

## Chapter 1

### Organic Light-Emitting Diodes

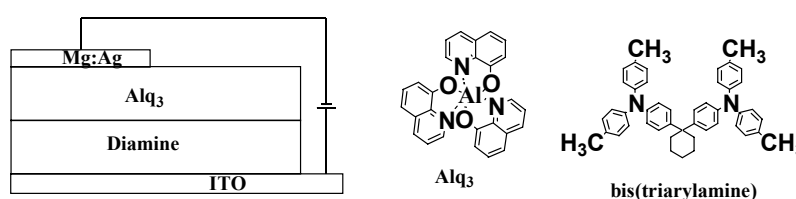
#### 1-1 Introduction

##### 1-1-1 Inorganic Light-Emitting Diodes (LEDs)

This phenomenon was first discovered for inorganic materials in 1936, when Destriau et al observed high field electroluminescence (EL) from a ZnS phosphor powder dispersed in an isolator and sandwiched between two electrodes.<sup>[1]</sup> In 1962, Holonyak et al. introduced commercially available light-emitting devices (LED) based on the inorganic semiconductor GaAsP.<sup>[2]</sup> GaAsP is one of the red light-emitting materials that are available for early day LEDs. Nowadays, inorganic LED materials that emit red, orange, yellow, or blue are compounds of elements from groups III and V of the periodic table such as GaAs, GaP, AlGaAs, InGaP, GaAsP, GaAsInP, and more recently AlInGaP.<sup>[3]</sup> Blue LEDs, however, were difficult to obtain since epitaxially grown semiconductors with large energy gaps are not stable. Nevertheless, blue diodes based on SiC, ZnSe, or GaN were developed, but exhibited distinctly lower efficiencies in comparison to other diodes.<sup>[3]</sup> Research is currently focused on the development of new highly efficient materials and technologies utilized to fabricate silicon integrated circuits. However, since materials used to fabricate LEDs are more complex than elemental silicon and are more difficult to produce and to process, the evolution of an analogous technology is still far behind technologies evolved for silicon. Although LED products have been successfully commercialized, i.e. lamps of car, traffic signals, the cost of LED fabrication is still high. Organic light emitting diodes (OLEDs) that are fabricated low cost organic materials by thermal vacuum deposition are relatively easy and low cost may be the other choice to replace LEDs.

## 1-1-2 Organic Light-Emitting Diodes (OLEDs)

Organic electroluminescence (EL) was first observed in 1963 by applying high voltage (~400 V) across single crystals of anthracene.<sup>[4]</sup> In 1982, the non-crystalline thin film of anthracene was deposited under vacuum emitted blue EL when subjected to lower drive voltages (~30 V).<sup>[5]</sup> These early stage development of OLEDs were hardly noted mostly due to their impractical performance. It was not until late eighties that a bilayer OLED reported by Tang and VanSlyke attracted worldwide attention.<sup>[6]</sup> The simple device structure comprising thermal evaporated two thin layers of organic compounds sandwiched between two electrodes one of which was transparent. The materials were selected on their ability to act as fluorophores and to transport charge carriers. Green EL was observed with devices comprising the bis(triarylamine) as the hole-transporting layer and tris(8-hydroxyquinoline)aluminium (Alq<sub>3</sub>) as both light-emitting and electron-transporting layer in the configuration ITO/bis(triarylamine)/Alq<sub>3</sub>/Mg:Ag, showed in **Figure 1-1**. Practically, a brightness of > 1000 cd/m<sup>2</sup> as well as the external quantum efficiency of 1% was achieved at an operating voltage below 10 V.

