3. Highly Efficient Green-emitting Devices

One of the key issues for us to get high-efficiency devices is that we have to spare no effort to balancing the currents of holes and electrons injecting from the anode and the cathode, respectively. Excessive holes or electrons increase the current density but there are no enough corresponding counterparts for holes or electrons to recombine with. These conditions result in increasing current density but keeping the same luminance. Thus the efficiency drops with no excuse.

There are probably two ways to find out the best way to balance the holes and electrons in the emissive layer(s). One is to change the concentration of hole-transporting material (for example TPD) or that of electron-transporting material (for example PBD) in the 4-material blend. Appendix A shows that blindly changing the blending ratio among the four materials will jeopardize the balance of holes and electrons. Besides, one (or more) of the four materials may act as the carrier-trap agent. This is also harmful to the hole-electron balance. The other possibility is to establish other kinds of device structures, such as producing more layers, or adjusting thicknesses of some layers in the device.

We produced devices with different cathodes, thicknesses of films, and also devices with single or double layers. We examine these devices and figure out which combination was the best to achieve the maximum luminous efficiency.

Among all the devices, the best efficiency of our own devices, 49 cd/A, was achieved with the single-layer structure, with the solution of the 4-material blend whose ratio was $PVK : PBD : TPD : Ir(mppy)_3 = 61 : 24 : 9 : 6$ as described in the literature. In the device, PCE was about 17 lm/W while the luminance was about 12,000 cd/m2. However, the performance at low voltages was worse than that in the literature. For our double-layer devices made by the buffer-layer technology, the luminance was about 20,000 at 17 volts, but in the device the efficiency decreased down to 18 cd/A, with the PCE of 5 lm/W. We impute this low efficiency to excessive injection of holes from TFB.

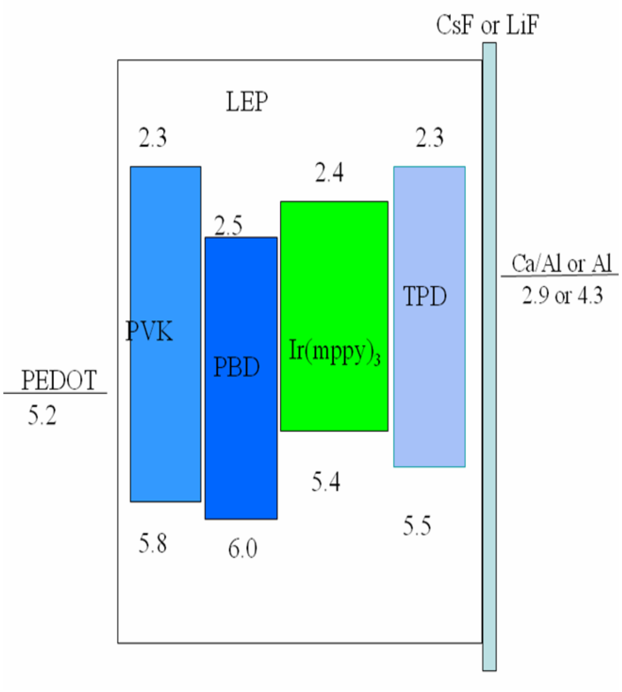

Figure 3.1: The energy diagram of the single-layer devices.

3.1 Single-layer devices with different insulating layers between the light emitting layer and the calcium cathode.

To begin with, we quite closely follow the article published by D. Neher et al [8][10]. Figure 3.1 is the energy diagram of the materials (PVK, PBD, TPD, and Ir(mppy)$_3$) and the work function of ITO and the cathode. The blend of the four materials is called "light emitting polymers (LEP)."

Notice that the host PVK has the largest band gap among all the materials. This is a very important criterion for us to choose a host. An energy diagram of the host and the guest which resembles that in Figure 3.2 is not a good choice because holes and electrons could be separated on each material, resulting in difficult recombination between a hole and an electron [18]. Another criterion for choosing a host is that the triplet energy level of it should be higher than that of a guest. Have it not been so, the triplet excitons would gather on the level of the host, not the guest [19].

Figure 3.3 shows the chemical structures of materials which are currently in

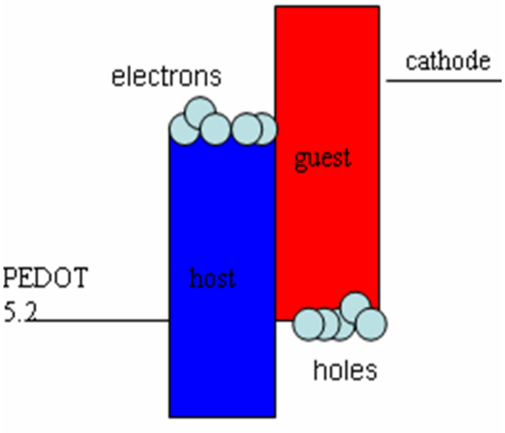

Figure 3.2: An example of a bad combination of shifted energy bands about the host and the guest. In this case, holes would be trapped on the IP of the guest while electrons would pass through the EA of the host. This results in separating the holes and electrons from one another and inefficient recombination of holes and electrons.

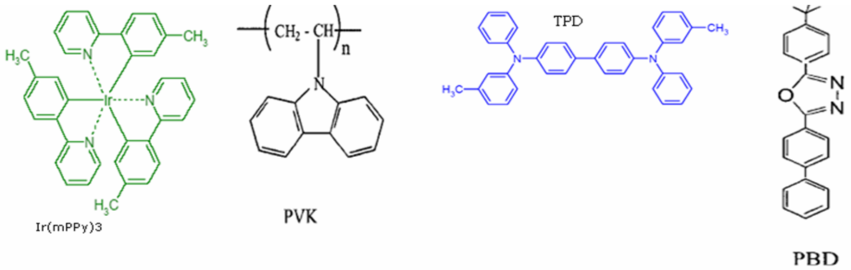

Figure 3.3: Chemical structures of the materials.

