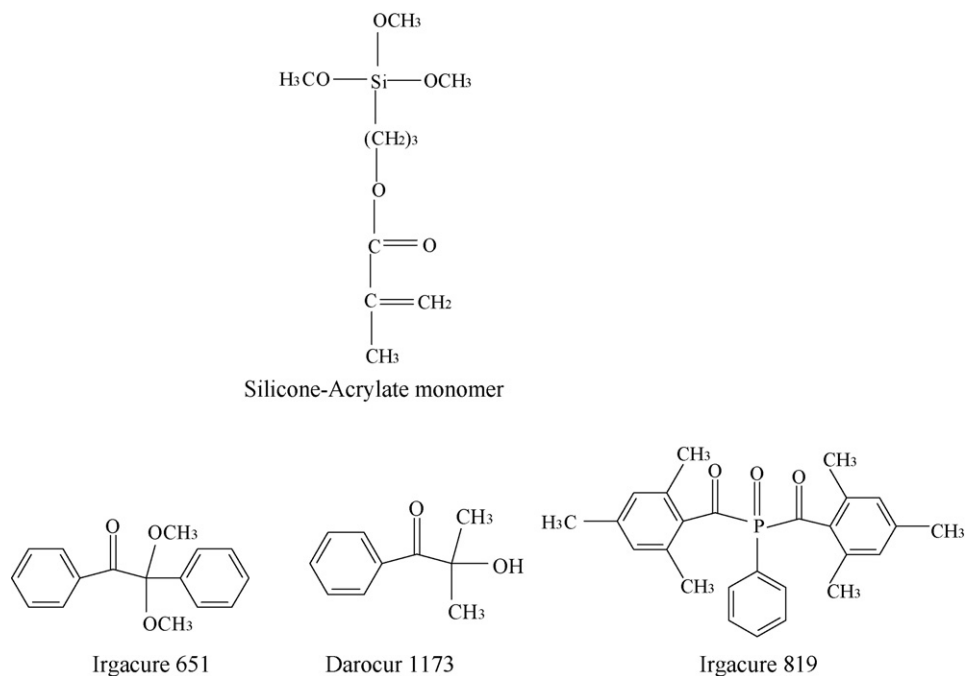
Fig. 1. The chemical structures of silicone-acrylate monomer and photoinitiators.

an Illinois-8501, respectively. Moreover, the EL properties and lifetimes of OLEDs were recorded by Keithley 2400 and Spectrascan PR650, respectively.

2.2. Fabrication of OLEDs

Firstly, we ultrasonically cleaned the ITO glass (sheet resistance = 5 $\Omega/\square$; substrate size = 5 cm × 5 cm) with the acetone, methanol as well as de-ionized water for 5 min and dried it with a stream of nitrogen as well as a 120 °C baking oven. After the treatment of oxygen plasma for 90 s, NPB (50 or 80 nm), ADS082BE (35 or 50 nm), Alq$_3$ (50 nm), LiF (3 nm), and Al (80 nm) were deposited sequentially layer-by-layer on the ITO glass by a vacuum evaporation system (Fig. 2; vacuum level = 4 × 10^{-6} Torr; deposition rate of organic materials = 0.3–0.5 Å/s; deposition rate of LiF and Al = 2–5 Å/s) to form the Device I as illustrated in Fig. 3(a). The similar procedure was executed in the fabrication of Device II (Fig. 3(b)).

The diversity of Devices I and II is that the electron blocking layers (Bpy-OXD) of 10, 20 or 30 nm thick are introduced in the Device II. In addition, the device sizes of Devices I and II are 1 cm × 1 cm.

2.3. Synthesis of UV-curable silicone-acrylate resin for OLED encapsulation

Silicone-acrylate monomer (180 g), Irgacure 651 (2 g), Darocur 1173 (1 g), Irgacure 819 (0.5 g), and alumina (20 g) were mixed and illuminated by a UV lamp (Entela UVP; wavelength = 365 nm) at the power of 100 W for 20 min (Scheme 1). The number-average molecular weight (M_n), weight-average molecular weight (M_w), M_w/M_n ratio, and viscosity of silicone-acrylate resin were 37,300, 83,200, 2.23, and 7200 cps, respectively.

