We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

4,100 Open access books available
116,000 International authors and editors
120M Downloads

154 Countries delivered to
TOP 1% Our authors are among the most cited scientists
12.2% Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
Organic Light Emitting Diode
for White Light Emission

M.N. Kamalasanan, Ritu Srivastava, Gayatri Chauhan, Arunandan Kumar, Priyanka Tayagi and Amit Kumar

Center for Organic Electronics, Polymeric and Soft Materials Section, National Physical Laboratory (Council of Scientific and Industrial Research), Dr. K.S. Krishnan Road, New Delhi 110012, India

1. Introduction

During the last few years, research based on energy saving technologies is being given high priority all over the world. General lighting is one area in which large quantity of electrical energy is being spent and substantial energy saving is possible by using energy saving technologies. Conventional light sources like incandescent filament lamps in which a major part of the energy is wasted as heat and is a less energy efficient technology is being phased out. Other technologies like gas filled electrical discharge lamps are more efficient but are polluting. Therefore there is a need for energy efficient and clean light source and solid state lighting is one of the ways to address the problem.

Organic light emitting diodes (OLED) is a new technology which has the potential to replace the existing lighting technologies. The attraction to organic semiconductors for lighting and display application has started during 1950-1960 because of the high fluorescence quantum efficiency exhibited by some organic molecules and their ability to generate a wide variety of colors. Study of electroluminescence (EL) in organic semiconductors have started in 1950s by Bernanose et.al (1953) using dispersed polymer films. This was followed by the study of electroluminescence in anthracene single crystals by Pope et al (1963) and W.Helfrich et.al. (1965) who has studied the fundamental aspects of light generation in OLEDs. Since the single crystal based anthracene OLEDs fabricated by Pope et al (1963) were very thick and worked at very high voltages, the devices were not commercialized. In 1987, Tang and VanSlyke (1987) of Eastman Kodak has demonstrated a highly efficient multi layer OLED device based on vacuum evaporated aluminum tris 8-hydroxy quonoline (Alq3) as the emitter material. The device had different layers for hole transporting, electron transporting and light emission. Transparent Indium Tin Oxide (ITO) and aluminum metal were the anode and cathode respectively. Quantum efficiency and luminescence efficiency of 1% and 1lm/W respectively were considered enough for commercial application. This work has stimulated a very intense activity in the field of Organic electroluminescence. Numerous improvements in device structure and addition of more layers having different functionalities were incorporated and are now on the verge of commercialization. Further, the developments in π-conjugated polymers by Heeger, MacDiarmid, and Shirakawa in
1977 for which they shared the 2000 Noble Prize in Chemistry as well as the report by Burroughes et al. (1990) of the first polymer (long chain molecules) light-emitting diode has also given a boost to the already expanding field of OLEDs. The new discovery of polymer light emitting diodes (PLEDs) have shown that even solution grown thin layers of a conjugated polymer can be used as an emitter material which has given new device concepts like ink jet printing and roll to roll processing of OLEDs. In 1998, Baldo et al. (1998) showed that the efficiency of OLEDs can be improved by the incorporation of phosphorescent dyes. In this way, the triplets generated in the electron-hole recombination process (~75%) which are otherwise not used in light generation can be harvested to get light emission. This new development has enhanced the internal quantum efficiency of organic LEDs to nearly 100%. Sun et al. (2006) introduced a different device concept that exploits a blue fluorescent in combination with green and red phosphor dopants, to yield high power efficiency and stable colour balance, while maintaining the potential for unity internal quantum efficiency. Two distinct modes of energy transfer within this device serve to channel nearly all of the triplet energy to the phosphorescent dopants i.e., retaining the singlet energy exclusively on the blue fluorescent dopant and eliminating the exchange energy loss to the blue fluorophore by direct excitation which allows for roughly 20 per cent increased power efficiency compared to a fully phosphorescent device. The device challenges incandescent sources by exhibiting total external quantum and power efficiencies that peak at 18.7 +/- 0.5 per cent and 37.6 +/- 0.6 lm/W, respectively, decreasing to 18.4 +/- 0.5 per cent and 23.8 +/- 0.5 lm/W at a high luminance of 500 cd/m².

