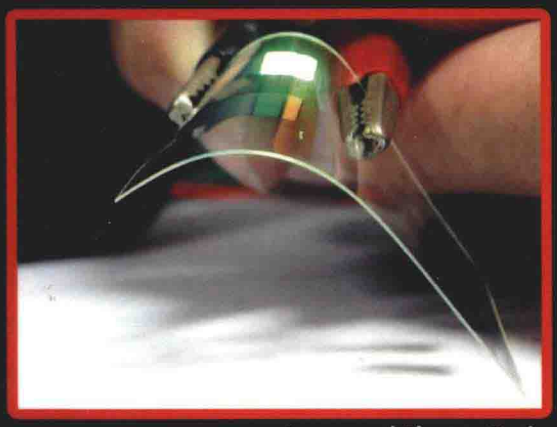
Douglas Rivera
Editor

Organic Light-Emitting Diodes (OLED)

Materials, Technology and Advantages



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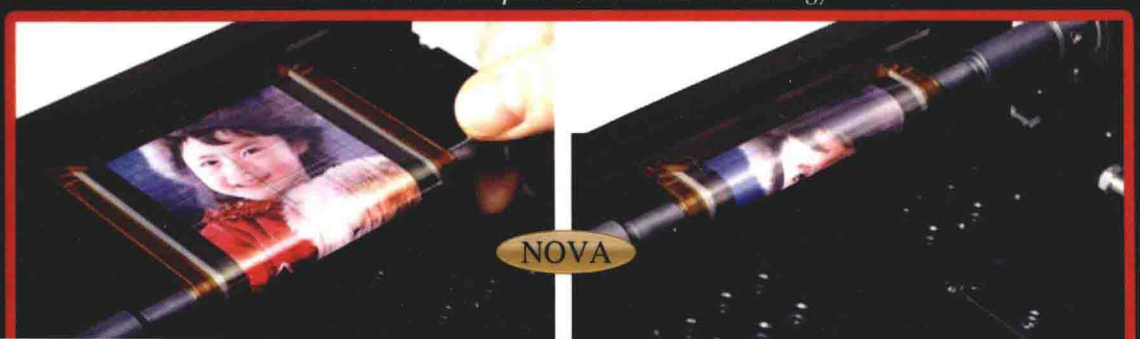

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ORGANIC LIGHT-EMITTING DIODES (OLED)

MATERIALS, TECHNOLOGY AND ADVANTAGES

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PREFACE

Organic light-emitting diodes (OLEDs) are considered as the most promising technology for next generation display and solid-state lighting for their advantages such as surface emitting, ease for large area manufacturing, viability for flexible and transparent applications, low energy consumption and potential to be low-cost. Chapter one of this book discusses tandem OLEDs, which are technologically interesting because not only can the luminance and current efficiency be improved linearly with the number of electroluminescent (EL) units in the tandem OLED, but also leakage current and breakdown of the electric field can be avoided due to the higher luminance at a low current density and the thicker organic films, resulting in a long lifetime. Chapter two mainly deals with the low cost synthesis and characterization of amino, amino-chloro, dichloro and trichloro substituted derivatives of diphenyl quinoline (DPQ). Chapter three aims at reporting the last strategies that have been developed to address the issue of roll-off.