The silicone-acrylate composite resin was subsequently used for the sealing of Device II containing 20-nm thick Bpy-OXD via spin-coating technique (stage I: 1000 rpm for 10 s; stage II: 2500 rpm for
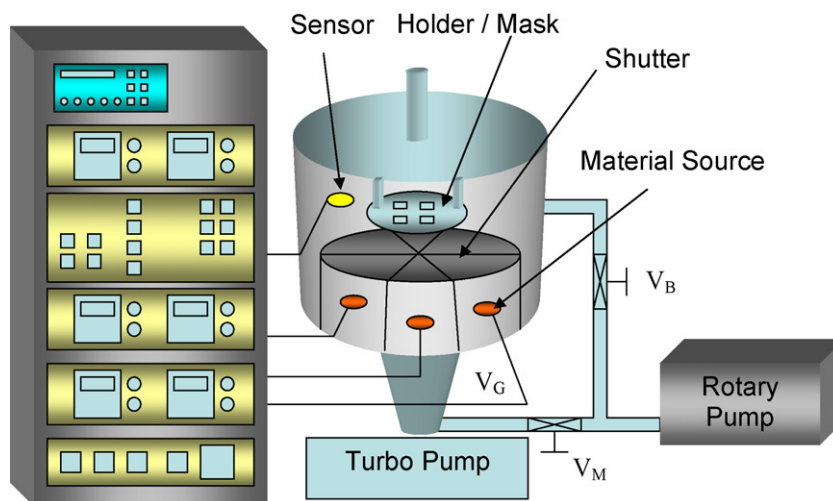
**Fig. 2.** The vacuum evaporation system used in the experiments.
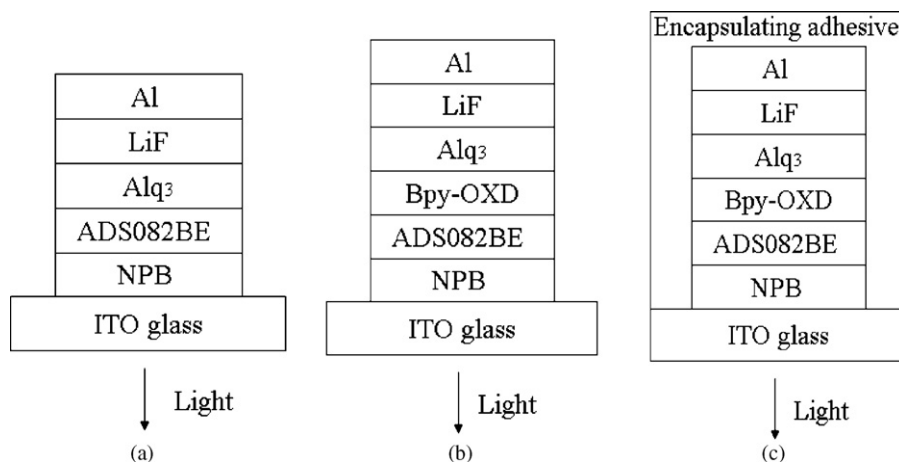
Fig. 3. The structures of lab-made OLEDs. (a) Device I: ITO glass/NPB (50 or 80 nm)/ADS082BE (35 or 50 nm)/Alq$_3$ (50 nm)/LiF (3 nm)/Al (80 nm); (b) Device II: ITO glass/NPB (80 nm)/ADS082BE (35 nm)/Bpy-OXD (10, 20 or 30 nm)/Alq$_3$ (50 nm)/LiF (3 nm)/Al (80 nm); and (c) Device III is the Device II containing 20 nm Bpy-OXD encapsulated with 50 μm silicone-acrylate sealing resin.

20 s) and cured by UV irradiation for 20 s at room temperature. The thickness of sealing resin was approximately 50 μm measured by a surface profiler (TENCOR P-10) and such an encapsulated sample is termed as Device III as shown in Fig. 3(c).