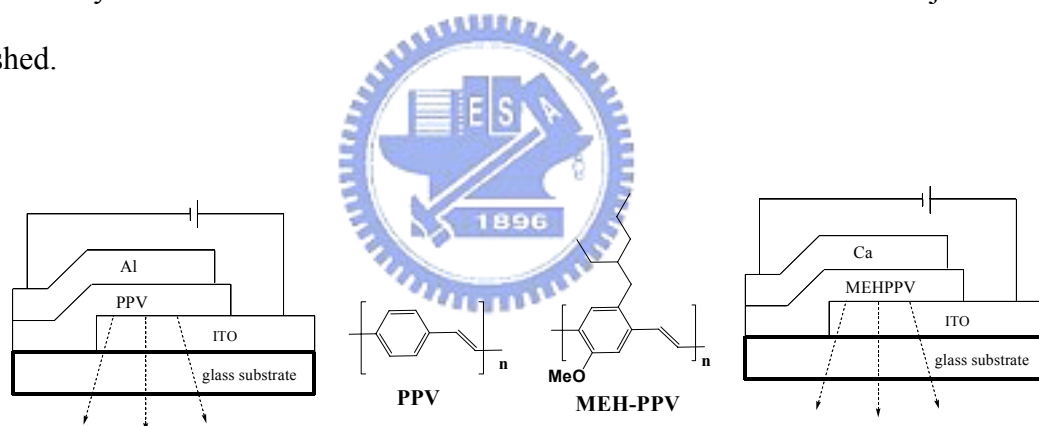


**Figure 1-1.** Configuration of ITO/bis(triarylamine)/Alq<sub>3</sub>/Mg:Ag device and molecular structures.

## 1-1-3 Polymer Light-Emitting Diodes (PLEDs)

In 1990, another essential breakthrough in polymer light-emitting devices (PLEDs) was reported by Friend et al. at University of Cambridge.<sup>[7]</sup> The Cambridge team demonstrated that a highly fluorescent thin film of conjugated polymer poly(p-phenylenevinylene) (PPV)

was fabricated on an ITO substrate by solution process method (**Figure 1-2**). PPV served as the active material emitting yellow–green light in PLED with the configuration of ITO/PPV/Al and the external quantum efficiency of 0.05% was achieved. The introduction of substituents to the PPV backbone provides derivatives which are soluble in organic solvents. In 1991 Braun and Heeger reported a red-orange emitting PLED based on poly[2-methoxy-5-(2-ethylhexyloxy)-p-phenylenevinylene] (MEH-PPV) in the configuration ITO/MEH-PPV/Ca with an external quantum efficiency of 1% (**Figure 1-2**).<sup>[8]</sup> These discoveries have led to intense worldwide interest in new materials for practical OLEDs applications, notably full-color flat-panel displays. Since 1987, hundreds of academic research groups around the world have contributed to the development of OLEDs, approximately 100 reviews and several thousand of articles on this subject have been published.

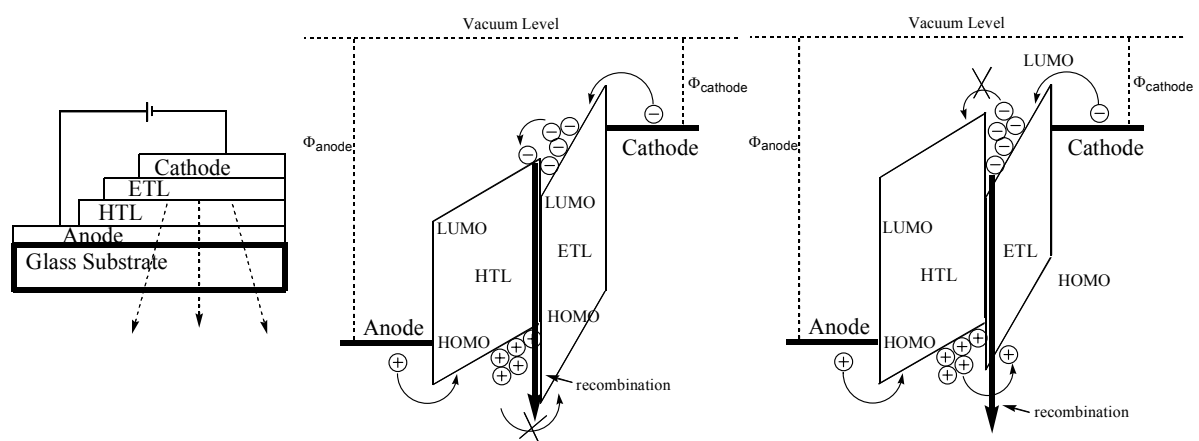


**Figure 1-2.** Configuration of devices based on PPV and MEH-PPV.

#### 1-1-4 Device configuration of OLEDs

An OLED contains mult-thin-layer structure (total thickness is usually less than 0.2 mm) is sandwiched by two electrodes (**Figure 1-3**). For an example, in a basic two-layer OLED structure, one organic layer is specifically chosen to transport holes and the other organic layer is chosen to transport electrons. The interface between the two layers provides an efficient site for the recombination of the injected hole and electron and consequent EL. When an electrical potential difference is applied between the anode and the cathode,