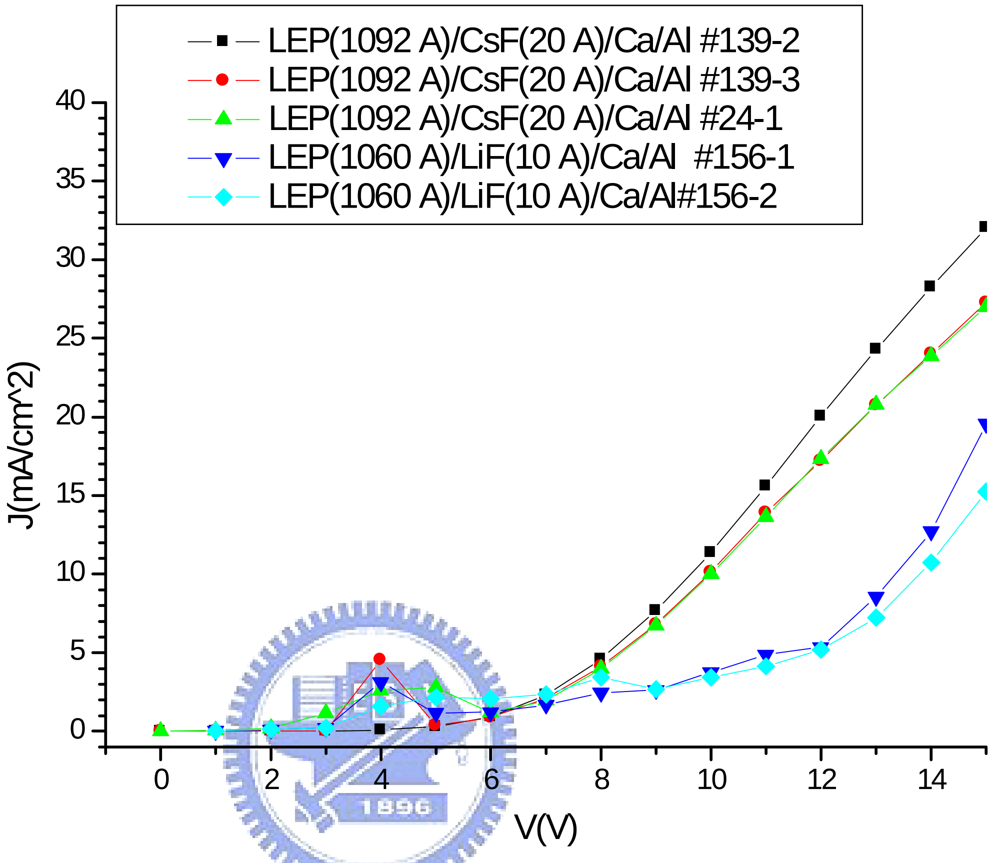

Figure 3.4: J-V diagram for single-layer devices with CsF/Ca/Al or LiF/Ca/Al

use.

We compare the device efficiencies with different cathodes— CsF/Ca/Al and LiF/Ca/Al. Figures 3.4 shows that the devices with CsF/Ca/Al have higher current density. The excessive amount of current density could be regarded as the excessive electrons because CsF injects electrons more efficiently than LiF does.

Figure 3.5 shows that devices with CsF/Ca/Al perform much better at low voltage range (around 6 volts to 15 volts) than those with LiF/Ca/Al. It is because the work function of CsF (about 1.9 eV) is lower than that of LiF (about 2.4 eV). Under low voltage the electrons have no barrier to inject for the former case while, under the low voltage, the electrons encounter a barrier for the latter case. On the contrary, however, for high voltages (voltage higher

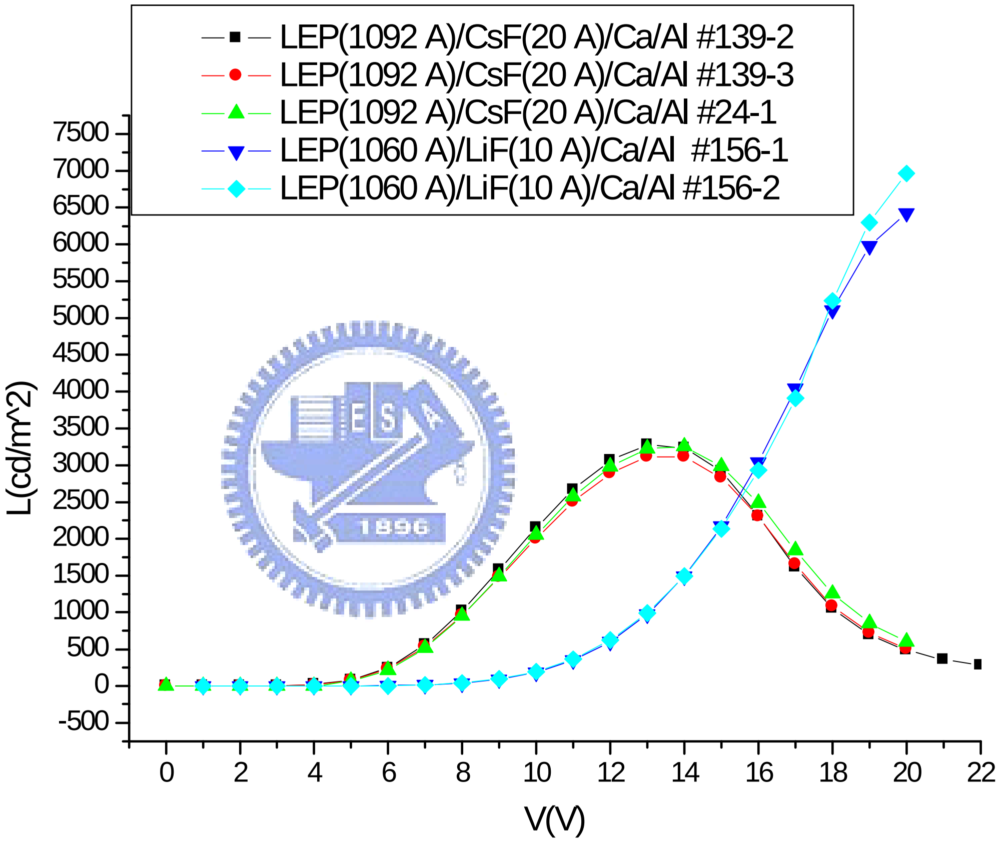

Figure 3.5: L-V diagram for single-layer devices with CsF/Ca/Al or LiF/Ca/Al

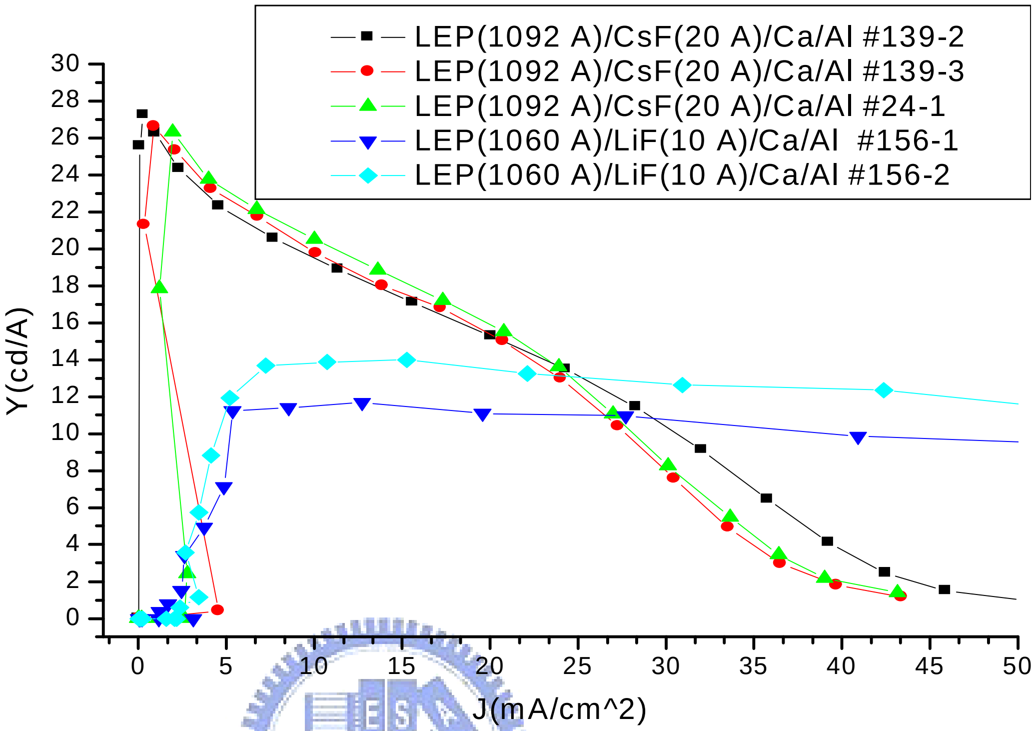

Figure 3.6: Y-J diagram for single-layer devices with CsF/Ca/Al or LiF/Ca/Al

than 15 volts), the devices with LiF/Ca/Al have higher luminance but the luminance of the devices with CsF/Ca/Al decreases dramatically at high voltages.

