1. Introduction

1.1 Polymeric light-emitting diodes and reasons for us to choose heavy metal complexes as dopants

A Polymer Light Emitting Diode (PLED) radiates by the relaxation of an exciton that is formed by the recombination of an electron injecting from the cathode to the LUMO (the Lowest Unoccupied Molecular Orbital) of the polymer and a hole injecting from the anode to the HOMO (the Highest Occupied Molecular Orbital) of it. Figure 1.1 shows the general structure of a PLED.

When an electron injects from the cathode, it theoretically goes through the line representing the electron affinity level (EA) of the emissive layer. On the other hand, when a hole injects from the anode, it in theory runs along the line standing for the ionization potential level (IP) of the emissive layer. The levels of EA and IP could in principle be measured by the cyclic voltammeter (CV). However in practice EA is more difficult to measure while IP is easier to get.

When the electron and the hole reach to the emissive layer, they recombine to form an exciton, relaxing to a photon. Figure 1.2 schematically shows the formation of an exciton from the recombination of holes and electrons in the emissive layer.

Since an exciton is formed from the recombination of holes and electrons whose spin quantum number are both $1/2$, we conclude that the exciton could have spin 0 or spin 1. The addition of spins of two particles both with
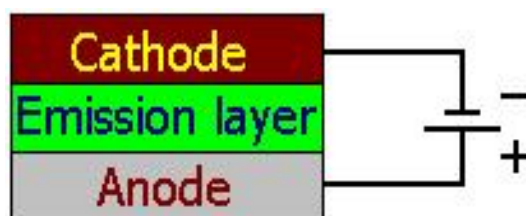

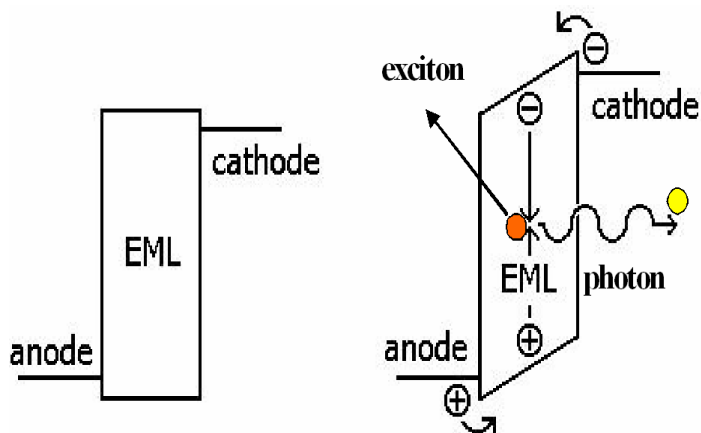Figure 1.1: Schematic structure of a Polymer Light Emitting Diode.

Figure 1.2: Left: the energy diagram of a device. Right: Schematic representation of recombination of holes and electrons in the region of the emissive layer in a device connecting to an external voltage source.

spin 1/2 results in four possible states. For spin 0, it is singlet and written as $|00\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$. For spin 1, it has three possible states (thus called triplet) and is written as $|11\rangle = \uparrow\uparrow$, $|10\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$, and also $|1-1\rangle = \downarrow\downarrow$.

The spin operator S is even under parity. Thus, transitions occur between states of the same parity. Also we know that the ground state of the system has total spin 0. Excitons with spin 0 are spin-allowed, relaxing in efficiently fluorescent photons; excitons with spin 1 are spin-forbidden, relaxing in inefficiently phosphorescent photons. Specifically, for an exciton decaying from the excited singlet state to the ground state, it takes about 1 nano-second to 100 nano-seconds. However, for an exciton decaying from the excited triplet states to the ground state, it takes much more than that — from 1 millisecond to 100 seconds. Therefore, in a typical polymeric light emitting diode, triplet excitons usually are non-radiative and they generally make no contributions to light emission. Because of this, the maximum internal quantum efficiency for a typical fluorescent (only singlet excitons work) PLED is about 25 per cent, for the statistical assumption of the ratio among the singlet and triplet excitons is one over three.

However, we may cope with the problem by inlaying in a heavy metal to the organic compound. This kind of (heavy metal) complex enables triplet excitons to relax to photons because it has strong spin-orbit coupling in the complex. The spin-orbit coupling operator $L \cdot S$ is also even under parity. Therefore it connects states of the same parity. Triplet excitons have spin of 1, and they may couple orbitals of the complex with quantum number

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of 1 to make total quantum number of 0. Therefore, triplet excitons could still decay to the ground state and relax to photons. It was shown that with the heavy-metal dye we could increase the internal quantum efficiency of the device up to 100 per cent [1].