Chapter 1 – Tandem OLEDs are technologically interesting because not only can the luminance and current efficiency be improved linearly with the number of electroluminescent (EL) units in the tandem OLED, but also leakage current and breakdown of the electric field can be avoided due to the higher luminance at a low current density and the thicker organic films, resulting in a long lifetime. Importantly, the state-of-the-art tandem OLEDs are very easy to vertically stack either individual red, green, and blue emission units or multiple white emission units in series via charge generation layers (CGLs) to achieve white emission. In tandem OLEDs, the CGL plays a critical role in the realization of high-performance tandem OLEDs since it functions as both an internal anode and a cathode to generate intrinsic charge carriers and to facilitate opposite electrons and holes being injected into the adjacent sub-OLED units. Although amounts of CGLs have been developed to use tandem OLEDs, the problems still remain including complicated processing and limited material combination. More importantly, since the driving voltage consumed by conventional tandem devices scales linearly with the number of electroluminescent units, the resulting power consumption would be the same for both the single-unit and tandem OLEDs to obtain the same luminescence, this means that the power efficiency cannot be increased for such tandem devices when using general CGLs. Therefore, developing new CGL structures have become important research topic in this field. In this chapter, the authors will review the progress of tandem OLEDs based on different CGLs from structure design to their working principles. The more discussion will be focused on the organic semiconductor heterojunctions as CGLs in tandem OLEDs. As the authors see, besides the luminance and current efficiency are double

enhancement, the power efficiency of resulting tandem OLEDs based on organic heterojunctions as CGLs is also greatly improved. Here, the authors will give detailed discussions on the structure design of organic heterojunctions as CGLs and the mechanism of their charge generation.

Chapter 2 – Since the preceding decade, OLEDs have become globally recognized exceptional area light source, which has enormous potential for the recent display applications and can overlay a novel path to create white light. In this regard, solid state lighting (SSL) - the new-fangled green technology has the prospective to go beyond the energy efficiencies of incandescent and fluorescent lighting and make the lighting eco - friendly and energy efficient. Such lighting can be achieved from light emitting devices based on either sublimely organics or polymeric materials and hence considerable attention has been grabbed in the scientific as well as in technological fields. Among the three primary RGB colours, the synthetic protocols and fabrication methods of green and red phosphors meet the necessary requirements. Conversely, the design and fabrication of blue phosphors and devices is still an ongoing challenge and hence research speaks volumes about the key challenges in attaining energy efficient blue light emitting organic emissive materials.

This chapter mainly deals with the low cost synthesis and characterization of amino, amino-chloro, dichloro and trichloro substituted derivatives of diphenyl quinoline (DPQ) by Friedlander condensation. The preparation of blended thin films with the synthesized complexes and binding polymers such as poly (methyl methacrylate) (PMMA) and polystyrene (PS) at different weight % are also illustrated. One of the main reasons for their synthesis and investigation of the present new conjugated polymeric compounds is to explore the molecular engineering approach as a means of the structural basis for the optimization of the desired solid-state properties. A single technique can not provide complete analysis of a solid and hence variety of instrumentation techniques were used for characterization of the synthesized materials. They include Fourier Transform Infrared Spectrometer (FTIR) and the X-ray diffraction (XRD) method, which are used to probe the structural properties. Spectrophotometer and spectroflurometer are used to study the optical properties by means of UV-Vis absorption and photoluminescence (PL) spectra. Thermal properties of the materials are analyzed by Thermo gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA). The results reveal that the starting materials are affordable for the chemical synthesis of DPQ derivatives; they are thermally stable and offer high intensity light emission in blue region of electromagnetic spectrum. Hence, these materials can be considered as an ultimate substitute for the existing blue organic light-emitting materials, generally employed for OLEDs, display devices and many more applications in this photonic age.

Chapter 3 – Since the early work of Tang and Van Slyke, Organic Light-Emitting Devices (OLEDs) attract broad attention of researchers due to their potential uses in flat panel displays and solid-state lighting. Some OLEDs proponents even believe that white OLEDs (WOLEDs) will soon replace the existing fluorescent and filament lamps for general lighting application. At present, OLEDs still suffer from an insufficient lifetime and the transfer of this technology to the mass market is another story. Doping the emissive layer with fluorescent or phosphorescent dyes is widely practiced for devices fabrication. To reach high efficiencies, a key requirement is that all electrically generated excitons must be harvested for light emission. However, even if emitters and especially metal complexes are usually doped into suitable host materials, quantum efficiency of phosphorescent OLEDs still tends to decrease at high current density because of competitive factors such as concentration

quenching and triplet-triplet annihilation. The efficiency roll-off i.e., the reduction of the quantum efficiency with increasing the current density is nearly general and constitutes the most significant problem facing OLEDs. This chapter aims at reporting the last strategies that have been developed to address this issue. Especially, a systematic understanding of the structure–property–performance relationships is proposed.