Figure 3.6 and 3.7 show that efficiency of devices is better under CsF/Ca/Al case.

The luminous efficiency of CsF/Ca/Al is about 28 cd/A and the Power Conversion Efficiency is about 20 lm/W. On the other hand, the luminous efficiency of devices with LiF/Ca/Al is only about 14 cd/A while the PCE is about 3 lm/W.

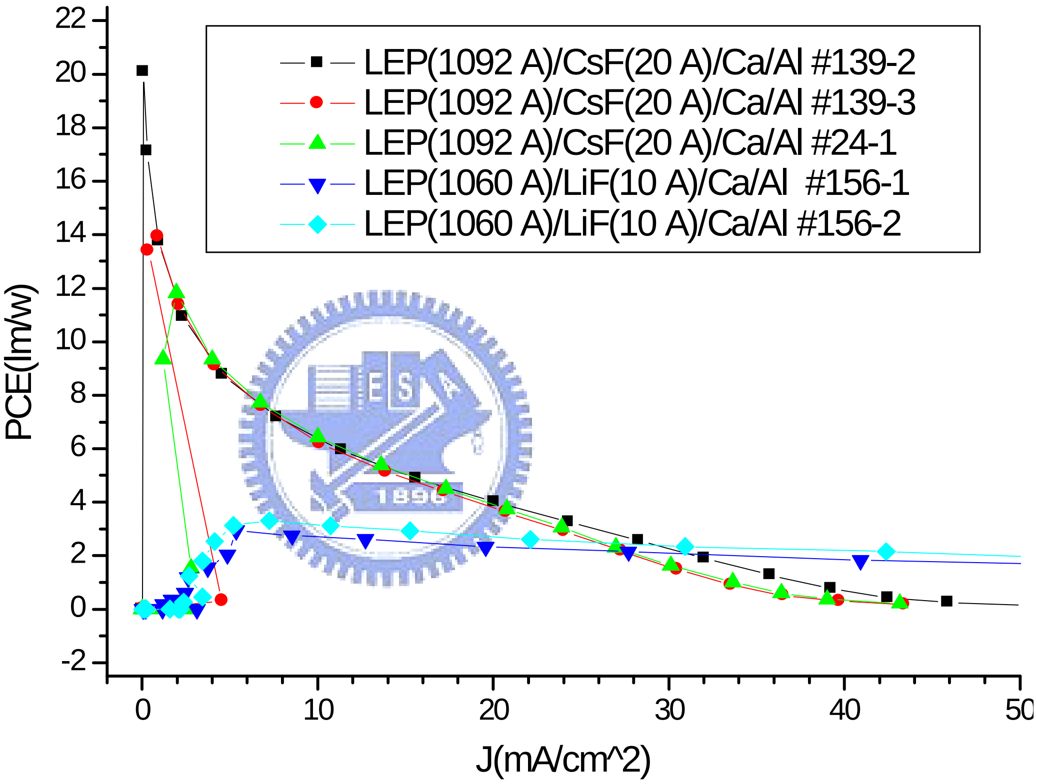

Figure 3.7: PCE-J diagram for single-layer devices with CsF/Ca/Al or LiF/Ca/Al

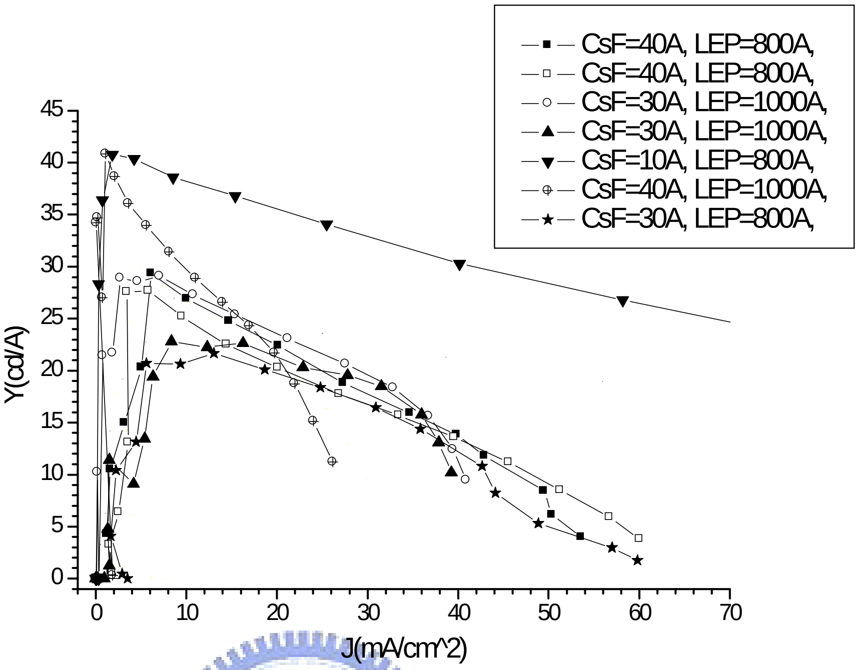

Figure 3.8: Y-J diagram for single-layer devices with various CsF thicknesses.

3.2 Single-layer devices with the CsF/Al cathode in conditions of different thicknesses of the light-emitting layer and of the CsF layer

In this section we will describe two very important comparisons about the optimal thickness of CsF layer and of the emissive layer (LEP). Our own experiments revealed that the best device had conditions of CsF about 10 Å and the emissive layer about 800 Å which were very close to the optimal production factors in the literature. For comparison, we produced devices with CsF of 10 Å, 30 Å, and 40 Å and with the emissive layer of 800 Å and 1000 Å. There were 6 combinations.

We observe in Figure 3.8 that there are two conditions for devices to get yield of 40 cd/A. One (with the symbol of ▼) is CsF with thickness of 10 Å and LEP with thickness of 800 Å. The other (with the symbol of ⊕) is CsF with thickness of 40 Å and LEP with thickness of 1000 Å. However, the Y-J diagram shows that the curve for the latter device drops much more quickly while the curve for the former still holds at high efficiency under larger current density. We also notice the curves representing the two devices in L-V (Fig 3.9) and J-V (Fig 3.10). ▼ has high luminance and large current

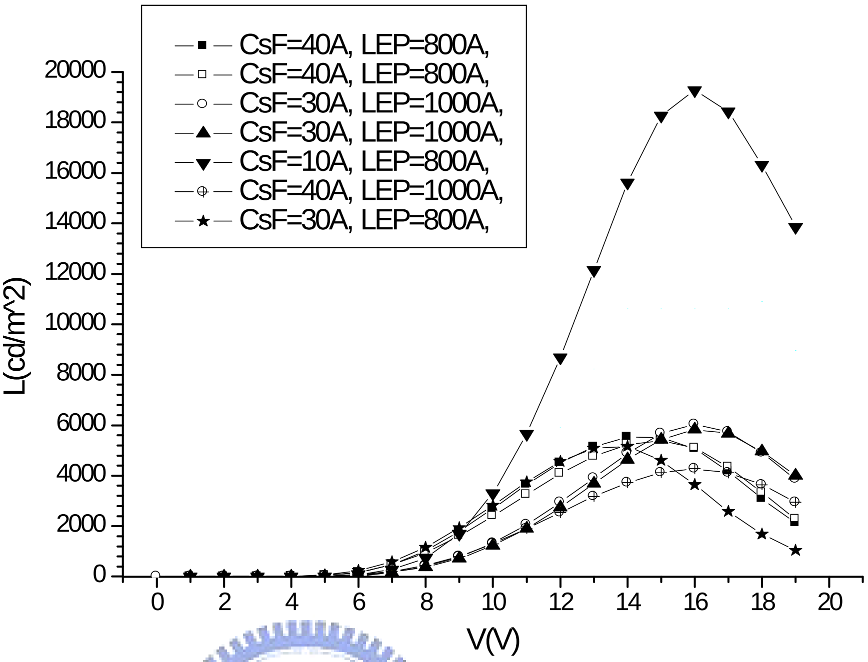

Figure 3.9: L-V diagram for single-layer devices with various CsF thicknesses.

density while ⊕ does not. We may deduce from these facts that thick Cesium fluoride film may block electron injections at high voltages.