1.2   Literature review

There are several various heavy metals that can be used to make complexes. For example, Copper (although it may not be qualified as a heavy metal) [2], Rhenium [3], Platinum [4], and Iridium. Among them, Iridium is of great interest because the triplet excitons in the Iridium heavy metal complexes have the shortest lifetime, leading to less possibility of triplet-triplet annihilation after the triplet excitons are formed. For example, the lifetime of the triplet exciton in PtOEP (Platinum Octaethyl Porphyrine) with Platinum in the organic compound is about 100 micro-seconds; the lifetime of the triplet exciton in $Ir(ppy)_3$(Tris(2-phenylpyridine) Iridium) with Iridium as the heavy metal is about 1 micro-second.

Recently, OLED used (blended) Platinum and Iridium to produce white OLED with efficiency of 20 cd/A [5] while PLED used two (blended) Iridium complexes to make white light PLED with efficiency of 9 cd/A [6] . Also, X. Gong et al. [7] published a highly efficient yellow-green PLED with the $Ir(DPF)_3$ as the dopant and PVK-PBD as the co-host. The efficiency was about 36 cd/A. The common drawback of the above achievements is that the primary emitting materials, such as Iridium heavy-metal complexes, have to be synthesized by one's own. Commercial unavailability makes it impossible to repeat the work for other groups, let alone to improve the efficiency of the devices with the same materials.

Fortunately, a commercially available Iridium heavy-metal complex, Tris (2-(4-tolyl) phenylpyridine) iridium ($Ir(mppy)_3$), was found, and has made great impression on researchers. $Ir(mppy)_3$was shown to possess a better efficiency compared with another similar complex called $Ir(ppy)_3$, which has no methyl units. The methyl units brace the complex to form a more solid structure, leading to a more homogeneous and amorphous film [8] [9]. To balance the holes and electrons in the emissive layer, D. Neher et al. [8] [10] added a hole-transport material, triphenyl diamine (TPD), and an electron-transport material, 2-(4-biphenylyl)-5-phenyl-1,3,4-oxadiazole (PBD), into the host, poly(N-vinylcarbazole) (PVK), which is also a weak hole-transport material. Thus, PVK, PBD, and TPD were treated as the co-host and the $Ir(mppy)_3$ was treated as the light-emitting dopant. The efficiency was more than 30

cd/A, and the luminance exceeded 10,000 cd/m^2 before 10 volts. The Power Conversion Efficiency (PCE) was about 24 lm/W. In these two articles, they also studied the best blending ratio among the four materials. They found that the best ratio among the four materials is PVK:PBD:TPD:Ir(mppy)$_3$ =61:24:9:6.

In addition to this, we may further improve the efficiency of devices by first spin coating another hole-transport layer at the anode. S.A. Choulis et al [11] added spin-rinsed poly(9, 9- dioctyl-fluorene-co-N-(4-butylphenyl)- Diphenylamine) (TFB) layer to serve as the hole-transporting layer, which improves the hole injection from the anode. By doing this, they got 45 cd/A of devices while the brightness was 8,000 at 8 volts. In addition, X. Yang et al [12] published the world-record phosphorescent PLED with luminous efficiency 67 cd/A, Power Conversion Efficiency 67 lm/W and External Quantum Efficiency 18.8%. They used two layers to serve as the hole-transporting layers. The first layer, either MUPD or OTPD, was spin-cast on PEDOT-PSS, and cross-linked by being irradiated with 365 nm light. The second layer was also done in the same way. PBD was replaced by OXD-7 and there seemed no TPD in the blend. In addition, a cross-linking catalyzer, 4 - octyloxydiphenyliodonium- hexafluorantimonate, was added in the first hole-transporting layer. To the best of our knowledge, this is the highest luminous efficiency in the world. On the other hand, S.A. Choulis et al [13] used spin-rinsed TFB and thermally-evaporated PBD as the hole-transporting layer and electron-transporting layer, respectively. By doing so, they also got devices of efficiency about 55 cd/A and PCE of 50 lm/W. But the luminance was decreased down to 2750 cd/m^2 at 8 volts.