Further, introduction of new technological concepts like electrical doping of transport layers has enhanced the OLED efficiency to more than 100 lm/W and enhanced life time of the devices to more than 100,000 hours which is better than the gas filled discharge lamps (Muran et al. 2005). However, efficiency and lifetime are still considered widely as the big obstacles on the road of OLED development. A further improvement in the OLED performance relies on the more detailed understanding of the EL physics and the new development in the OLED materials, structure and fabrication.

Even though OLEDs of different colours have been developed with enough efficiency for commercialization, white light emitting organic LEDs have a special significance. It can be used for general lighting, back light for LED displays and for display applications. Since Organic materials are band emitters, OLEDs using these materials are mono chromatic and have low half width. Single broad band emitters developed so far has low efficiencies. To get white light emission from organic materials special efforts have to be made. Many methods like optical doping using fluorescent and phosphorescent materials as well as down conversion using inorganic phosphors have been used to get white light emission. Compared to other sources, OLEDs are thin, flat, lightweight, flexible and emits cold light. WOLED having high energy efficiency of 62 lm/W have been demonstrated on R&D level by OSRAM Opto Semiconductor GmbH (Nov. 2009) and >100 lm/W reachable in future. They can produce high quality white light (CRI ~ 80), which are diffuse and non glaring large area light source. Further, they can be instantly on/off and are driven at low voltages. They have various colors and different color temperatures functionality. Numerous white OLEDs have been fabricated (Kido et al. 1994, 1996, Dodabalapur et al. 1994, Yang et al. 1997). In the fabrication of full colour display all three primary colours have equal importance but white light emission has drawn particular attention because any desired colour range can be achieved by filtering of white light (Strukeji et al. 1996, Zhang et
al 2001). To obtain high quality (high CRI) white light, all the three primary colors red, green, and blue have to be produced simultaneously. Since it is difficult to obtain all primary emissions from a single molecule, excitation of more than one organic species is often necessary, thus introducing color stability problems. Due to the different degradation rate of the employed organic compounds, the emission color of the device can, in fact, change with time.

The first white OLED was produced by Kido and his colleagues in 1994. This device contained red, green and blue light emitting compounds that together produce white light. But there were some problems with these devices such as their efficiency was less than 1 lm/W, required large driving voltage and burned out quickly. But now the efficiency of these devices has increased very fast. White emission from OLEDs can now be achieved in both small molecule and polymer systems (Strukeji et al 1996, Granstom et al 1996, Jordan et al 1996). The yearly progress in the efficiencies of conventional LEDs, nitride LEDs and white OLEDs is shown in Fig.1.

![Progress in LED Efficiency](Image)

**Fig. 1.** The yearly progress in the efficiencies of conventional LEDs, nitride LEDs and white OLEDs

Fig. 2. 1”x1” prototype type of a multilayer phosphorescent efficient WOLED developed at National Physical Laboratory, New Delhi, India

![WOLED](Image)
National Physical Laboratory New Delhi has taken up a program for developing WOLEDs for general lighting applications. In this effort a 1”x1” prototype of a multilayer phosphorescent efficient WOLED has been demonstrated (Fig.2). In this review, we like to highlight on the development of white organic LEDs for general lighting.

2. Basic OLED Structure and Operation principles

White organic light emitting diodes are thin-film multilayer devices in which active charge transport and light emitting materials are sandwiched between two thin film electrodes, and at least one of the two electrodes must be transparent to light. Generally high work function (∼4.8 eV), low sheet resistant (20 Ω/□) and optically transparent indium tin oxide (ITO) is used as an anode, while the cathode is a low work function metal such as Ca, Mg, Al or their alloys Mg:Ag, Li:Al. An organic layer with good electron transport and hole blocking properties is typically used between the cathode and the emissive layer. The device structure of an OLED is given in Fig. 3. When an electric field is applied across the electrodes, electrons and holes are injected into states of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), respectively and transported through the organic layer. Inside the semiconductor electrons and holes recombine to form excited state of the molecule. Light emission from the organic material occurs when the molecule relaxes from the excited state to the ground state. Highly efficient OLEDs which are being developed at present, contains many layers with different functionality like hole injection layer(HIL), hole transport layer (HTL),electron blocking layer(EBL), emissive layer(EML), hole blocking layer(HBL), electron transport layer(ETL) and electron injection layer(EIL) etc apart from electrodes. A schematic diagram of multilayer structure is shown in Fig. 4.