CONTENTS

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Chapter 1

TANDEM ORGANIC LIGHT EMITTING DIODES

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ABSTRACT

Tandem OLEDs are technologically interesting because not only can the luminance and current efficiency be improved linearly with the number of electroluminescent (EL) units in the tandem OLED, but also leakage current and breakdown of the electric field can be avoided due to the higher luminance at a low current density and the thicker organic films, resulting in a long lifetime. Importantly, the state-of-the-art tandem OLEDs are very easy to vertically stack either individual red, green, and blue emission units or multiple white emission units in series via charge generation layers (CGLs) to achieve white emission. In tandem OLEDs, the CGL plays a critical role in the realization of high-performance tandem OLEDs since it functions as both an internal anode and a cathode to generate intrinsic charge carriers and to facilitate opposite electrons and holes being injected into the adjacent sub-OLED units. Although amounts of CGLs have been developed to use tandem OLEDs, the problems still remain including complicated processing and limited material combination. More importantly, since the driving voltage consumed by conventional tandem devices scales linearly with the number of electroluminescent units, the resulting power consumption would be the same for both the single-unit and tandem OLEDs to obtain the same luminescence, this means that the power efficiency cannot be increased for such tandem devices when using general CGLs. Therefore, developing new CGL structures have become important research topic in this field. In this chapter, we will review the progress of tandem OLEDs based on different CGLs from structure design to their working principles. The more discussion will be focused on the organic semiconductor heterojunctions as CGLs in tandem OLEDs. As we see, besides the luminance and current efficiency are double enhancement, the power efficiency of resulting tandem OLEDs based on organic heterojunctions as CGLs is also

greatly improved. Here, we will give detailed discussions on the structure design of organic heterojunctions as CGLs and the mechanism of their charge generation.

1. INTRODUCTION

Organic light-emitting diodes (OLEDs) are considered as the most promising technology for next generation display and solid-state lighting for their advantages such as surface emitting, ease for large area manufacturing, viability for flexible and transparent applications, low energy consumption and potential to be low-cost [1-5]. Since the breakthrough by Kodak in 1987, considerable efforts have been made to improve both their efficiency and lifetime in order to meet the requirements for mass production [6].

OLEDs are actually current driving device, with increasing current density through, the luminance would rise while operational lifetime would reduce [7-9]. Since tandem OLEDs (TOLEDs) can obtain the same luminance under several folds of lower current density (depend on the number of EL units), its lifetime can be significantly lengthened.

Furthermore, the tandem structure provides the feasibility that EL units of different colors can be vertically stacked together for color tuning and white emission [10-12]. Duing to the unique advantages over traditonal single unit OLEDs, TOLEDs have been attracting extensive research interests ever since their first appearance in 2003 [13].

A typical TOLED is fabricated by vertically connecting several individual electroluminescent (EL) units together in series via interconnectors called charge generation layers (CGLs), with the entire device driven by a single power source (Figure 1) [14-17]. When certain voltage is applied on the electrodes, each EL lights up individually under the same current that flows through the whole device. From the viewpoint of the simplest terms, the current efficiency and the external quantum efficiency of the tandem devices would be the sum of each EL unit; while the power efficiency might be inferior to the single EL unit ones, considering the extra voltage drop across the interconnector and the interfaces it brings in.