For devices with other combinations, the yield is lower than 30 cd/A even though the current densities of theirs are higher than that of the ⊕. Next we disscuss effects of film thickness.

There are two groups in respect to a fixed LEP thickness. For devices with LEP thickness of 800 Å which are represented by ■, □,▼, and ★ in Figure 3.9 of L-V, and for devices with LEP thickness of 1000 Å, which are represented by ◯,▲, and ⊕, we observe that the thinner the CsF, the higher the luminance. On the other hand, for a fixed CsF thickness (for example, ■, □, and ⊕ stand for devices with CsF of 40 Å and ◯, ▲, and ★ represent for those with CsF of 30 Å), devices with LEP thickness of 800 Å get higher luminance at low voltages than those with LEP thickness of 1,000 Å.

The luminance for the device with CsF=10 Å and LEP=800 Å was about 12,000 cd/m^2 at only 13 volts. Notice that the ⊕ curve, whose yield was also 40 cd/A, got low luminance. For the other devices, the value of luminance was lower than 6,000 cd/m^2 even at 16 volts.

Although the best power conversion efficiency (PCE), about 22 lm/W, is

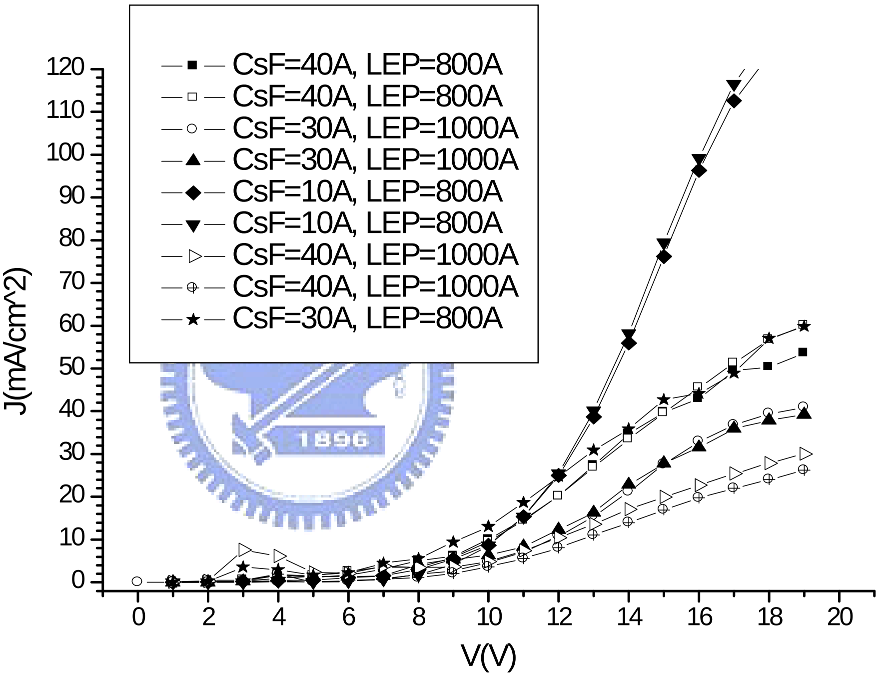

Figure 3.10: J-V diagram for single-layer devices with various CsF thicknesses.

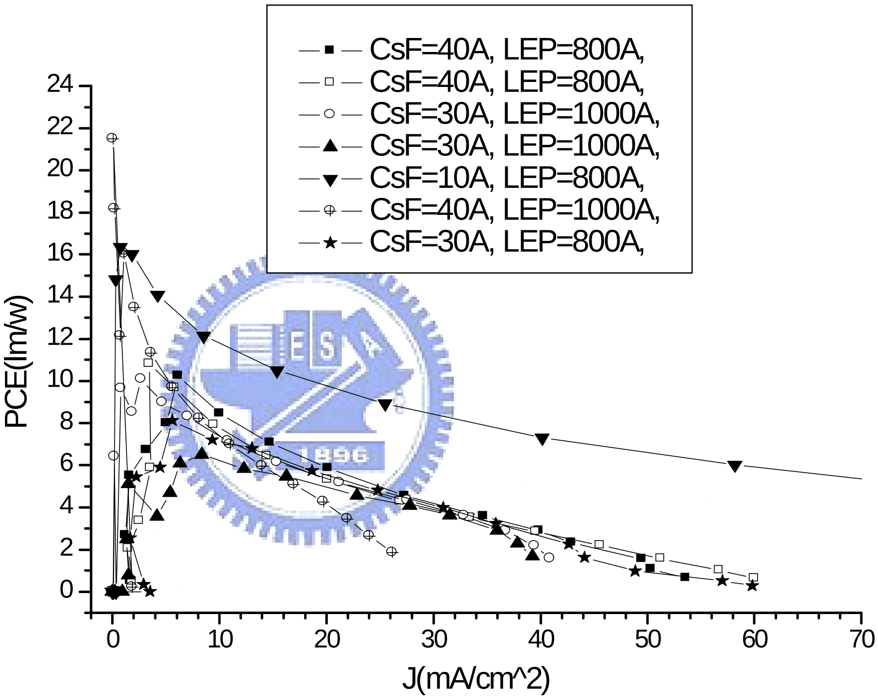

Figure 3.11: PCE-J diagram for single-layer devices with various CsF thicknesses.

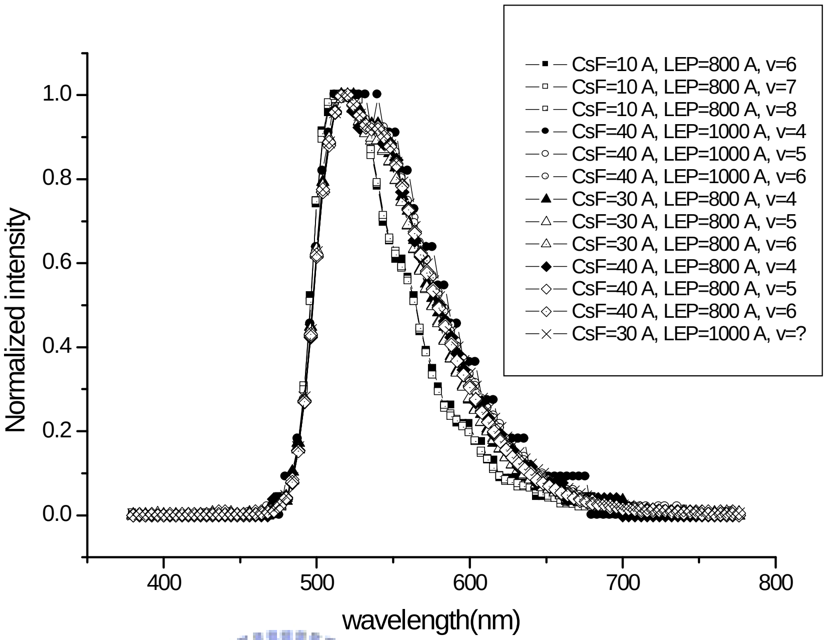

Figure 3.12: Spectra of devices. There is no significant difference for the spectra among different device conditions.

achieved by the device with the condition of CsF =40 Å and LEP =1000 Å, it drops very quickly when going through high current density. On the other hand, even though the inverted triangle curve does not get the highest value of PCE, it stands at much higher PCE than any other devices under large current density. Therefore we conclude that the best device is still the one represented by the inverted triangle curve.