Fig. 3. The device structure of an OLED
Organic Light Emitting Diode for White Light Emission 183
National Physical Laboratory New Delhi has taken up a program for developing WOLEDs for general lighting applications. In this effort a 1"x1" prototype of a multilayer phosphorescent efficient WOLED has been demonstrated (Fig. 2). In this review, we like to highlight on the development of white organic LEDs for general lighting.

2. Basic OLED Structure and Operation principles
White organic light emitting diodes are thin-film multilayer devices in which active charge transport and light emitting materials are sandwiched between two thin film electrodes, and at least one of the two electrodes must be transparent to light. Generally high work function (\(\sim 4.8 \text{ eV}\)), low sheet resistant (20 \(\Omega/\square\)) and optically transparent indium tin oxide (ITO) is used as an anode, while the cathode is a low work function metal such as Ca, Mg, Al or their alloys Mg:Ag, Li:Al. An organic layer with good electron transport and hole blocking properties is typically used between the cathode and the emissive layer. The device structure of an OLED is given in Fig. 3. When an electric field is applied across the electrodes, electrons and holes are injected into states of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), respectively and transported through the organic layer. Inside the semiconductor, electrons and holes recombine to form excited state of the molecule. Light emission from the organic material occurs when the molecule relaxes from the excited state to the ground state. Highly efficient OLEDs which are being developed at present, contains many layers with different functionality like hole injection layer (HIL), hole transport layer (HTL), electron blocking layer (EBL), emissive layer (EML), hole blocking layer (HBL), electron transport layer (ETL) and electron injection layer (EIL) etc apart from electrodes. A schematic diagram of multilayer structure is shown in Fig. 4.

![Fig. 4. A schematic diagram of multilayer structure of OLED](image)

3. Characterization of White OLEDs
3.1 Colour quality
In order for a light-emitting device to be acceptable as a general illumination source, it clearly must provide high-illumination-quality light source. White light has three characteristics (i) the Commission International d’Eclairage (CIE) coordinates (ii) the correlated colour temperature (CCT) and (iii) the colour rendering index (CRI)

3.1.1 Commission International d’Eclairage (C-I-E) coordinates
The color of a light source is typically characterized in terms of CIE colorimetry system. Any colour can be expressed by the chromaticity coordinates \(x\) and \(y\) on the CIE chromaticity diagram (Fig. 5). The boundaries of this horseshoe-shaped diagram are the plots of monochromatic light, called spectrum loci, and all the colours in the visible spectrum fall within or on the boundary of this diagram. The arc near the centre of the diagram is called the Planckian locus, which is the plot of the coordinates of black body radiation at the temperatures from 1000 K to 20 000 K, described as CCT. The colours of most of the traditional light sources fall in the region between 2850 and 6500 K of black body. For general illumination a light source should have high-energy efficiency and CIE-1931 chromaticity coordinates \((x, y)\) close to the equal energy white (EEW) \((0.33, 0.33)\).
3.1.2 Colour rendering index (CRI)

For a given light source, the CRI attempts to quantify how different a set of test colors appears when illuminated by the source compared to when the same test colors are illuminated by the standard illuminant with the same correlated color temperature. It is measured in 0-100 scales and the highest possible CRI value is 100, and this occurs when there is no difference in color rendering between the light source and the standard illuminant. An example of such a light source is the incandescent lamp. When a color rendering difference exists, the CRI is less than 100. Achieving illumination-quality white light generally requires a CRI value of 80 or greater.

3.1.3 Correlated colour temperature (CCT)

The color of a light source is typically characterized in terms of its color temperature. If the x,y coordinates of an illumination source do not exactly sit on the blackbody locus, the color of a light source is characterized in terms of its CCT. The CCT is the temperature of a blackbody radiator that has a color that most closely matches the emission from a non-blackbody radiator. For high quality white light illumination the CCT should be between 2500K and 6500 K. There is an accepted method (Wyselki et al 1982) to determine lines of constant correlated color temperature in x, y space. CIE, CCT and CRI for common white light sources are given in Table 1 for comparison purpose (Misra et al 2006).
3.1.2 Colour rendering index (CRI)
For a given light source, the CRI attempts to quantify how different a set of test colors appears when illuminated by the source compared to when the same test colors are illuminated by the standard illuminant with the same correlated color temperature. It is measured in 0-100 scales and the highest possible CRI value is 100, and this occurs when there is no difference in color rendering between the light source and the standard illuminant. An example of such a light source is the incandescent lamp. When a color rendering difference exists, the CRI is less than 100. Achieving illumination-quality white light generally requires a CRI value of 80 or greater.