3. Results and discussion

3.1. Color modulation and EL effect of OLEDs with distinct NPB/ADS082BE layer thicknesses

As shown in Fig. 4(a)–(c) as well as Fig. 5, the EL hue and luminance strongly depend on the thickness of NPB (hole transport layer) and ADS082BE (blue-color emitting layer). While the bias voltage = 7 V and the NPB thickness = 80 nm, the OLED with thinner ADS082BE (35 nm) emits blue light (CIE$_{x,y}$ = (0.18, 0.27)) and that with thicker ADS082BE (50 nm) emits deep-blue light (CIE$_{x,y}$ = (0.12, 0.20)). Moreover, the luminance of former (350 cd/m^2) is higher than that of the latter (10 cd/m^2). This result indicates that the device with thicker ADS082BE can effectively confine all the holes in the ADS082BE layer, whose emitting efficiency is lower, so that the recombination almost takes places in the blue-color emitting layer; however, the device with thinner ADS082BE cannot completely restrict the holes in the ADS082BE layer and some holes can overcome the energy barrier between the ADS082BE and Alq$_3$ layers as shown in Fig. 6(a) [6] so that a small portion of recombination occurs in the green-color emitting layer (Alq$_3$), whose emitting efficiency is higher, inducing the red-shift of EL color and strong luminance.
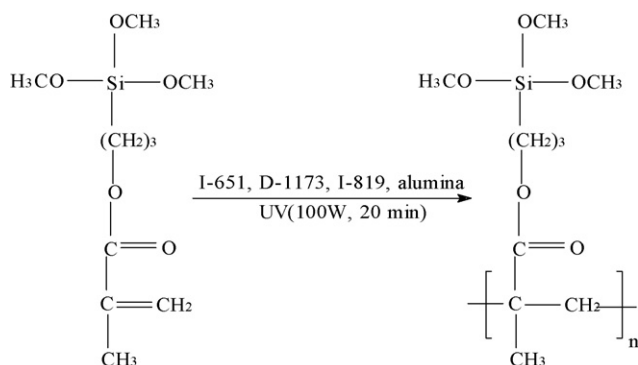
When the layer thickness of NPB was reduced to be 50 nm, nevertheless, the OLED with thinner ADS082BE (35 nm), which is lighted up at 7 V, irradiates blue-green light (CIE$_{x,y}$ = (0.23, 0.30)), revealing the decrease for electrical resistance of NPB can further increase the mobility of hole and raise the possibility of the recombination in the Alq3 layer. In addition, its luminance (450 cd/m^2) at 7 V is highest among Device I due to its lowest electrical resistance. Since the EL efficiencies of NPB as well as ADS082BE are diverse and the location of recombination can be manipulated by the layer thickness of NPB/ADS082BE, the color/luminance tunable OLEDs can thus be fabricated.

3.2. Introduction of electron blocking layer

In order to promote the EL properties of blue-light OLEDs (i.e., Device I containing 80 nm NPB and 35 nm ADS082BE), Bpy-OXD (the electron blocking layer) was introduced into the device. Without Bpy-OXD, the electron can freely arrive at either ADS082BE or Alq$_3$ layer and the recombination occurs when the hole and electron meet as shown in Fig. 6(a). With Bpy-OXD, however, the hole can be impeded in the boundary of Bpy-OXD/Alq3 since it cannot overcome the energy barrier between the Bpy-OXD and Alq3 as shown in Fig. 6(b) [7] and the recombination consequently takes place in the Alq3 layer, whose emitting efficiency is higher, irradiating strong luminance. As shown in Fig. 7, introduction of Bpy-OXD can drastically not only raise the luminance but also lower the turn-on voltage to be 3 V, whereas the turn-on voltage of the OLED without Bpy-OXD is 5 V. This illustrates that Bpy-OXD may hinder the entry of holes into the Alq3 layer and the recombination readily occurs while electrons arrive at Alq$_3$/Bpy-OXD boundary, decreasing turn-on voltage. Despite addition of Bpy-OXD into OLEDs may heighten the EL intensity, the OLED with 30 nm Bpy-OXD exhibits weaker luminance (60 cd/m^2 at 4 V; 650 cd/m^2 at 7 V) than that with 20 nm Bpy-OXD (200 cd/m^2 at 4 V; 1550 cd/m^2 at 7 V). This result comes from that the hole may be trapped in the Bpy-OXD layer while the layer thickness of Bpy-OXD is larger than 20 nm, causing the electrical resistance is high enough to obstruct the migration of the hole and lessen the recombination in the Alq$_3$ layer.