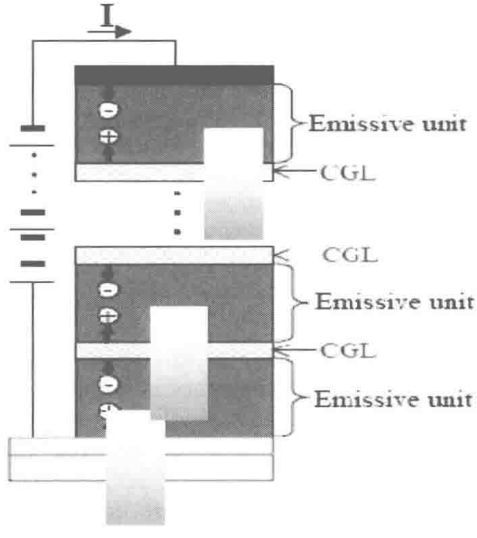


Figure 1. Structure and working processes of tandem OLEDs.

However, this shortcoming can be overcome as we will discuss in the article latter.

Understandably, rational interconnector selection and design are crucial to the performance of TOLEDs. A good CGL must meet several requirements: efficient hole-electron generation, minimal energy barrier for charge injection, high conductivity, transparent in visible spectral range, high operational stability and easy for deposition.

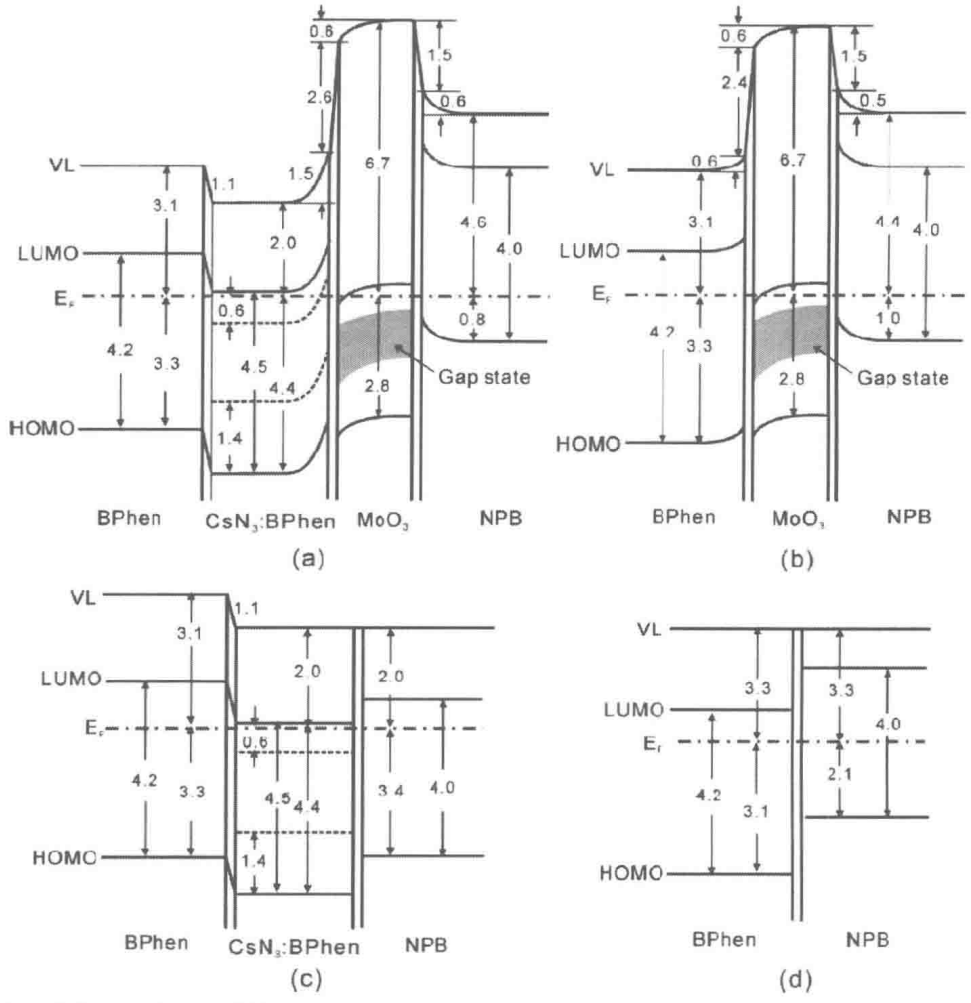
In fact, the researchers are working hard towards this goal, and most published papers on TOLEDs are focusing on interconnector design and its influence on device performance. Various types of interconnectors have been put forward, of which the most widely used structures include: metal-oxide, n-doped/p-doped organic bilayer and organic heterojunction (OHJ) [15-17].