3.1.3 Correlated colour temperature (CCT)
The color of a light source is typically characterized in terms of its color temperature. If the \(x, y\) coordinates of an illumination source do not exactly sit on the blackbody locus, the color of a light source is characterized in terms of its CCT. The CCT is the temperature of a blackbody radiator that has a color that most closely matches the emission from a non-blackbody radiator. For high quality white light illumination the CCT should be between 2500K and 6500 K. There is an accepted method (Wyszelki et al 1982) to determine lines of constant correlated color temperature in \(x, y\) space. CIE, CCT and CRI for common white light sources are given in Table 1 for comparison purpose (Misra et al 2006).

<table>
<thead>
<tr>
<th>Light source</th>
<th>Chromaticity coordinate</th>
<th>CCT (K)</th>
<th>CRI</th>
</tr>
</thead>
<tbody>
<tr>
<td>High pressure sodium lamp</td>
<td>0.519 0.417</td>
<td>2100</td>
<td>24</td>
</tr>
<tr>
<td>Xenon lamp</td>
<td>0.324 0.324</td>
<td>5920</td>
<td>94</td>
</tr>
<tr>
<td>Tungsten Halogen lamp</td>
<td>0.448 0.407</td>
<td>2856</td>
<td>100</td>
</tr>
<tr>
<td>Daylight</td>
<td>0.313 0.329</td>
<td>6500</td>
<td>90</td>
</tr>
<tr>
<td>Fluorescent cool white lamp</td>
<td>0.375 0.367</td>
<td>4080</td>
<td>89</td>
</tr>
<tr>
<td>Fluorescent warm white lamp</td>
<td>0.440 0.403</td>
<td>2940</td>
<td>72</td>
</tr>
<tr>
<td>Incandescent bulb</td>
<td>0.448 0.408</td>
<td>2854</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 1. Chromaticity coordinates (CIE), correlated colour temperature (CCT) and colour rendering indices (CRI) for common white light sources.

3.2 Device Efficiency
The efficiency of OLEDs is characterized by quantum efficiency, power efficiency and luminous efficiency. Over the past several years, the power (\(\eta_p\)) and external quantum (\(\eta_{ext}\)) efficiencies of white OLEDs have been steadily improving.

3.2.1 Quantum efficiency.
The quantum efficiency of a device can be differentiated into two categories i.e internal and external quantum efficiencies.

**Internal quantum efficiency (IQE)**- This is the total number of photons generated inside the device per electron– hole pair injected into the device. It is represented by \(\eta_{int}\).

For OLEDs the internal quantum efficiency in the case of fluorescent materials is given by (OIDA 2002)

\[
\eta_{int} = \gamma \eta_s \Phi_f, \tag{1}
\]

where \(\gamma\) is the fraction of injected charges that produce excitons and is called the charge balance factor, \(\eta_s\) is the fraction of singlet excitons called singlet exciton efficiency and \(\Phi_f\) is the fraction of energy released from material as light and called the quantum efficiency of fluorescence.

Generally based on spin statistics fluorescent organic materials exhibit 25% singlet and 75% triplet states in EL and 100% singlet states in PL (Baldo et al 1998, Friend et al 1999). In fluorescent materials triplet energy states have a low emission quantum yield and thus do not contribute to electroluminescence. This means the quantum efficiency for EL can only be about 25% of the PL efficiency. But some organometallic complexes (phosphors) have a strong triplet emission quantum yield and provide the possibility of a high efficiency EL device by using these materials. A research group from Princeton University demonstrated the efficiency limitation breakthrough in OLEDs by energy transfer from fluorescent host to a phosphorescent guest material (Baldo et al 1998). The phosphorescent dopants are doped in host materials with a wide energy gap. In electrophosphorescence the energy from both the singlet and triplet states of the fluorescent host is transferred to the triplet state of the phosphorescent guest molecule or the charges are directly trapped to the phosphor triplet. This harvesting of both singlet and triplet states has been resulted result in 100% internal
quantum efficiency (Adachi et al. 2001). But exciton-exciton quenching (Baldo et al. 2000), polaron-exciton quenching (Young et al. 2002) and exciton dissociation (Szymtkowski et al. 2002) may reduce the internal quantum efficiency to much lower values. One of the important developments of WOLEDs is the demonstration of phosphorescence sensitization of EL (Kanno et al. 2006). It has been observed that addition of a small quantity of a phosphorescent dopant in a guest host system enhances the fluorescence efficiency of a co-dopant. Cheng et al. (2003) reported that the internal efficiency of fluorescence can be enhanced to 100% by using a phosphorescent sensitizer to excite the fluorescent dye through resonant energy transfer between the triplet excitons in the phosphor and singlets in the fluorescent dye. Using the blue emission from a spatially separated hole transport layer NPB and Ir(ppy)$_3$ sensitized DCJTB in a CBP host the authors obtained the high efficiency white OLEDs. The colour tuning has been achieved by varying the concentration of the sensitizer as well as the thickness of the co-doped emitter layer.