Furthermore, we have also observed the voltage-dependent EL effect in Device II containing 20 nm Bpy-OXD. As shown in Fig. 8 and Table 1, the EL spectra of OLEDs fluctuate with the applied potential and their emitting colors also vary accordingly in the range of 4–9 V, manifesting that the migration speed of electrons may accelerate and the recombination zone gradually locates in the ADS082BE
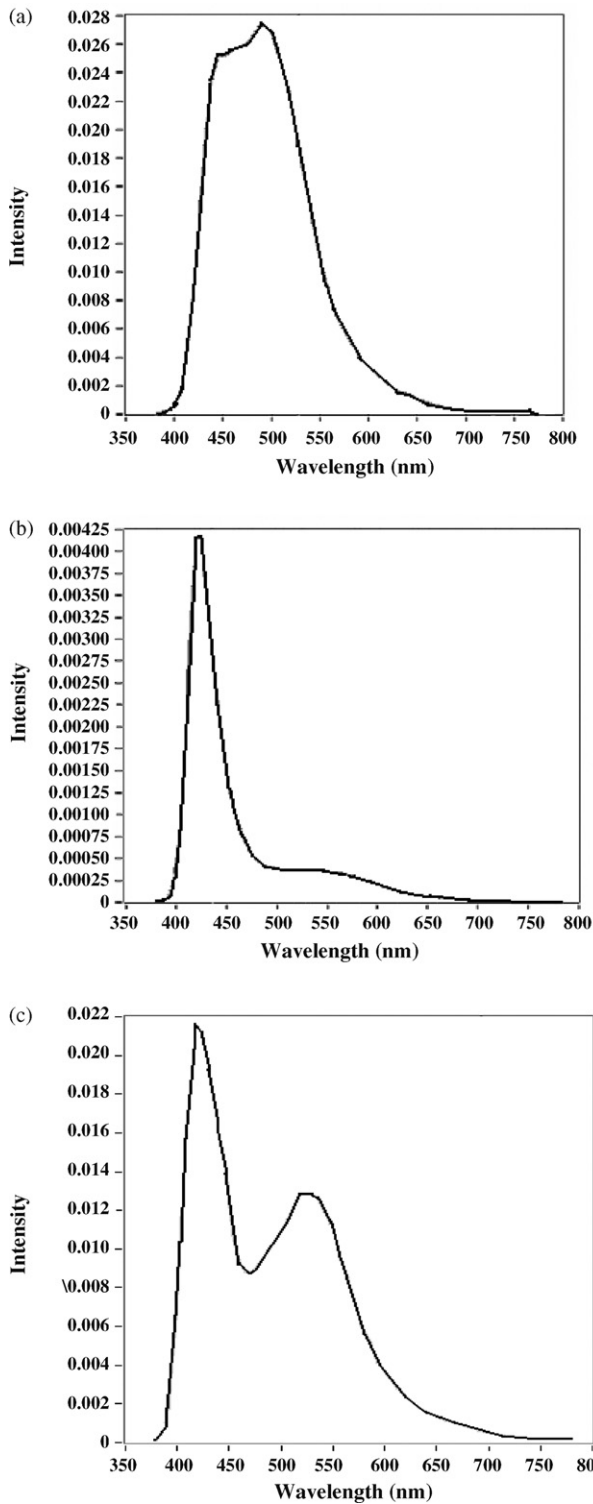

Scheme 1.