injection of holes occurs from the anode into the hole-transport layer (HTL), while electrons are injected from the cathode into the electron-transport layer (ETL). The injected holes and electrons each migrate toward the oppositely charged electrode, and the recombination of electrons and holes occurs near the junction in the luminescent HTL. Upon changes recombination, electrical energy is transferred to light-emitting material as photonic energy goes through the light-transmissive anode (Indium Tin Oxide, ITO) and substrate (glass). As shown in **Figure 1-3**, the highest occupied molecular orbital (HOMO) of the HTL is above that of the ETL, and holes can be blocked in front of ETL, and the lowest unoccupied molecular orbital (LUMO) of the ETL is slightly below that of the HTL, so that electrons are easily injected to the HTL. The hole was block in the HTL causes a build up in hole density, and thus enhance the collision capture process after electrons injected from the ETL. Furthermore, by spacing this interface at a sufficient distance from the electrode contact, the probability of quenching near the metallic surface is greatly reduced. On the other hand, if the HOMO of ETL is slightly below HTL and the LUMO of ETL is significantly below that of the HTL, hole-electron pair will recombine in ETL and the light of ETL will be emitted. The simple structure can be modified into a three-layer structure, in which an additional luminescent layer (EL) is introduced between HTL and ETL to function primarily as the site for hole-electron recombination in EL and thus EL.

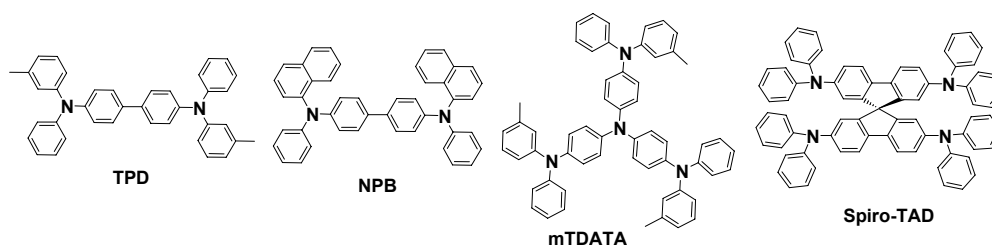


**Figure 1-3.** A configuration of Anode/HTL/ETL/Cathode device and energy level diagram.

## 1-1-5 Materials in OLEDs

### 1-1-5-1 Hole-transporting materials

Most Hole-transport materials are based on aromatic amines and known for their high hole mobility ( $\sim 10^{-3}$ - $10^{-4}$  cm/Vs) as compared to other organic molecules. Generally, aromatic amines have low oxidation potential and a small electron affinity associated with a large energy gap. 1,4-Bis(1-naphthylphenylamino)biphenyl (NPB) *N,N'*-di-*m*-tolyl-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (TPD)<sup>[9]</sup> are two most commonly used HTL (Figure 1-4). These two materials are composed by tri-arylamines with a bi-phenyl center core which greatly improved both EL efficiency and operational stability of OLED.<sup>[10]</sup> One of the reasons for its popularity is because sublimed TPD or NPB can be easily fabricated into homogeneous thin film, although their  $T_g$ s (glass transition temperatures) at 65 °C and 98 °C are trifle low which may affect the thin film morphological stability because of the joule heat released by the operating OLED. Therefore, studies on the design and synthesis of new HTLs have been continually focused on finding materials with high thermal and thin film morphological stabilities and on finding ways to control and optimize carrier injection and transport. Starburst type (e.g. mTDATA)<sup>[11]</sup> and spiro-linked (e.g. Spiro-TAD)<sup>[12]</sup> amorphous molecule not only increase the thermal stability but also form homogenous thin film easily (Figure 1-4).