2. TANDEM OLEDS BASED ON TRANSITION METAL-OXIDE CGLS

The first TOLED reported by Kido et al. used ITO or V_2O_5 as interconnector between two EL units. Ever since, various interconnectors employing transition metal-oxides (TMOs) have been reported, of which MoO_3 and WO_3 are frequently used [15, 18-29]. The typical TMO type interconnector structure is to insert a thin layer of TMO between the hole-transporting layer (HTL) of one sub-EL unit and the electron-transporting layer (ETL) of another sub-EL unit.

For a long time, TMOs like MoO_3 has been considered as a p-type material which leads the misinterpretation of charges to generate at the interface of TMO and ETL [30]. In 2009, Kahn et al. found that TMOs actually have very low-lying LUMOs, 6.7 eV for MoO_3, for example [31]. Now it is generally considered that the charges are generated at the interface of TMO and adjacent hole transporting material (HTM) [19, 20]. For a typical TMO/HTM system, The TMO serves as a strong electron acceptor, when the electrons are drawn from the HTM HOMO to the LUMO of TMO, the holes would be left at the HTM HOMO side, thus electrons and holes are generated in pairs. Afterwards, the generated electrons and holes would separate and transport in opposite directions under certain bias, and are injected to adjacent ETL and HTL, respectively. This process is confirmed by several groups by the energy level alignment obtained from the ultraviolet photoemission spectroscopy (UPS) measurements [19, 20, 24, 25]. Among them, the results reported by Tang et al. are shown in Figure 2. The HTL and ETL interfaces without MoO_3 shows flat vacuum level alignment (Figure 2c and 2d), and no charge generation process is observed from additional C-V test [25]. The large energy level offset between NPB's HOMO and CsN_3:BPhen's (or BPhen's) LUMO indicates that the charge generation process is hard to occur at that interface unless higher driving voltage is applied. In contrast, the insertion of MoO_3 between HTL and ETL can induce large vacuum level bending, which is crucial for the electron-hole generation and injection (Figure 2a and 2b). Apart from the charge generation mechanism previously mentioned, the authors also suggest that the electron transfer in MoO_3 may happen spontaneously via thermal diffusion from various defect states to the conduction band; then under bias, the left holes in these gap states (Figure 2a and 2b) will tunnel into the HOMO of NPB, and the electrons in the conduction tunnel into the LUMO of BPhen.

Since TMOs have rather deep LUMOs, which is lower than the HOMOs of most common HTMs, the charge generation and the hole injection are relatively easy.



Reproduced from reference [25].

Figure 2. Schematic energy level diagrams: a) BPhen/CsN_3:BPhen/MoO_3/NPB, b) BPhen/MoO_3/NPB, c) BPhen/CsN_3:BPhen/NPB, and d) BPhen/NPB interfaces on ITO substrate, respectively. All the values shown are in the unit of eV.

However, the electron transporting materials (ETMs) in OLEDs usually have their LUMOs around 3.0 eV, therefore the electron injection from LUMO of TMO into the adjacent ETL is hard unless the vacuum level bending is involved (like in Figure 2). So the design of proper TMO/ETL interface is critical to the performance of TMOs based tandem devices. In Table 1, some of the reported TMO/ETL interfaces and their device performances are given. The vacuum level bending at the interface of intrinsic ETM and TMO is not very efficient, for example, the vacuum level is 3.1 eV above the Fermi level at the intrinsic BPhen side (Figure 2b), but only 2.0 eV above Fermi level if a n-doped ETL is added into BPhen (Figure 2a). Actually, the n-doped ETL is a commonly used solution to increase band bending at ETL/TMO interface. As seen in Table 1, most of the reported devices' ETL is n-doped, such as Mg, Li, Cs and their compounds are mostly used dopants. In comparison ([22] in Table 1), if the ETL is intrinsic, the device performance would be obviously inferior to the n-doped one.

