

Light-Emitting Devices with Polymer-Organic Heterostructure

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Highly quantum efficient and multi-color emissible polymer light emitting devices have been realized utilizing poly((1-dodecyloxy-4-methyl-1,3-phenylene)(2,5"-terthienylene)) (hereafter, mPTTh polymer) as an emitting layer and tris(8-hydroxyquinoline) aluminum (Alq3) as an electron transport layer. A single layer EL device of mPTTh polymer emits orange-colored light. EL efficiency increases as the thickness of Alq3 layer increases, but the emission color becomes visually broad when the Alq3 layer thickness is greater than 30 nm since the relative peak intensity of green EL from Alq3 layer grows. EL color is changed from orange to greenish orange as the thickness of Alq3 layer increases. EL efficiency of the double layer device was greatly enhanced by 3000 times compared with that of a single layer device. Alq3 layer in device acts as a hole blocking electron transporting layer and an emitting layer as a function of the thickness of Alq3 layer.

I. INTRODUCTION

Since electroluminescence (EL) from thin films of the π -conjugated polymer was first demonstrated [1], interest in light emitting devices (LEDs) utilizing π -conjugated organic molecules and polymers has fueled research into EL devices based on polymer thin layers, which are one of the most promising next-generation flat panel display and light emitting diodes. Color tuning is one of the best advantages of using the π -conjugated polymer, since the π - π^* band gap can be easily engineered by adjusting the chemical structure [2]. Thermochromism in the polythiophene system demonstrated the possibility to define the band gap by designing the planarity of the chain [3]. Some of the present authors (BSK, SCS) showed the wavelength tunability of the polythiophene by inserting the phenylene block in the main chain [4].

Heterostructure device combining the emission layer and the charge transport layer is one of the best way to improve the quantum efficiency [5]. Polymer-polymer multiple layer device fabrication has some difficulties in finding the best solvents which dissolve one polymer but not the other. Organic-organic multiple layer devices can be fabricated more easily, but there may be some interdiffusion between two organic layers causing degradation during device operation [6].

In this paper, we studied the EL and the electrical properties of a device made from polythiophene containing *m*-phenylene block in the backbone. A multilayer device utilizing the poly(1-dodecyloxy-4-

methyl-1,3-phenylene)(2,5"-terthienylene)) (mPTTh polymer) and Alq3 was made and the EL properties were characterized. Multicolored light emission from a double layer device was obtained and the device showed highly enhanced performance over a single layer EL device using mPTTh polymer only.

II. EXPERIMENTS

Single and double layer devices were fabricated with mPTTh polymer and tris(8-hydroxyquinoline) aluminum (Alq3) as an emitter layer (EML) and electron transport layer (ETL), respectively. The chemical structure of the polymer and the device structure used in this study are shown in Fig. 1. Synthetic procedures and molecular properties of the synthesized polymer were shown in detail in reference [4]. The Dodecyloxy group on the phenyl ring improves the solubility. The device was fabricated by spin coating the chloroform solution of mPTTh polymer onto ITO coated glass. Thickness of the polymer layer was about 50 nm. The Alq3 layer was formed by vacuum deposition onto mPTTh polymer layer at a deposition rate 1-2 Å/sec. Al top electrode was thermally evaporated at 10 Å/sec. Details of the device fabrication process were described in reference [7].

The PL spectra were obtained by excitation with ultraviolet light at 351 nm from an Ar ion laser (Coherent Innova-305). Luminescence spectra measurements used a monochromator (ISA HR320) with a photomultiplier tube (PMT, Hamamatsu R955) as detector, and were recorded at 1 nm resolution by computer while applying direct current from the current/voltage

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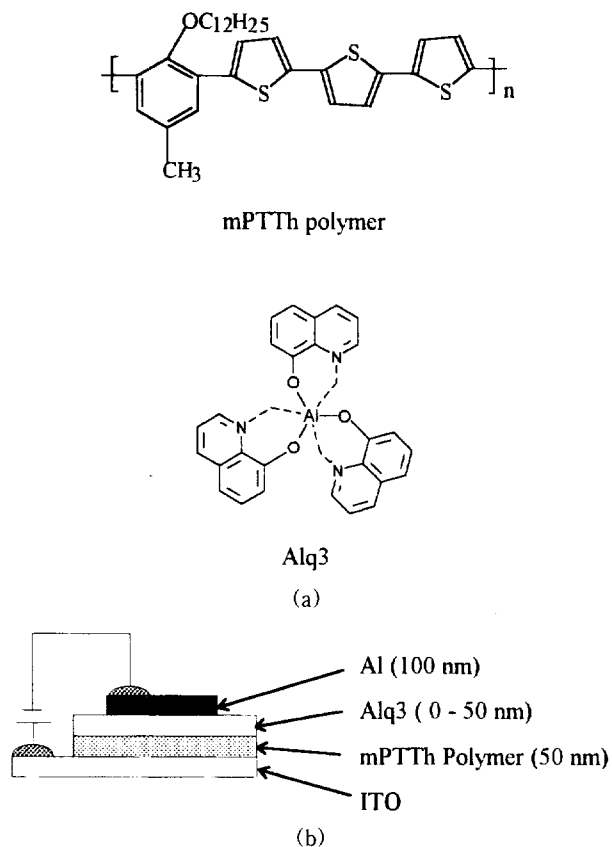