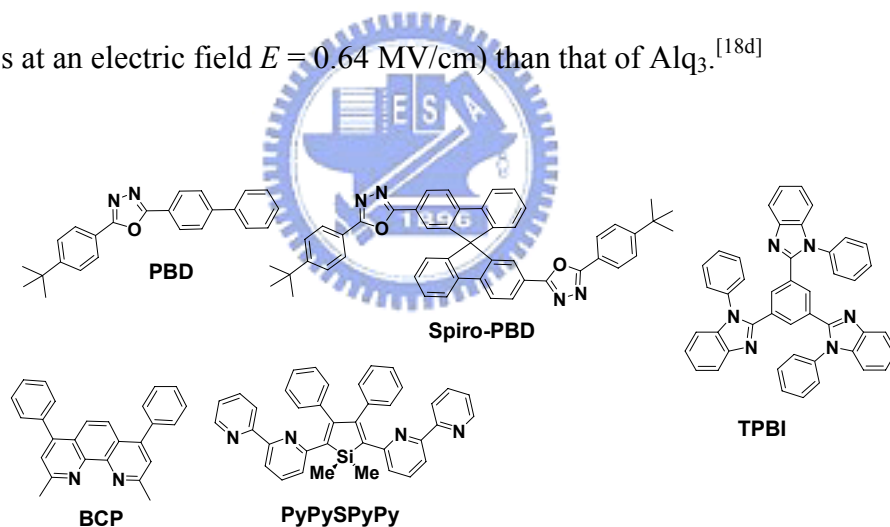


**Figure 1-4.** The structures of TPD, NPB, mTDATA and Spiro-TAD.

### 1-1-5-2 Electron-transporting and hole-block materials

To date, the most widely used electron-transport and host emitting material in OLEDs is

still Alq<sub>3</sub>, although the electron mobility of Alq<sub>3</sub> is relatively low ( $\sim 10^{-4}$ - $10^{-6}$  cm<sup>2</sup>/Vs).<sup>[13]</sup> This is because Alq<sub>3</sub> is thermally and morphologically stable to be evaporated into thin films, easily synthesized, and purified. One of the most widely used electron-transport and hole blocking materials is 2-biphenyl-4-yl-5-(4-*t*-butylphenyl)-1,3,4-oxadiazole (PBD).<sup>[14]</sup> It has been branched, spiro-linked to be Spiro-PBD (Figure 1-5)<sup>[12]</sup> to prevent from crystallization in thin films. The other hole-blocking layer also used in front of Alq<sub>3</sub> is 2,9-dimethyl-4,7-diphenyl-[1,10]phenanthroline (BCP).<sup>[15]</sup> Tao et al.<sup>[16]</sup> used 2,2',2''-(benzene-1,3,5-triyl)-tris(1-phenyl-1*H*-benzimidazole) (TPBI)<sup>[17]</sup> as an excellent efficient electron-transport and hole blocker material for OLEDs. Another class of electron-transport materials for OLEDs is 2,5-diarylsiloles.<sup>[18]</sup> It was reported by Kafafi et al. that the bipyridylsilole derivative, PyPySPyPy, showed higher electron-transporting abilities ( $2.0 \times 10^{-4}$  cm<sup>2</sup>/V s at an electric field  $E = 0.64$  MV/cm) than that of Alq<sub>3</sub>.<sup>[18d]</sup>