Fig. 4. The EL spectra of Device I: (a) NPB = 80 nm; ADS082BE = 35 nm; (b) NPB = 80 nm; ADS082BE = 50 nm; and (c) NPB = 50 nm; ADS082BE = 35 nm.

Fig. 5. The electroluminescent properties of Devices I (+: NPB = 50 nm; ADS082BE = 35 nm; ◊: NPB = 80 nm; ADS082BE = 35 nm; □: NPB = 80 nm; ADS082BE = 50 nm).
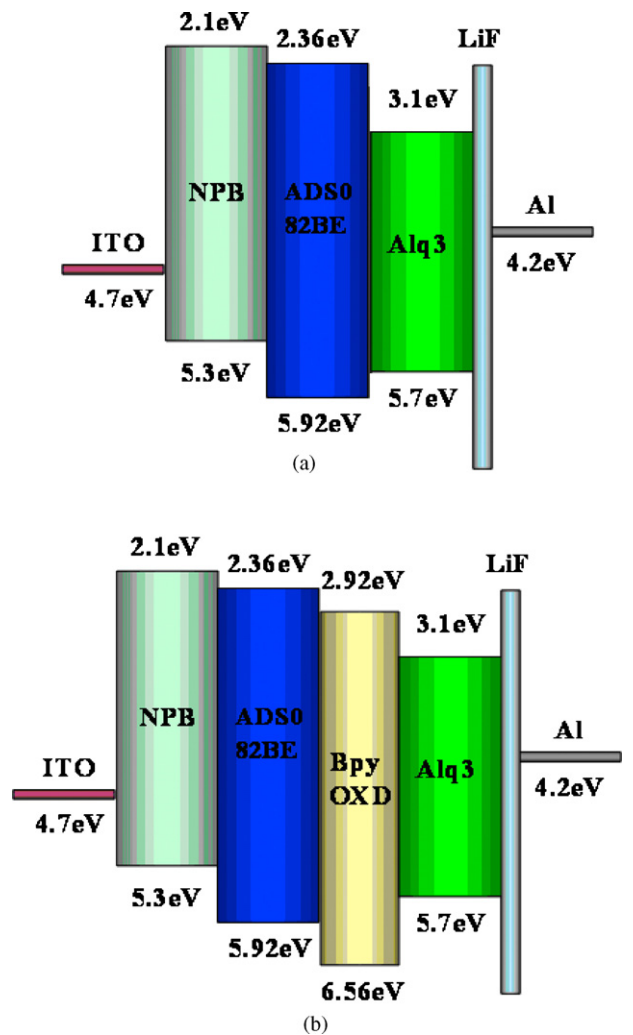
Fig. 6. The energy level diagrams: (a) Device I and (b) Device II.

layer (blue emitting layer) when the applied voltage is increased. This induces the change of EL hue from deep green to light blue.