Figure 3.12 shows the spectra of the devices. We can see that different thicknesses of Cesium fluoride and LEP layers lead to almost the same spectra.

With almost the same production process, except for using O_2 plasma after UVOzone treatment, we produced a device, shown in Figure 3.13, with luminous efficiency of about 49 cd/A. However, there was no evidence that using both treatments would increase the device efficiency. The PCE was about 18 lm/W. High efficiencies were achieved at low current density. It is worth notifying that the current density in this device was lower than usual. We attributed this to an accurate and smooth fabrication proceeding. Nevertheless, the luminance was not high at low voltages. The spectra under different voltages of course remained the same as before.

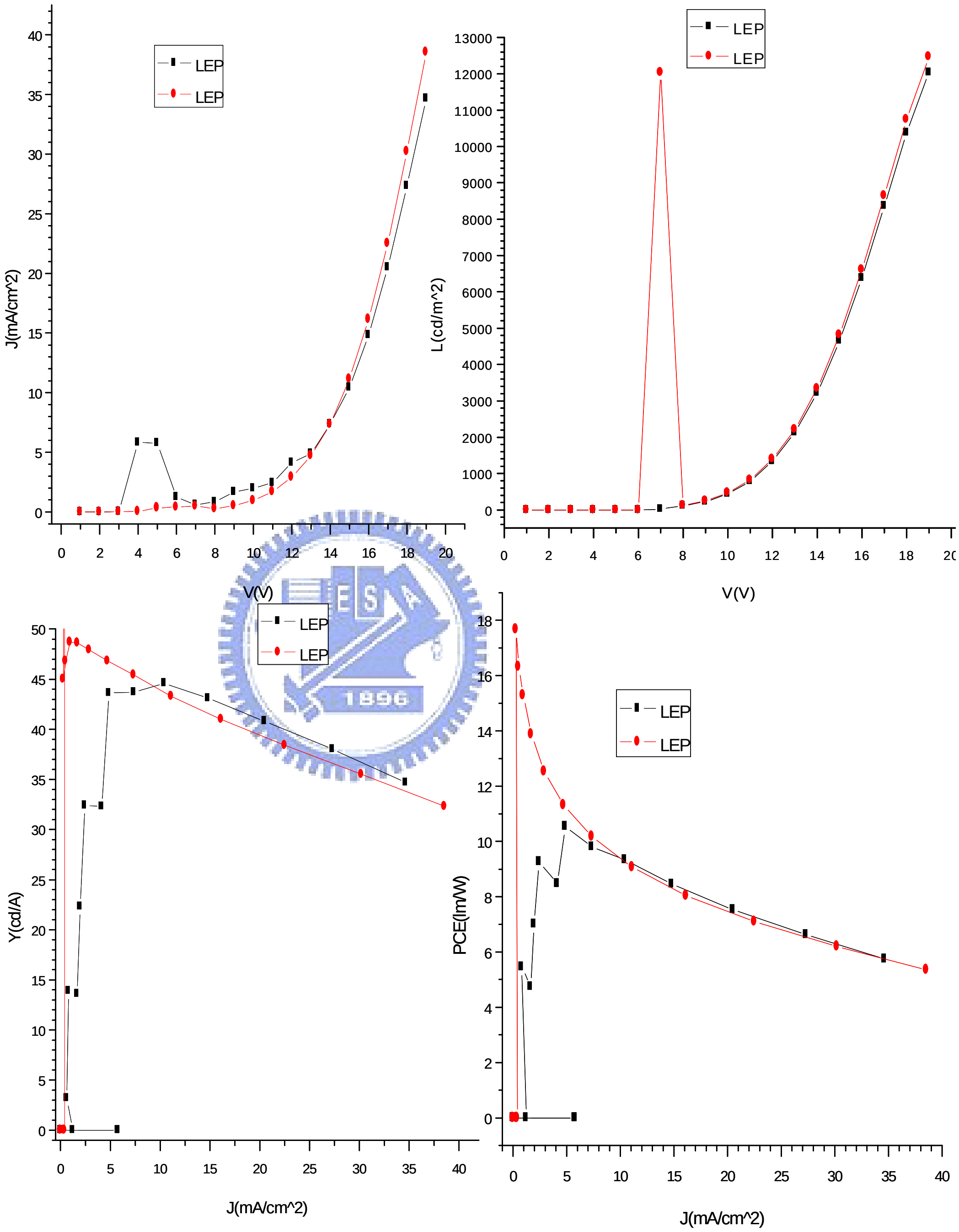

Figure 3.13: Devices with luminous efficiency of 49 cd/A.

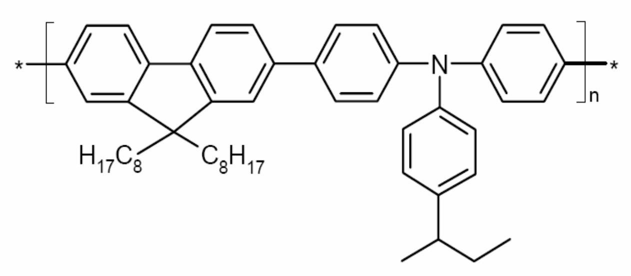

Figure 3.14: Chemical structure of TFB.

3.3 Double-layer devices with combinations of different insulating layers and different cathodes

This section studies the double-layer devices with three different conditions of cathodes. One is the device with CsF/Al as the cathode. Another is with CsF/Ca/Al/. The other is with LiF/Ca/Al as the cathode. The double layers consist of Poly [(9, 9-dioctylfluorenyl-2, 7-diyl)-co- (4, 4'-(N-(4-sec-butylphenyl)) diphenylamine)] (TFB), whose chemical structure is shown in Figure 3.14 , and the four-material blend LEP. For each kind of layer, the thickness is kept in close thickness in every device. The different insulating layers, LiF and CsF, are kept with thickness about 10 Å.

Figure 3.15 shows the EA-IP relationships of the PEDOT, TFB, LEP materials, Cesium Fluoride, and Calcium or Aluminum cathode.

It seemed reasonable at the first time to conjecture that the luminous efficiency could be increased by using TFB as the hole-transporting material. However, the curves with the symbol ■ in the following figures indicate that the idea is wrong. If we compare the curves represented as inverted triangles (▼) (single-layer device with structure of LEP/CsF/Al) in the preceding section with the square ones (■, bi-layer device with structure of TFB/LEP/CsF/Al) in this section, we find that the luminous efficiency of the latter drops significantly from 40 cd/A to 21 cd/A. PCE slightly declines from 16 lm/W to 9 lm/W. The spectra of the two devices are almost the same. We impute this to excessive holes that are injected from TFB. This breaks the originally balanced holes and electrons in the single-layer device. We also suggest that the ordinary single-layer structure of LEP/CsF/Al, with the LEP referring to the four-ingredient blend, whose ratio among the four materials $PVK : PBD : TPD : Ir(mppy)_3 = 61 : 24 : 9 : 6$, makes a very balanced condition holes and electrons.