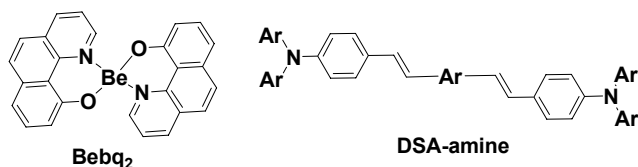


**Figure 1-5.** The structures of PBD, Spiro-PBD, TPBI, BCP and PyPySPyPy.

### 1-1-5-3 Light-emitting materials

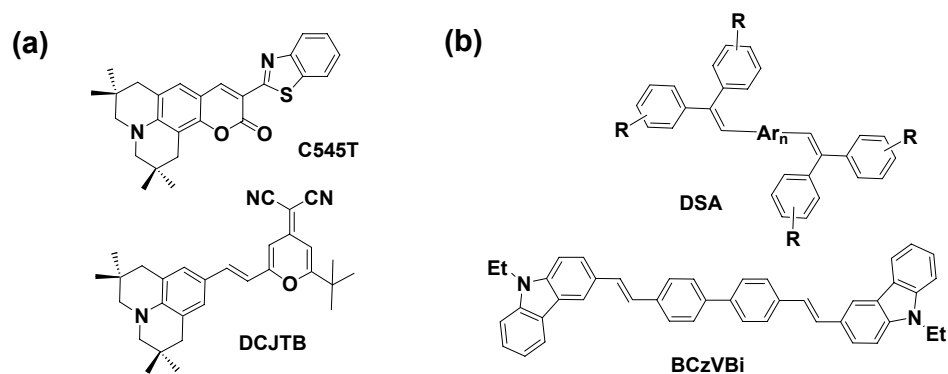
When HTL or ETL possesses a bipolar carrier-transporting characteristic and highly efficient fluorescence, these molecules can be a candidate for the light-emitting layer. So far, a variety of fluorescent molecules with high fluorescent efficiency in solid states have been reported to be useful as a light-emitting layer. The first case is electron transporting light-emitting. Alq<sub>3</sub><sup>[19]</sup> and Bebq<sub>2</sub> (Figure 1-6)<sup>[20]</sup> are two typical green metal chelates

light-emitters. The second category is hole transporting light-emitter, DSA-amine (**Figure 1-6**).<sup>[21]</sup> There are various kinds of styrylamine derivative having a strong fluorescence in solid states. The unique combination of a triarylamine unit and a styrylbenzene unit provide strong blueish emission (**Figure 1-6**).



**Figure 1-6.** The structures of Bebq<sub>2</sub> and DSA-amine.

Dopant materials are other keys for obtaining high EL quantum efficiency as well as durable devices performance. Various organic fluorophores show nearly 100% of fluorescence quantum efficiency, such as laser dyes in a dilute solution. although in solid state, they are not fluorescent because of the concentration quenching. Green fluorescent dopant is the first successfully demonstrated in a commercial product and it is also by far the most efficient one. One of the best green dopants is C545T<sup>[22]</sup> which belongs to the highly fluorescent class of coumarin laser dyes (**Figure 1-7(a)**). Among the RGB dopants used in OLEDs, red emission, due to its low efficiency, remains to be the weakest link in realizing the full potential of OLED display. Among the red dopants which are often not bright or efficient, DCJTB<sup>[23]</sup> still shows the best EL efficiency (**Figure 1-7(a)**). The blue dopants of OLEDs often necessitate the judicious selection or design of an appropriate blue host material which has a wide enough bandgap energy and a set of matching LUMO/HOMO level to effect the sensitization.<sup>[24]</sup> In commercial circles, one of the best blue emitters used in OLED is believed to have been patented by Idemitsu Kosan Co. based on the basic structure of distyrylarylene (DSA) host doped with a hole transporting amine-substituted DSA dopant, such as BCzBi (**Figure 1-7(b)**).<sup>[21]</sup>



**Figure 1-7.** The structures of C545T, DCJTb, DSA, and BCzVBi.

## 1-2 Motivation

For dopant or nondopant OLEDs, controlling the reproducibility of device performance and the lifetime (stability) of the device become major issues in organic optoelectronics devices, challenging material scientists and device engineers. Taking fluorene and spirobifluorene for illustration, the perpendicular arrangement of the two molecular halves leads to a high steric demand of the resulting rigid structure, efficiently suppressing molecular interactions between the  $\pi$ -systems. Furthermore, this result in a higher solubility of the spiro compounds compared with the corresponding non-spiro-linked parent compounds. The sterically demanding structure of fluorescent emitters, based on the spiro concept, also suppresses excimer formation, frequently encountered in solid-state fluorescent dyes. In addition, increase of the molecular weight in combination with the cross-shaped molecular structure along with the rigidity of spiro compounds causes entanglement in the amorphous state and hinders recrystallization. The spirobifluorene core provides us a good chance to reduce the fluorescence quenching of the light-emitting materials in solid state. In this thesis, we will develop a series of fluorene or spirobifluorene based red, green, and blue emitters possessing high morphological stability and fluorescence quantum yields for OLEDs.



### 1-3 References

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