FIG. 1. (a) chemical structures of the mPTTh polymer and Alq3, (b) the structure of ITO/mPTTh/ Alq3/Al double layer device.

source(Keithley 238).

Current - voltage ($I - V$) and light intensity - current ($L - I$) characteristics were measured using the current/voltage source(Keithley 238) and the optical power meter (Newport 835). The injected current was measured by the voltage supply while applying the bias and recorded by computer. At the same time, the emitted light was collected by a Si photodetector (Newport 818SL) placed in front of the device and recorded by the computer. Since the solid angle of light detection is very small, a great loss in the light detection is unavoidable. All the measurements were performed in air and at room temperature.

III. RESULTS AND DISCUSSION

Fig. 2 shows the photoluminescence (PL) spectra of the devices made from mPTTh polymer and Alq3 as a function of the Alq3 layer thickness. The spectra were obtained for the devices with the Alq3 layer thickness of 0, 5, 15, 30, 50 nm and by shining the pumping light onto the polymer side through the quartz substrate. The PL peaks at 584 nm, and 523 nm originate from the pristine mPTTh polymer and Alq3, respectively. The PL emission peak at 523 nm increases abruptly for

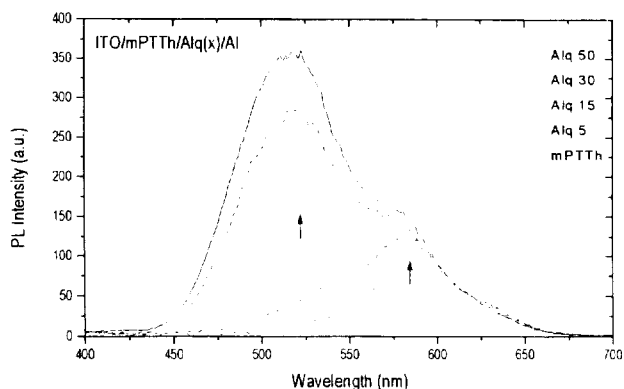


FIG. 2. Fig. 2. PL spectra of the heterostructure devices as a function of Alq3 layer thickness. The spectra were obtained for the devices with the Alq3 layer thickness of 0, 5, 15, 30, and 50 nm.

the device with the Alq3 layer thickness of 15nm, and there are two peaks with almost the same intensity. For the devices with thicker Alq3 layer, the emission from the Alq3 layer becomes dominant. These trends are consistent even when we shine the pumping light in the opposite direction. According to the PL spectra, the exciton formation responsible for the emission is more efficient in the Alq3 layer than in the polythiophene derivative layer.

However, EL spectra show a different behaviour. Fig. 3 shows the EL spectral change of the devices as a function of Alq3 layer thickness. 'Alq3 5' stands for the devices with the Alq3 layer thickness of 5 nm. As shown in Fig. 3, the emission peaks at 584 nm and 630 nm correspond to the vibronic structure from the pristine mPTTh polymer. For the heterostructure devices, the EL emission intensity of the mPTTh polymer increases with Alq3 layer thickness. The EL intensity at 525 nm corresponding to the Alq3 layer is also enhanced with the increase in Alq3 thickness. However, in contrast to PL, the emission intensity from the Alq3

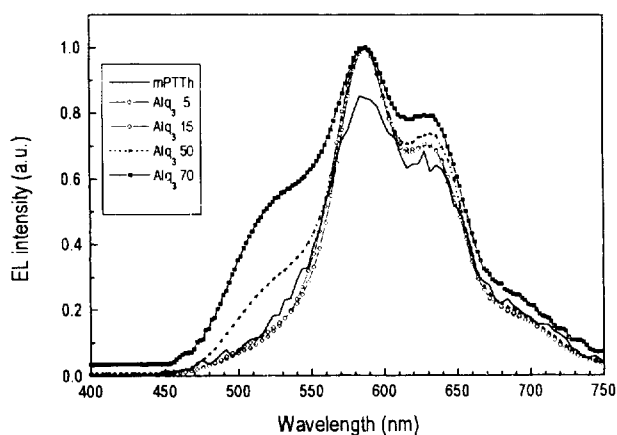


FIG. 3. EL spectra of the heterostructure devices as a function of Alq3 thickness. 'Alq3 5' stands for the devices with the Alq3 layer thickness of 5 nm.