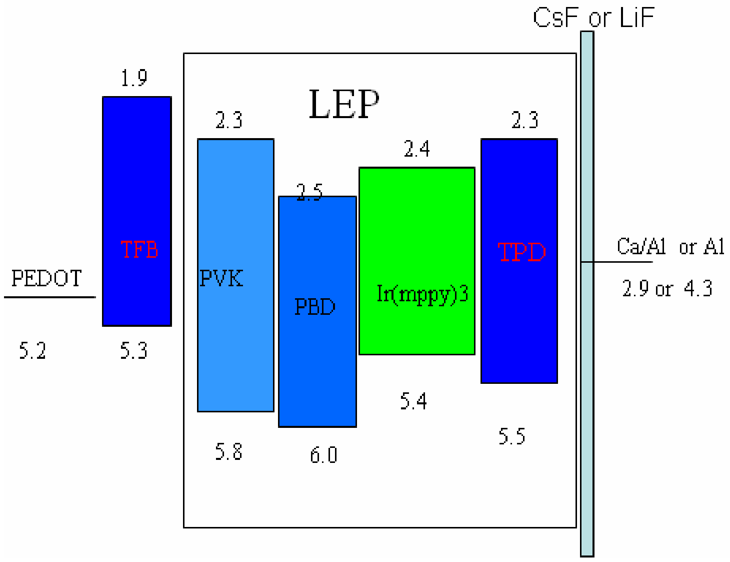

Figure 3.15: Energy diagram of the bi-layer structure.

We may further suggest that one deposit, in double-layer devices, Calcium between the insulating layer and the Aluminum cathode. We have noticed earlier that the CsF/Ca/Al combination injects more electrons. See Section 3-1 or the calculation of free energy in Section 2-6. That the structure TFB/LEP/CsF/Al is hole-excessive may just indicate that using Ca between the CsF and Al suits our need, because in this way more electrons will be carried in the device. However, the results represented by the solid circles in the following diagrams would disappoint us. In observation of Figure 3.16 and Figure 3.17, even though the device with CsF/Ca/Al has larger current density than that with Cs/Al, we do not see efficiency improvement in the Cs/Ca/Al device. Even worse, it shows that the device with CsF/Ca/Al has slightly low luminous efficiency than that of the device with CsF/Al. Just like the case in single-layer devices, Figure 3.18 shows that under low voltage range, devices with Ca performs better than those without Ca. We may rule out the possibility of fabrication errors in the device.

Figure 3.19 and Figure 3.20 show the PCE versus current density and the spectra of theses devices, respectively. We see that the spectra of bilayer devices are almost the same as the spectra of single-layer ones.

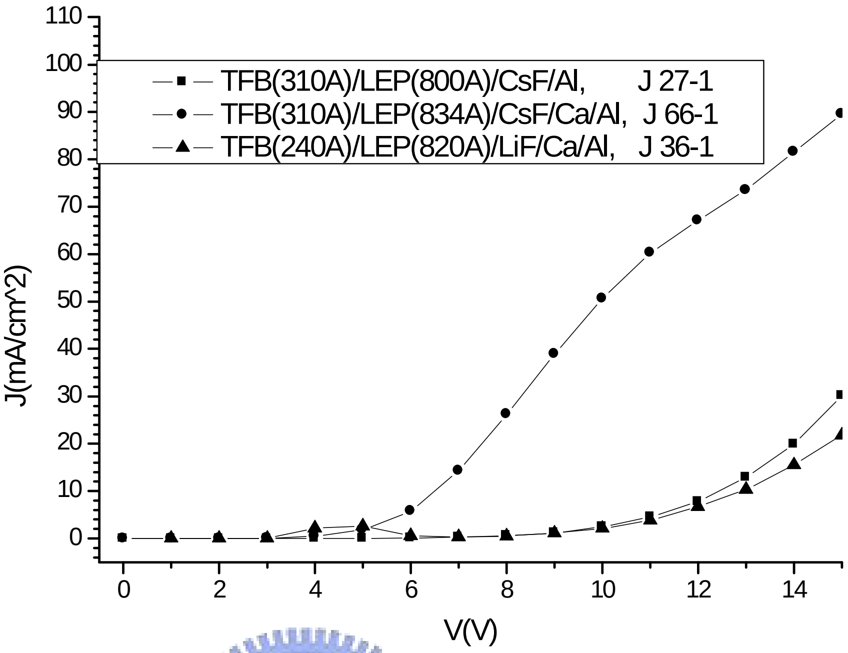

Figure 3.16: J-V diagram for bilayer devices.

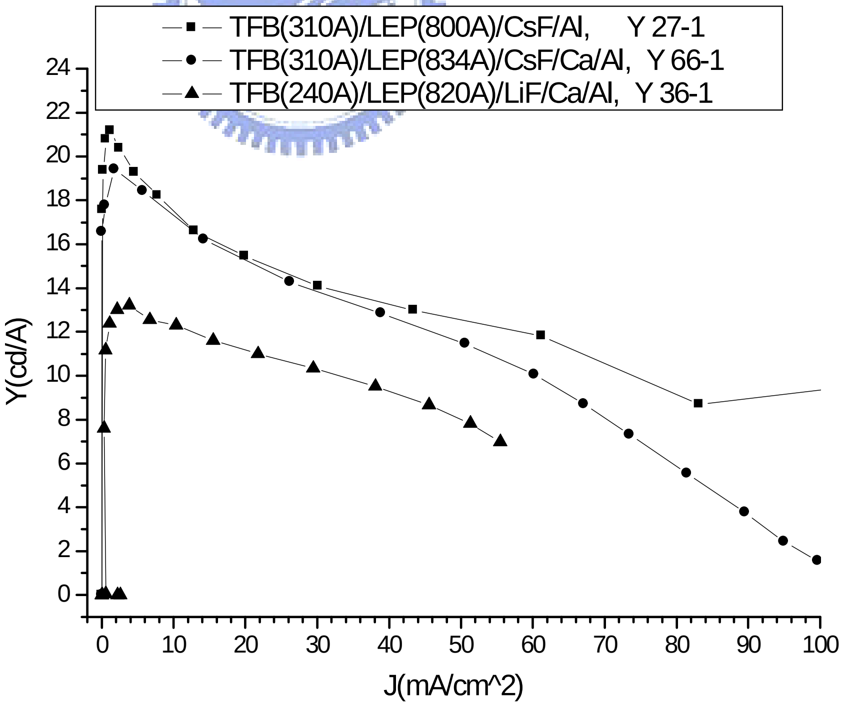

Figure 3.17: Y-J diagram for bilayer devices.