Table 1. Comparison of the reported TMO based tandem devices

TMO/ETL interface	emitter	Tandem VS Single (max value given in References for two unit device)		References
		PE(lm/W)	CE(Cd/A)	
MoO_3/$CsCO_3$:BCP	DPAVBi	6.15/5.05	17.1/9.3	[18]
WO_3/Li:Alq	C545T	5.67/4.71	23.1/9.9	[15]
MoO_3/CsN_3:BPhen	Ir $(ppy)_3$	NA/57	84/41	[21]
MoO_3/$CsCO_3$:BPhen	C545T	4.19/3.84	22.16/10.7	[24]
MoO_3/Mg:Bphen	Ir $(ppy)_3$	NA/NA	67.9/33.2	[29]
MoO_3/LiF:BPhen MoO_3/Al/LiF:BPhen	Alq	1.2/2.0 2.5/2.0	7.0/3.5 8.8/3.5	[23]
MoO_3/Al/Liq/B3PyPB MoO_3/Al/Liq/Liq:B3PyPB	FIrpic	33.6/56.5 40.8/56.5	78.2/51.6 90.0/51.6	[22]

Reproduced from reference [22].

Another popular method to increase band bending at ETL/TMO interface is adding a thin layer of metal (about 1 nm) Al or Ag in between. From [23] in Table 1, we can see that the addition of a thin layer Al can improve the device performance significantly, especially in power efficiency, because the voltage drop at the electron injection interface is reduced. The mechanism of enhancing the charge generation by inserted metal is thought to be that the metal cluster can induce more gap state to assist charge tunneling [32, 33].

As we know, TMOs always have high evaporation temperature, which is one main drawback of TMOs based CGLs [15]. Moreover, there are also some concerns about the operating stability of TMO CGLs. In fact, the TMO interconnectors' stability is in close relation to the n-dopant in adjacent ETL, as reported by Tang et al. [26].

The authors prepared several tandem devices with MoO_3 as CGL, and only vary the n-dopants in ETL, the results exhibit rather significant difference in the EL spectra, as shown in Figure 3. The tandem devices use a green emitter in one EL unit and a red emitter in another EL unit. Tested for a period of time, the device with Mg:Alq/MoO_3 interface shows a synchronous decrease of both spectral intensity, but the devices with $CsCO_3$:Alq/MoO_3 and CsN_3:Alq/MoO_3 interfaces show a fast decrease of green spectral, which means that some degradations are taking place in the green EL unit. The author then exchanged the place of green and red EL units, finding that the red EL unit is degrading faster this time, the influence of electrodes are also excluded with other experiments.

All the phenomena points out that the degradation may happen at the interface of ETL/ MoO_3 interface. The degradation is attributed to the electric field induced migration of cesium ions towards ETL/MoO_3 interface, which will further lead to the reaction of cesium cations with MoO_3 to form complexes. Considering Li and Cs are the most frequently used n-dopant in OLEDs, the degradation problem of TMOs based CGLs might be common in tandem OLEDs based on metal-oxide CGLs.