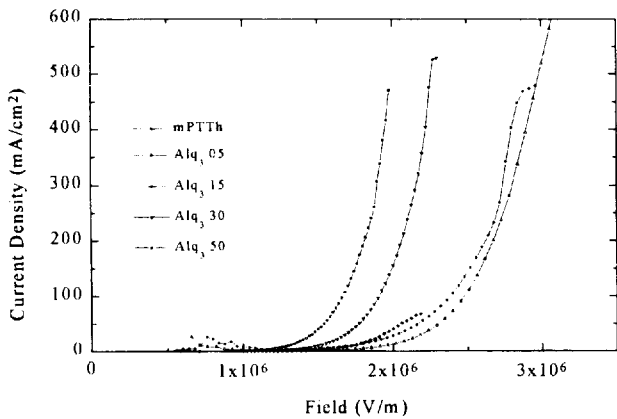


FIG. 4. Current density - electric field curves for the heterostructure devices as a function of Alq3 layer thickness. Alq3 05 stands for the device of ITO/mPTTh /Alq3(5 nm)/Al structure.

layer does not appear up to the Alq3 layer thickness of 30 nm. The emission color changes from orange to greenish orange for the device with Alq3 layer thickness of 50 nm. However, we did not find color tunability in any device depending on varying the electric field. These results suggest that the Alq3 layer may act not only as a hole-blocking electron transport layer but also an emitter layer when the Alq3 layer becomes thick. We expect the recombination zone may be extended from the mPTTh layer near to the mPTTh-Alq3 interface to the Alq3 layer by the exciton diffusion into the Alq3 layer [8].

Fig. 4 shows the current density - electric field (J - F) characteristic curves obtained for the ITO/mPTTh /Alq3/Al devices. These data were obtained from the first run of the I -V measurement. There are some spikes at low bias which also showed in other papers [9], and these vanished after the second run. As shown in Fig. 4, the current starts to flow at lower electric field with the increase of Alq3 layer thickness. Accord-

ing to the Fowler-Nordheim plots of the devices (see Fig. 5), the slopes of the linear portion of the curves become smaller for the thicker devices, which means the energy barrier for the carrier injection is getting smaller. For the same electric field, the current density is large in the case of a thicker device. These suggest that Alq3 assists the carrier injection and/or the space-charge build up more efficiently in the thick device. This is supported by the light - current density characteristic curves as shown in Fig. 6. According to Fig. 6, more luminescence comes out as the Alq3 layer thickness increases. For the same amount of current, more light comes out for the thicker device. As seen in the inset of Fig. 6, which has the expanded luminescence scale, the turn-on voltage is low for the thicker device, consistent with the results of the Fowler-Norheim plot. However, the luminescence is almost constant even when the Alq3 layer is thicker than 30 nm. The external quantum efficiency for ITO/mPTTh/Alq3 (30 nm) /Al device is 3000 times higher than the single layer device (Table 1). Since the luminescence from the device with 50 nm of Alq3 layer contains the emission from Alq3, the real quantum efficiency contributed by the emission from mPTTh polymer only must be less than the observed. This shows that there is an optimum thickness of Alq3 layer to obtain the highest quantum efficiency contributed by only mPTTh poly-

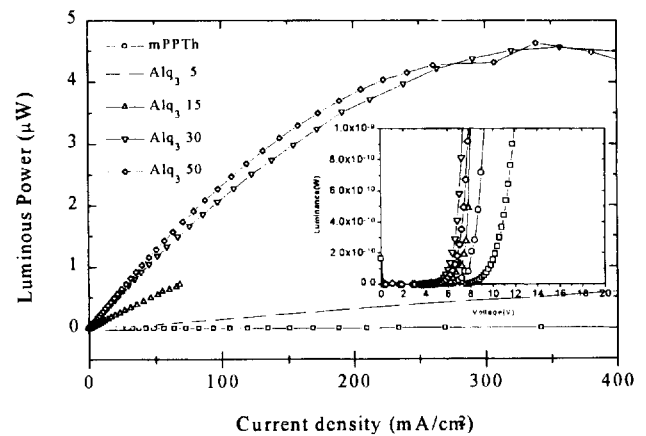


FIG. 6. Light power - current density curves for the heterostructure devices as a function of Alq3 layer thickness. The inset shows the light power vs the applied voltage curves in expanded scale of luminous power.