**External quantum efficiency (EQE)** - This is defined as the total number of photons emitted from the device per electron-hole pair injected into the device. It is represented by $\eta_{ext}$. The external quantum efficiency is related to the internal quantum efficiency and is given by (OIDA 2002)

$$\eta_{ext} = R_e \eta_{int}$$

where $R_e$ is the extraction or outcoupling efficiency representing the number of photons emitted from the device per number of photons generated in the device.

### 3.2.2 Power Efficiency

The luminous efficacy or power efficiency is the lumen output per input electrical power of the device. It is measured in lumen per watt (lm/ W) or candela per ampere (cd/ A). It is represented by $\eta_p$. In order to compete with the fluorescent lighting market, the efficiency of OLED sources should be 120 lm/ W or more. To meet the above requirement the OLED sources must have an electrical to optical power conversion efficiency of 34%. For white light with a CRI of 90 the maximum value is 408 lm/W and for a CRI of 100 it is 240 lm/W (Kamtekar 2010).

The projection for WOLED is that by 2015, efficiency will exceed 100 lm/W with desirable life time and brightness and will start to replace indoor and outdoor light. Murano et al. demonstrated white pin-OLEDs based on phosphorescent and fluorescent emitters and stacked OLEDs. This intentional doping of the transport layer led to a very high power efficiency of well above 20 lm/W at 1000 cd/ m$^2$ (Murano et al. 2005). The CRI properties of emitted light are very high, between 85 and 95. Universal Display Corporation (UDC) announced the demonstration of a white OLED lighting panel with a high power efficiency of 30 lm/ W using the company’s phosphorescent OLED technology. This efficiency was achieved at a colour temperature of 4000 K, which is comparable to the colour temperature and power efficiency of a cool fluorescent lamp. The colour-rendering index was >80 across the measured colour temperatures because of the broad spectral output of the combined colours. D’Andrade et al. (2004) reported power efficiency of 42 lm/ W for a white OLED that exceeds that of incandescent lamps. Therefore WOLEDs have great potential for energy saving and the replacement of traditional incandescent light sources.
3.2.3 Improvement of Efficiency
One of the measure problems in OLEDs is its low efficiency. Various techniques are used to improve the efficiency of OLED devices.

3.2.3.1 Triplet Harvesting
Due to spin statistics the efficiencies of OLEDs are limited, as only the singlets are responsible for light emission in EL in undoped devices. The recent developments in harvesting of triplet states, using phosphorescent materials, led to an increase in the efficiency and selectivity of colours. Electrophosphorescence achieved by doping an organometallic phosphor into a host has been successfully used for generating the primary colours necessary for display applications (Baldo et al 1998, Holmes et al 2003, Adachi et al 2001). Due to extensive work, the power efficiency of white organic light emitting devices (WOLEDs) has continuously increased over the past decade and it has attained the level required for WOLEDs acceptance into the lighting market. Universal Display Corporation is a world leader in developing and commercializing innovative OLED technologies and materials for use in the electronic flat panel display and other markets. Universal Display is working with a network of world-class organizations including Princeton University, the University of Southern California, DuPont Displays, Samsung SDI Co., Seiko Epson Corporation, Sony Corporation, Tohoku Pioneer Corporation and Toyota Industries Corporation. NOVALED GmbH, Dresden Germany, is another emerging company in the field of organic displays. NOVALED works in close cooperation with Technical University Dresden and Fraunhofer Dresden Institute IPMS. According to a press release in 2005 from Dresden, Germany, NOVALED has developed a green emitting OLED with efficiency of 110 lm/W.