To begin with, we first try to find the best production process of our own to repeat the green emitting, high-efficiency devices. Chapter 2 will describe the detailed fabrication conditions of our devices throughout our experiments. In order to achieve the maximum luminous efficiency, we compare devices with different conditions such as different cathodes, thicknesses of light-emitting films, etc. To produce bi-layer devices, the buffer-layer technique [14], designed for preventing adjacent layers from dissolving each other, is uniquely developed. The method is not affected by the nature of solvents of the subsequent layers. Therefore theoretically it does not delimit any particular solutions.

It is intuitive to introduce a kind of electron-transporting material at the cathode. To achieve better electron transportation, we may also spin coat or thermal-evaporate 2,2 ',2 "-(1,3,5-phenylene) tris (1-phenyl-1H-benzimidazole) (TPBI) at the cathode, which has high LUMO level to enable electrons to
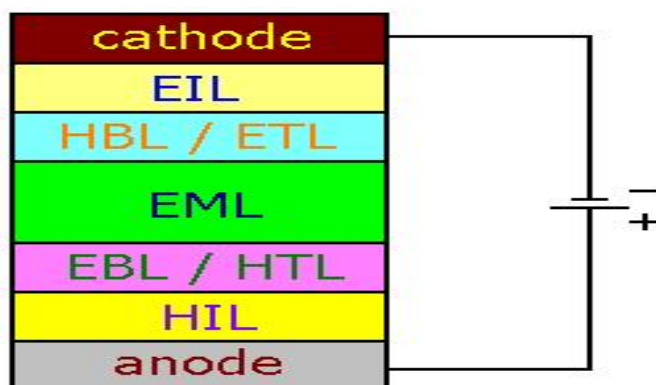
Figure 1.3: Schematic structure of a Polymer Light Emitting Diode after improvements with multiple layers.

inject more easily and also has high HOMO level to block the holes. Therefore, the TPBI acts not only an electron-trasporting material but also a hole-blocking one. All in all, an idealized structure of multilayer PLEDs should consist of, from the anode to the cathode, a hole-injection material (for example PEDOT-PSS), an electron-blocking (or hole- transporting) layer (for example TFB), an emissive layer (for example the 4-material blend described in the literature), an electron- transporting (or hole-blocking) layer (for example TPBI), and finally the electron injection material (this is not used in our work), as shown in Figure 1.3.

Figure 1.4 shows the ideal injections of holes from the anode and electrons from the cathodes. The carriers recombine in the region of the emissive layer, but not recombine in the other carrier-transporting layers.

Some data of devices will be discussed and described in Chapter 3.

Next, based on the above devices with high efficiency, we go further to white-emitting PLEDs. Up to now, the world record of phosphorescent, white polymeric light emitting diodes was achieved by X. Gong et al. [15], who used $Ir(HFP)_3$ as the dopant and PFO-ETM (or PFO-F) as the host to achieve high efficiency of 10 cd/A and brightness of more than 10,000 at 10 volts. In our work, in order to achieve white PLED with high efficiency, we produced bi-layer devices, with the first layer being a blend of TFB and DCJTB (DCJTB is a red-emitting, small molecule), and the second layer being the 4-material blend plus the PFO, which is a blue emitter. Detailed discussion about this work and some possible future directions of research will be given in Chapter 4.
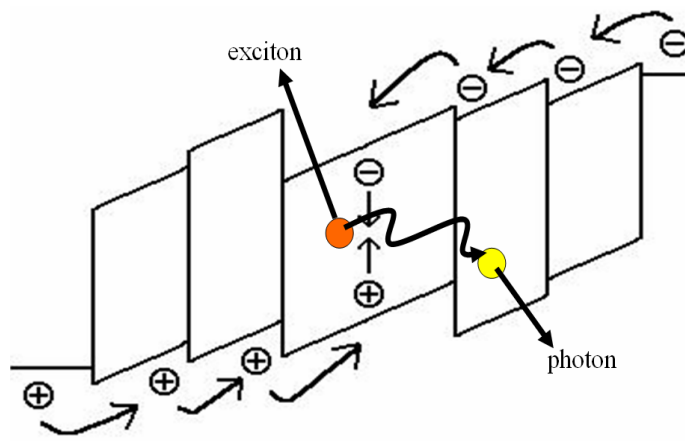
Figure 1.4: Energy diagram of the biased PLED with the multilayer structure. Holes and electrons only recombine in the region of emissive layer, not in the other carrier-transporting layers.