Although the modulation of EL colors for OLEDs can be executed by the modification of light-emitting materials, the process for the tune of colors by the variation of layer thickness, introduction of electron blocking layer, and manipulation of applied voltage is relatively easier, cheaper, and more convenient. Nonetheless, as
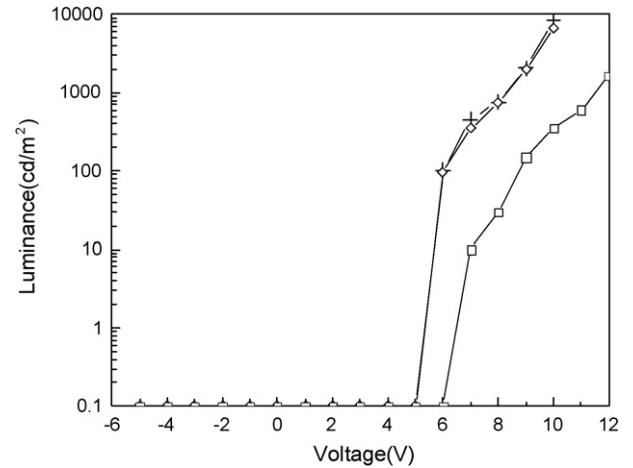
Fig. 7. The electroluminescent properties of Device II (◇: Bpy-OXD = 10 nm; □: Bpy-OXD = 20 nm; △: IBpy-OXD = 30 nm).
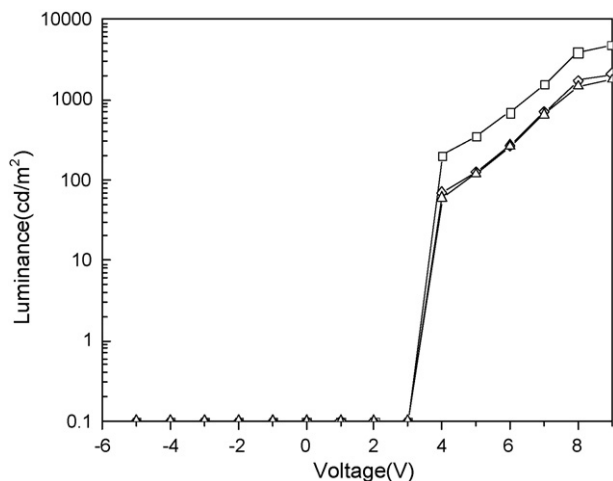
Table 1
The voltage-dependent EL properties of Device II with Bpy-OXD = 20 nm.

Applied voltage (V)	$CIE_{x,y}$	Luminance (cd/m²)	EL color
4	(0.30, 0.55)	200	Deep green
5	(0.28, 0.50)	350	Green
6	(0.26, 0.46)	700	Light green
7	(0.24, 0.40)	1550	Green-blue
8	(0.22, 0.34)	3900	Blue-green
9	(0.20, 0.30)	4850	Light blue

shown in Fig. 9, the luminance drastically decreases when Device II (NPB = 80 nm; ADS082BE = 35 nm; Bpy-OXD = 20 nm) is actuated at 7 V and the half-lifetime, defined as the duration while the luminance decays from the original amount to its half, is only 9 h, representing the moisture and oxygen in the ambient lead to the corrosion of organic layers and Al electrode. To further improve the lifetimes of OLEDs, we have synthesized the encapsulating resin with high gas barrier capability and applied it for the package of lab-made OLEDs.

3.3. UV-curable encapsulating resin and its application for lifetime enhancement of OLEDs

Since UV is the electromagnetic radiation (180–400 nm) and exhibits high energy to result in the dissociation of photoinitiators as well as free-radical polymerization [8], a new UV-curable encapsulating resin, i.e., the silicone-acrylate resin, has been synthesized in order to eliminate above deficiencies. The reaction of silicone-acrylate *via* UV synthetic process takes only 20 min, while that with conventional thermal methods takes numerous hrs for completion. In addition, the viscosity for silicone-acrylate resin prepared by UV irradiation (7200 cps) is larger than that by conventional thermal methods (5300 cps; reaction duration = 20 h) and no solvent is nec-
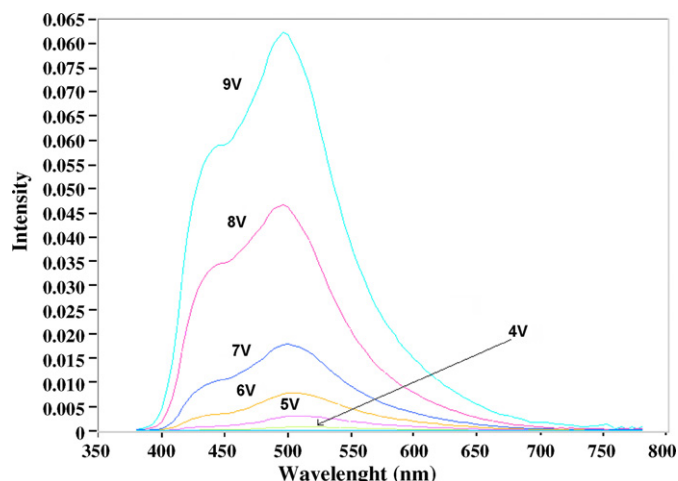
essary in the UV procedure. These advantages fit the demand for the clean, low-cost, and fast production of packaging materials.