3.2.3.2 Optical doping
The doping of the emissive layer in an OLED has been used extensively as a way of improving efficiency and lifetime, in addition to being used to modify the emission color (Optical doping has been explained in guest host system). Tang et al. (1989) first introduced fluorescent dyes, 3-(2-benzothiazolyl)-7-diethylamino coumarin (coumarin 540 or coumarin 6 and DCMs, as dopants in Alq3 to improve the efficiency and color purity of devices. Since then, a wide range of fluorescent dopants have been used in OLEDs (Sano et al 1997, Hamada et al 1995). The ground state of most materials has a single spin state. Emission of a photon in fluorescent materials conserves spin, therefore only singlet excited states typically emit light. Decay from the triplet excited states is typically a nonradiative process for most organic materials and so these triplet excitons are lost from the perspective of light emission. The maximum possible internal quantum efficiency that can be obtained in an OLED using fluorescent material is limited by the ratio of these excited states or the so-called exciton singlet-to-triplet ratio, which is approximately 1:3 (Baldo et al 1999, 1999a). This limits fluorescent OLEDs to a maximum internal quantum efficiency of approximately 25%.

3.2.3.3 Electrical doping
In typical OLEDs, the applied voltage (V) is usually 5–8 V, when illuminated at 500–1000 cd/ m², i.e., greater than twice the voltage of the emitted photon Vg. The voltage drop across the emission layer itself is usually 2 to 3 V, depending upon the emission wavelength.
The remaining voltage is dropped predominantly across the ETL, across the HTL, and at the heterojunction interfaces. Charge transport in low-mobility organic films is space-charge limited (Marks et al 1993) and high electric fields are required to inject the necessary charge to generate the desired photon flux. Band misalignments at the heterojunction interfaces also result in voltage loss. However, the drive voltage can be significantly reduced by electrical doping of the transport layers (Blochwitz 2002). Electrical doping was demonstrated using green Ir(ppy)$_3$-doped PHOLEDs by Pfeiffer et al (2002). It was observed that the drive voltage necessary to produce 100 cd/ m$^2$ was 2.65 V, i.e., only slightly higher than $V_g$. This device used p-type (tetra fluoro tetra cyano quino dimethane (F$_4$TCNQ)) and n-type (Li) doping of the HTL and ETL, respectively. In this effort Murano et al from NOVALED demonstrated efficient white OLEDs based on an intentional doping of the charge carrier transport layers and the usage of different state of the art emission principles (Murano et al 2005). Large quantity of (~50%) low work function metal like Li is usually co-evaporated with conventional electron transport materials like Bphen to achieve n-type doping. In corporation of low work function metals induces stability problems in OLEDs. Recently Tyagi et al (2010) have demonstrated efficient n-type doping by doping Liq in electron transport material Alq$_3$. An increase in current density by two orders of magnitude has been achieved with 33 wt% of Liq doped in Alq$_3$. Organic light emitting diode with p-i-n structure was fabricated using F$_4$-TCNQ doped a-NPD as hole transport layer, Ir(ppy)$_3$ doped CBP as emitting layer and 33 wt% Liq doped Alq$_3$ as electron transport layer. Comparison of OLEDs fabricated using undoped Alq$_3$ and 33 wt% Liq doped Alq$_3$ as electron transport layer shows reduction in turn on voltage from 5 to 2.5V and enhancement of power efficiency from 5.8 to 10.6 lm/W at 5V.

### 3.2.3.4 Improving out coupling efficiency

It is well understood that the generated light from the active OLED medium propagates via various modes, that is, external modes (escape from the substrate surface), substrate-, and ITO/organic-waveguided modes due to total internal reflection (TIR) (Gu et al 1997, Madigan 2000, Moller and Forrest 2002). According to the ray optics theory, about 80% of the generated light is lost in waveguided modes due to glass substrate and ITO/organic material which means that the majority of generated light is either trapped inside the glass substrate and device, or emitted out from the edges of an OLED (Gu et al 1997, Madigan 2000, Moller and Forrest 2002). For the purpose of applications in general illumination and flat panel displays, light emitted from the substrate surface (external modes) is most useful which is only about 20% of the total emitted light from the OLED.