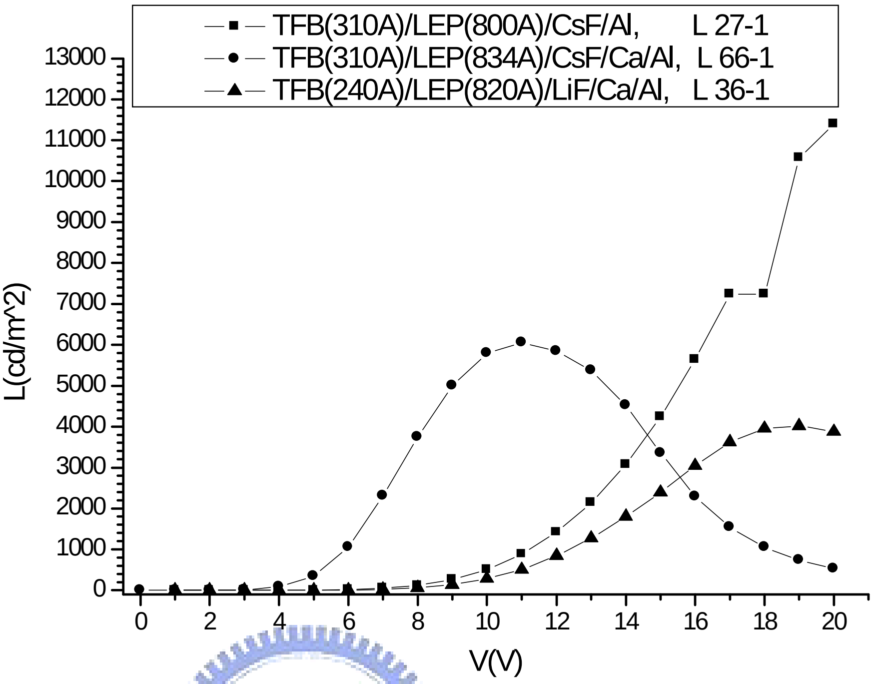

Figure 3.18: L-V diagram for bilayer devices.

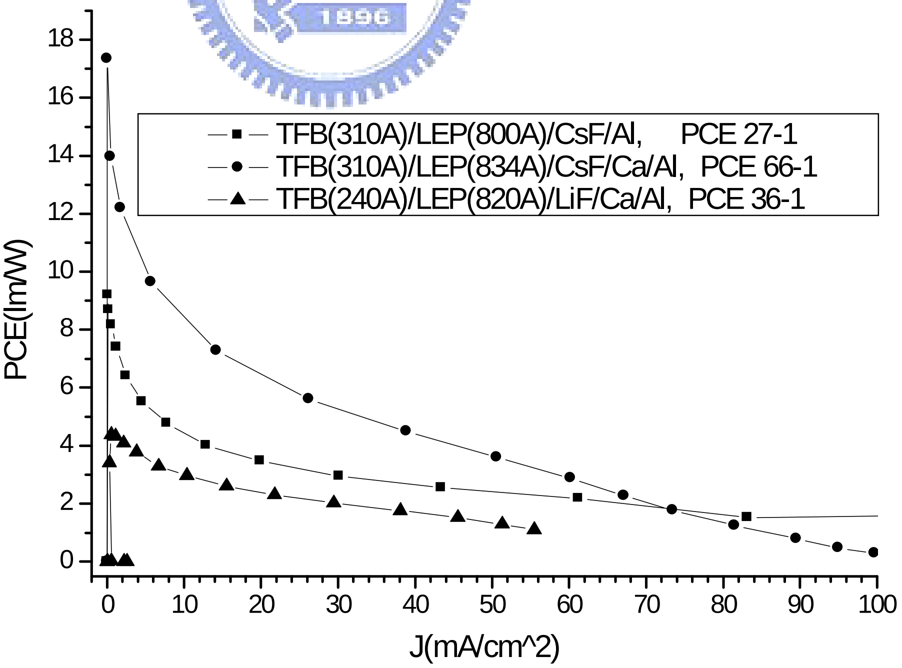

Figure 3.19: PCE-J diagram for bilayer devices.

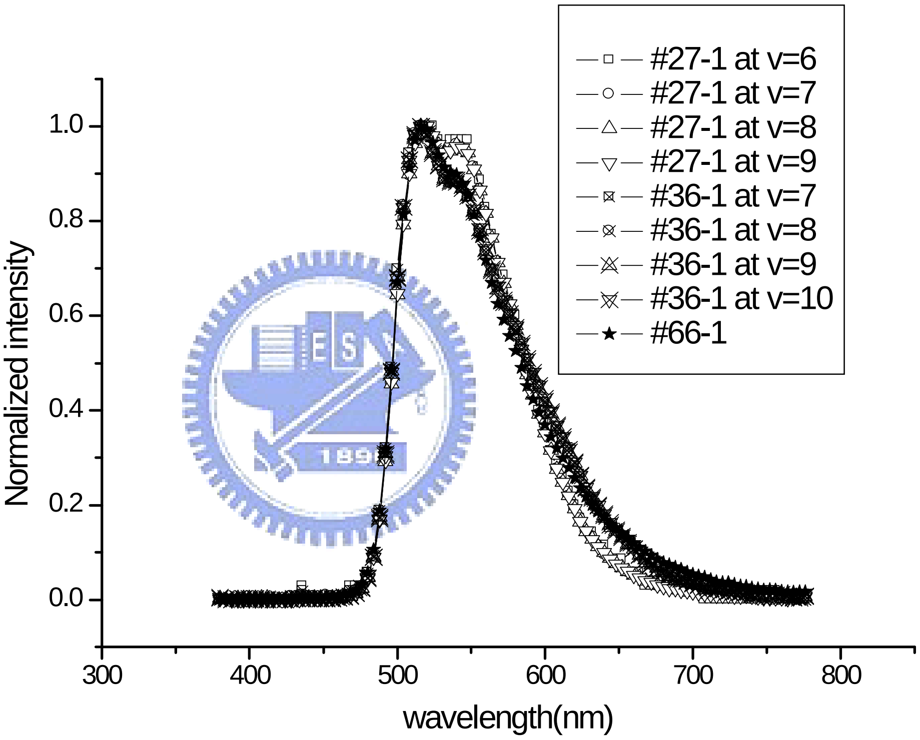

Figure 3.20: Spectra of bilayer devices.

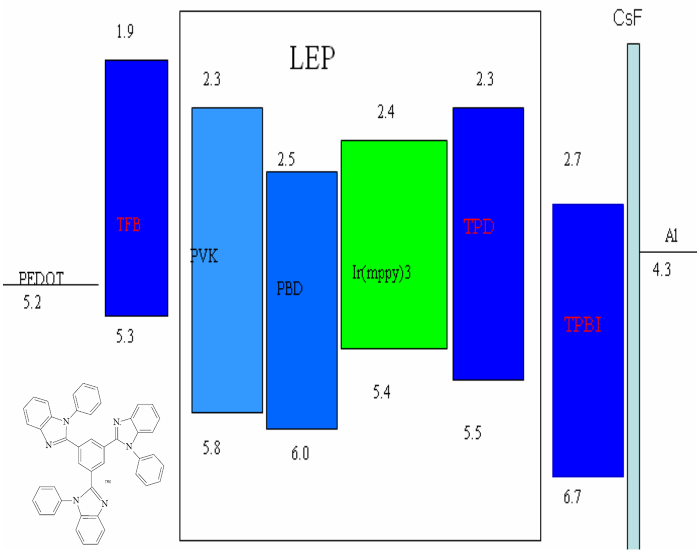

Figure 3.21: The tri-layer energy diagram and (inset) the chemical structure of TPBI.

3.4 Tri-layer structures with TPBI as the electron-transporting layer

The first idea is simple. We know that it is hole-excessive for the device structrue of TFB/LEP/Cs/Al. Therefore probably using 2, 2 ’, 2 ”-(1, 3, 5-phenylene)tris(1-phenyl-1H-benzimidazole) (TPBI) as the hole-blocking layer at the cathode side may just improve the device efficiency by lowering the hole current. Figure 3.21 shows the energy diagram of tri-layer devices. We observe that the reason for TPBI to block holes is that it has a very large IP compared with all the other materials. Inset in the Figure shows the chemical structure of TPBI.