Pure polymers, such as acrylics and epoxy resins, have been extensively utilized for the preservation of food as well as beverages [9]. However, their gas resistance is not satisfactory. In order to further promote the gas barrier performances, some researchers have recently added fillers (e.g. silica, alumina, clay, etc.) into the polymer matrix to increase their gas barrier capability [10–14]. In recent years, the literatures about the lifetime improvement for the package of OLEDs with cover glass [15,16] and organic/inorganic multilayer (e.g. Barix technique developed by Vitex Systems Co., etc.) [17] have been reported. Although the gas blocking performances of cover glass and organic/inorganic multilayer are good, the procedure of OLEDs encapsulation with them is high-cost and complicated. Consequently, we have tried to package OLEDs with low-cost UV-curable silicone-acrylate encapsulating resin/alumina composite by simple spin-coating technique and fast UV-curing process.

Fig. 9 shows the lifetime measurement of Device II without encapsulation and with the encapsulation of EPO-TEK OG115 (Epoxy Technology Inc.) as well as lab-made silicone-acrylate composite resin at room temperature. Furthermore, all the luminance measurements versus time were carried out non-stop at constant voltage (7 V). The half-lifetimes of OLEDs with silicone-acrylate composite resin substantially achieves to be 98 h in comparison with 9 h for those without package, showing that the silicone-acrylate composite resin, whose permeation rates for oxygen and moisture are respectively 0.11 and 0.08 g/m²day, can effectively restrict the permeation of moisture and oxygen in the air into the devices. The gas resistance of silicone-acrylate composite resin suppresses the degradation of Al electrode as well as organic materials and eventually increases the lifetimes. Compared with the com-
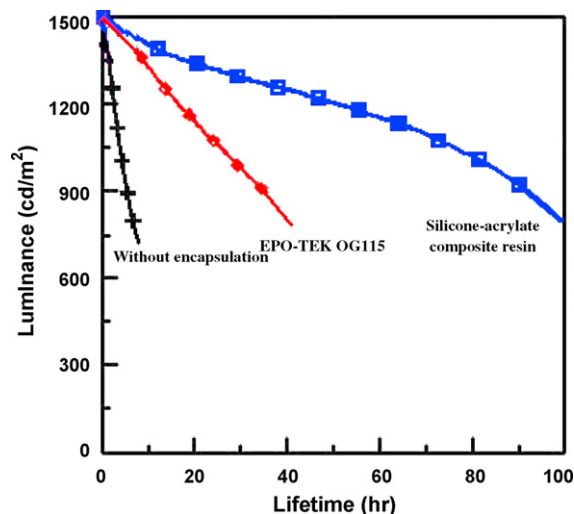

Fig. 8. The EL spectra of Device II with Bpy-OXD = 20 nm at 4–9 V.

Fig. 9. The non-stop lifetime curves for Device II at room temperature without encapsulation and with the encapsulation of EPO-TEK OG115 as well as lab-made silicone-acrylate composite resin at 7 V.

mercial packaging adhesive (EPO-TEK OG115), the silicone-acrylate composite resin exhibits better gas barrier capability and shorter curing time because the half-lifetimes and curing time of OLEDs with EPO-TEK OG115 are 41 h and 5 min, respectively. Experimental results manifest that the lab-made sealing resin, which consists of silicone-acrylate matrices, finely dispersed alumina fillers and proper prescription of photoinitiators, possesses good gas barrier property than the commercial available epoxy resins-based materials.

4. Conclusions

By the manipulation of NPB/ADS082BE layer thickness and addition of electron blocking layer, we have successfully manufactured color/luminance tunable OLEDs with high electroluminescent intensity and low turn-on voltage. Moreover, the lifetimes of lab-made OLEDs with encapsulation have been promoted to be approximately 11-folds longer than those without encapsulation.

Acknowledgement

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