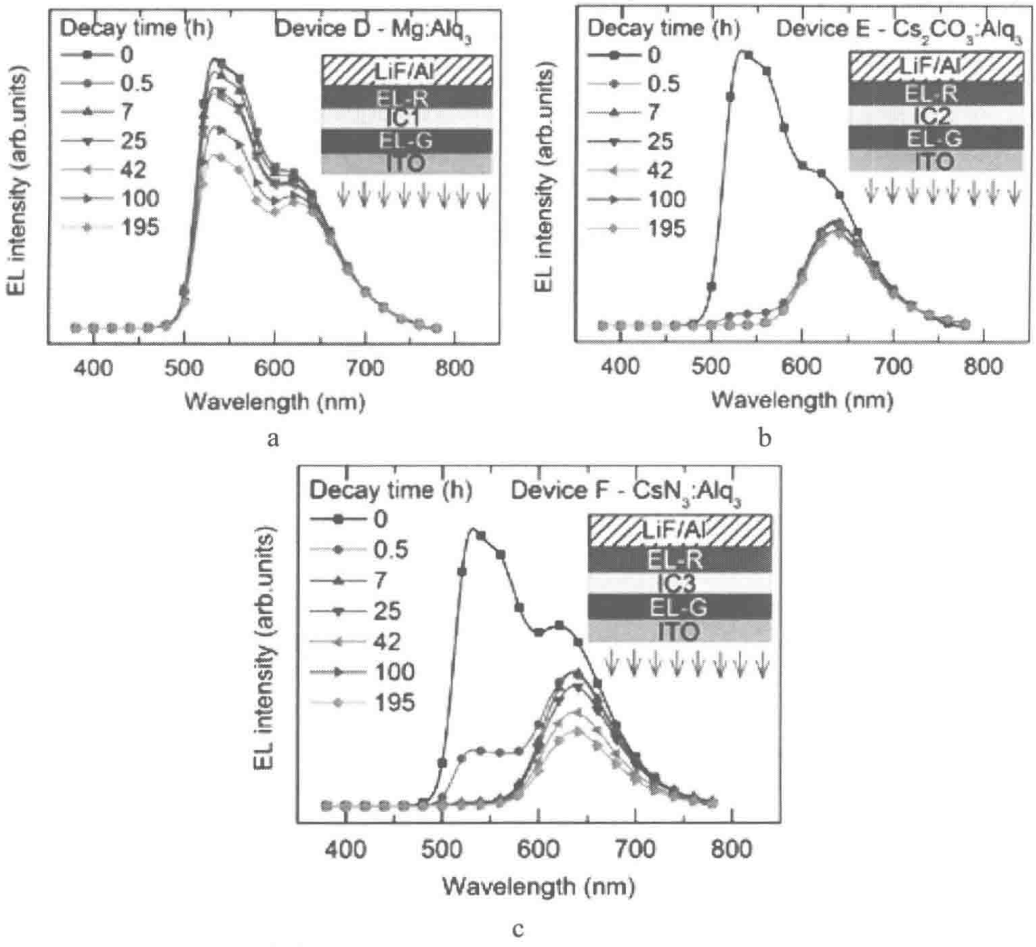


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Figure 3. Time dependence of the emission characteristics of TOLEDs using various CGLs. EL spectra of devices (a) D, (b) E and (c) F versus operational time at a current density of 5 mA/cm^2. The insets show the device structures.

3. Tandem OLEDs Based on N-Doped/P-Doped Organic CGLs

The first CGL interconnector employing a n-doped organic layer and a p-doped organic layer forming bilayer n/p structure was reported in 2004 by Liao et al. [34]. They used Li:Alq/ $FeCl_3$:NPB as CGL to achieve a TOLED with current efficiency of 81.7 cd/A for two-unit device and 136.3 cd/A for three-unit device using $Ir(ppy)_3$ as emitter, which are about two and three times higher than single unit one, proving the validity of the n/p CGL. This type CGL is considered to offer several advantages over the TMOs, including excellent optical and electrical properties, as well as the ease of fabrication by thermal evaporation [34, 35]. A lot of other works using n/p type CGL interconnectors have been published in the last decades, among them, a Lewis acid or low LUMO materials such as F_4-TCNQ are always used as acceptor in the p-doped layer and alkali metals are used as donor in the n-doped layer [10, 16, 24, 34-40].