There are two possible ways to add the TPBI layer. One is to adulterate a little amount of Poly(methyl methacrylate) (PMMA), which is an insulator, into the TPBI. This will be disscussed in Appendix B. The other is to thermal-evaporate the TPBI powder. Thermal-evaporation seems an easier way with regard to production process. It also gives us more compact films. However, thermal-evaporation may limit us to small-area fabrication, which makes it impossible to produce the flat-panel displays in a large area. In our experiment here, the thicknesses of the TFB, LEP, TPBI are about 200 Å, 800 Å, and 150 Å, respectively.

Figure 3.22 shows that there seems no difference between the tri-layer device

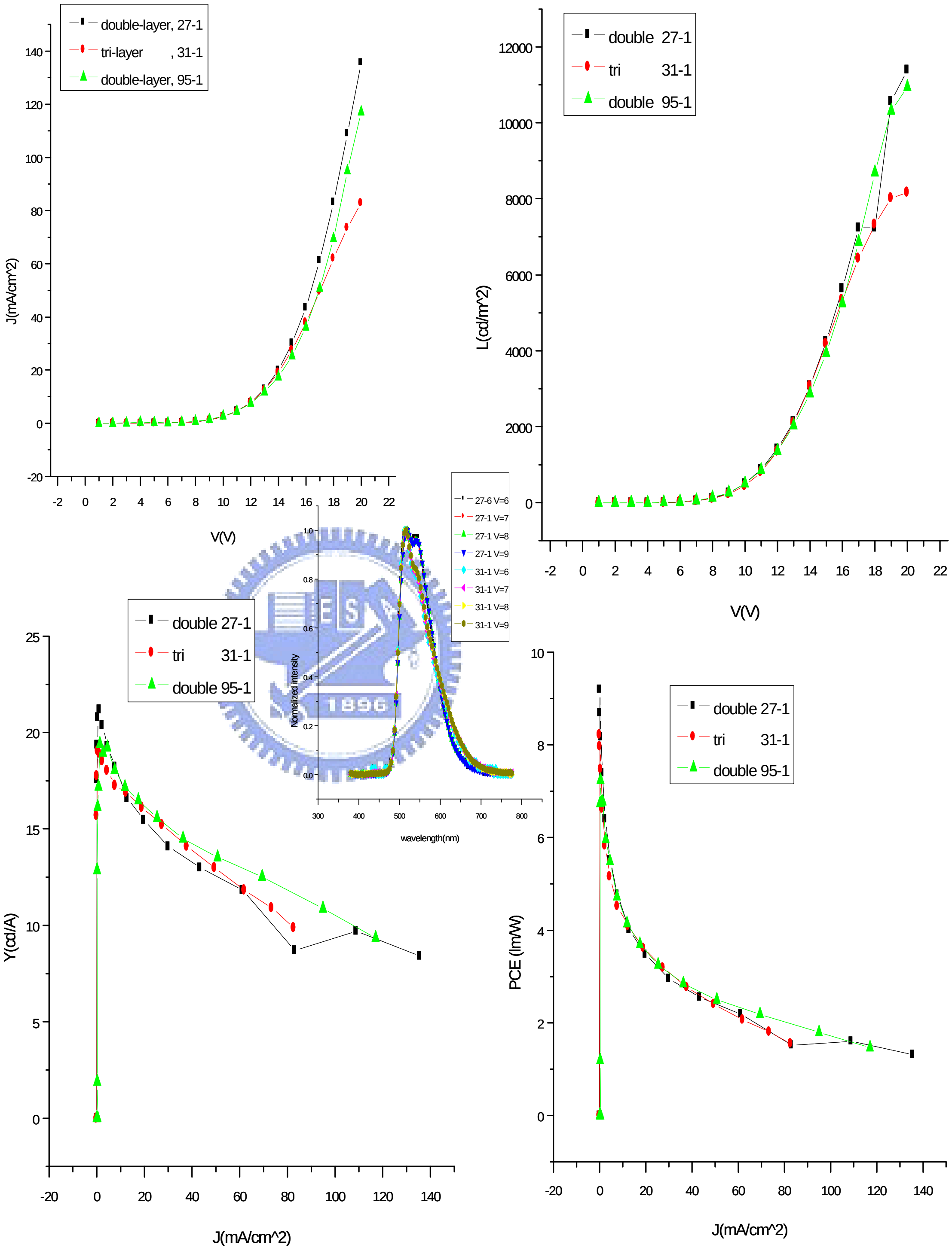

Figure 3.22: Performance of a tri-layer device.

and the double-layer ones. The reason to cause the failure may be that the EA of TPBI is as high as 2.7 eV. Therefore electrons are accumulated at the interface of TPBI and the LEP. We should replace TPBI with PBD in the future.

3.5 Conclusions of Highly Efficient Green-emitting Devices

We talulate the maximum efficiencies of different device structures in the following table. Unless noted, LEP refers to the four-material blend with the blending ratio of $PVK : PBD : TPD : Ir(mppy)_3 = 61 : 24 : 9 : 6$.

We suggest that we do more experiments on the various concentrations of PBD in single-layer devices. For double-layer devices with CsF/Ca/Al as the cathode, we may change the thicknesses of CsF and Ca. We may adjust the PBD concentration in the 4-material blend as well. For the tri-layer ones, we should convert our attention to PBD. PBD has lower EA of 2.5 eV. This may cause electrons to inject directly to the Iridium emitter [13].

[1]	single layer	bi-layer[2]
10Å	LiF/Ca/Al LEP=800Å LEP=1000Å (051027,51-2,10.9,2.8) (051027,156-2,13.9,3.1) (051021,208-1,19.6,3.3)[3] (051021,62-1,10.2,1.7)[4] CsF/Al (060407,147-2,40.8,16.4)[6] × (060419,9-1,44.6,10.5)[6] × (060419,9-2,48.7,17.7)[5,6] ×	LiF/Ca/Al CsF/Al 0% TPD (060530,36-1,13.2,4.4) (060512,51-2,26.9,12.0) 3% TPD × (060519,50-1,23.8,7.0) 9% TPD × (060419,257-1,18.1,4.8)[6]
20Å	CsF/Ca/Al LEP=1000Å LEP>1000Å (060324,139-2,27.2,20.1) (060324,98-2,17.0,10.4)	LiF/Ca/Al (051216, 113-2,11.9,2.6)[7] CsF/Ca/Al (060329,66-1,19.4,17.3) CsF/Al (060329,44-1,22.8,11.6)
30Å	CsF/Al LEP=800Å LEP=1000Å (060407,199-1,21.7, 8.1) (060407,3-1,29.1,10.1)	×
40Å	CsF/Al LEP=800Å LEP=1000Å (060407,2-1,29.3,10.2)[6] (060407,165-2,40.8,21.5)	×

Table 3.1: Efficiencies of devices with various structures

The left column refers to thickness of the insulating layer. The top row stands for the device structures. In the main body, the four numbers in parenthesis (a,b,c,d) stand for date (in order of year, month, day) of production, number of the sample, luminous efficiency in unit of cd/A, and power conversion efficiency in unit of lm/W of the device, respectively.

Bi-layer devices have the structure of TFB/LEP. Unless notified, the thicknesses of TFB and LEP are about 300Å and 800Å, respectively.

Without TPD. LEP=700Å.

Without TPD. LEP=1100Å.

The highest efficiency that was achieved in our lab.

Measured with an attenuator which reduces luminance, yield, and PCE to $\frac{1}{10}$ of the original values.

PBD concentration 246 (72%)