TABLE 1. External quantum efficiency as a funtion of Alq3 layer thicknesses for ITO/mPTTh/Alq3/Al devices

Thickness of Alq3 layer (nm)	Efficiency (photons/electron)
0	1.08×10^{-7}
5	1.83×10^{-5}
15	1.40×10^{-4}
30	3.29×10^{-4}
50	3.64×10^{-4}

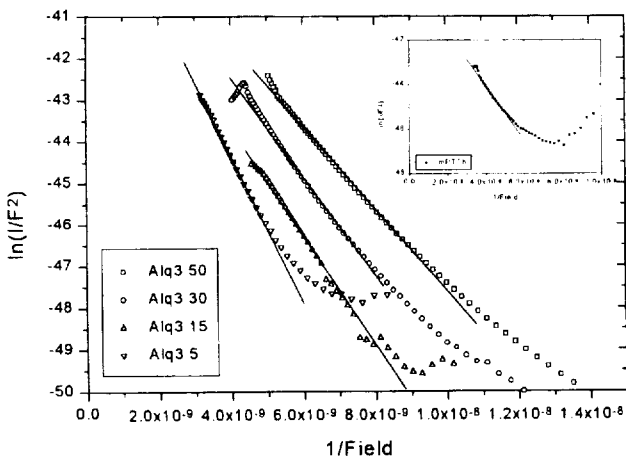


FIG. 5. Fowler-Nordheim plot of the devices with various Alq3 layer thickness.

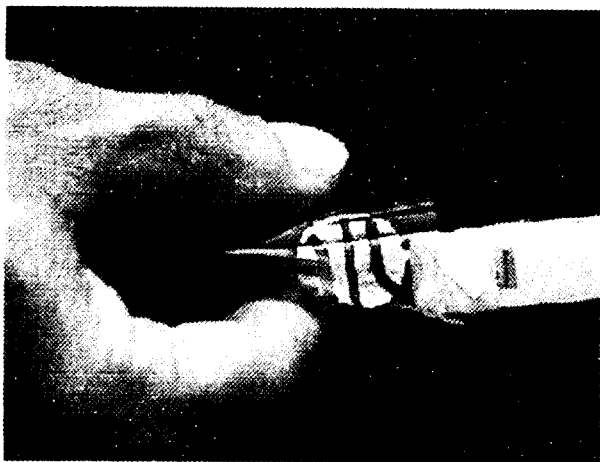


FIG. 7. Picture of the yellow-orange light emission from the device of ITO/mPTTh/Alq3/Al heterostructure on the plastic substrate.

mer. For the organic-organic heterostructure device, it also shows that there is a peak in the quantum efficiency depending upon layer thickness [10].

Building up more space-charge in a thicker Alq3 layer device can be achieved by more efficient hole blocking. Based on the results above, Alq3 layer should work more efficiently as an electron injection layer and a hole blocking layer. The reason why the hole blocking is more efficient in a thicker Alq3 layer device is discussed as follows. For the same electric field, the field across the polymer layer in the thicker Alq3 layer device should be less than that in the thin Alq3 layer device if we assume that the current densities flowing in the polymer layer and in the organic layer are the same. Therefore, the polymer-organic interfacial blockade height for the major carrier should be less for the thick device. This is confirmed by the Fowler-Nordheim plot which shows that the thinner device has the steeper slope. The device possessing the higher interfacial barrier shows less total device current and steeper slope in the Fowler-Norheim plot [11]. To confirm the hole blocking behaviour of Alq3 in the device, we applied reverse bias to the same samples of Fig. 3. As a result, the luminescence under reverse bias was observed only for the single layer of ITO/mPTTh /Al device. Under reverse bias, there is no hole blocking and a high energy barrier exists for the hole injection from the Al electrode in view of the band alignment, so that it is hard to obtain light emission. From the results, it may be suggested that there should be an optimum thickness of the charge transport layer in the heterostructure for balancing the charge injection.

The polymer EL device has the advantage of an application to flexible flat panel display. The devices on the plastic substrate were formed successfully and a picture of the light emission is shown in Fig. 7. The

device can be bent during light emission without failure.

IV. CONCLUSION

Highly efficient and multi-color EL devices were fabricated utilizing mPTTh polymer as an emitting layer and Alq3 as an electron transport layer. Depending on the thickness of Alq3 layer in the heterostructure, the EL intensity increased and emission color changed from orange to greenish orange. EL efficiency of the heterostructure device was greatly enhanced compared to that of a single layer device. Also there is an optimum thickness of the electron transport layer in order to obtain the highest quantum efficiency. It may be suggested that the Alq3 layer acts as a hole blocking electron transporting layer and an emitting layer as a function of the thickness of the Alq3 layer. The Alq3 layer assists the carrier injection and/or the space-charge build up more efficiently in the heterostructure device.

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