Detailed optical modelling (Kim et al 2000) predicted that the fraction of the light emitted in the forward direction is reduced by a factor of $(4/3)n^2$, where $n$ is the index of refraction of the emitter layer. Through a series of experiments using an integrating sphere, Cao et al (Cao et al 1999) demonstrated that the measured reduction factor is approximately 2-2.5, less than the theoretical value $2n^2 - 6$. Forrest and coworkers found that the total external efficiency is larger by a factor of 1.7-2.3 than observed in the forward viewing direction (D’Andrade et al 2004). The poor light extraction is the most important factor which limits the external quantum efficiency of devices and hence better outcoupling methods are to be developed to get higher efficiencies. To extract the trapped and waveguided light into external modes, various approaches based on light refraction and scattering to reduce TIR at
the interfaces have been reported, such as, the use of a shaped substrate (Gu et al 1997, Madigan et al 2000), use of micro-lenses on the backside of substrate surface (Moller et al 2002, Peng et al 2005, Lim et al 2006), formation of mono-layer of silica micro-spheres as scattering medium (Yamasaki et al 2000, Neyts and Nieto 2006), and use of high refractive index substrate (Lu et al 2000). In another approach, an extremely low refractive index silica-aerogel layer (Tsutsui et al 2001) was inserted between the ITO transparent electrode and glass substrate.

A 50% light extraction efficiency from OLEDs was recently reported by insertion of a two-dimensional photonic crystal structure (Do et al 2004, Kitamura et al 2005, Liu et al 2005, Lee et al 2005), and using nano-porous and nano-patterned films (Lee et al 2003, Kim et al 2005). More recently, use of diffusive layer lamination (Nakamura et al 2004), holographic technique (Liu et al 2005), and shaped substrate OLED luminair (Andrade et al 2006) has also been investigated for the improvement of out-coupling efficiency in conventional OLEDs. An index-matching layer has also been used for top emitting OLED (Hung et al 2001).

To extract the trapped light, Saxena et al (2008) used simple AR coating technique and demonstrated pronounced enhancement in light out-coupling of conventional OLED. Single-layer MgF$_2$ was coated on backside of glass substrate of conventional OLED with thickness of $\lambda/4$. About two-fold enhancement in luminance with anti-reflection coating of MgF$_2$ has been observed. Fig. 6 shows the schematic diagram of the phenomenon of anti-reflection (AR) coating using single-layer MgF$_2$ for the extraction of substrate-waveguided modes.

![Fig. 6 Schematic diagram of the phenomenon of anti-reflection (AR) coating using single-layer MgF$_2$ for the extraction of substrate-waveguided modes.](image)

3.3 Stability

One issue that limited the early adoption of OLEDs in commercial products was device stability both during storage and in operation. Suggested causes of degradation include indium migration from the ITO anode (Lee et al 1999), morphological instability of the organic materials (Higginson et al 1998), fixed charge accumulation within the device (Kondakov et al 2003), damage to the electrodes, and the formation of non emissive dark
spots (Burrows et al 1994, Aziz et al 1998, Cumpston et al 1996). Water and oxygen are known to cause problems in OLEDs. Therefore, a great deal of effort has been directed toward the encapsulation of devices. Encapsulation is typically carried out under a nitrogen atmosphere inside a glove box.

In addition to extrinsic environmental causes of degradation in OLEDs, some groups have explored the stability problem related to the individual device materials to transport charge and emit light. For example, Aziz et al 1999 have proposed that in simple Alq3 devices hole transport through the Alq3 layer is the dominant cause of device degradation due to the instability of the Alq3+ cationic species. A useful overview of the factors affecting device reliability is given by Forrest et al. (1997) and Popovic and Aziz (2002).

3.4 Encapsulation
In the OLED fabrication process encapsulation is the final step to ensure a long device lifetime. OLEDs (Tang and Vanslyke 1987, Adachi et al 2000, Burroughs et al 1990) built on glass substrates have been shown to have lifetimes of tens of thousands of hours (Shi and Tang 1997, Burrows et al 2000). There have been many proposed mechanisms for the decay in luminance, but most theories agree that one of the dominant degradation mechanisms in unencapsulated OLEDs, which have far shorter lifetimes than encapsulated devices, is the exposure of the organic–cathode interface to atmospheric oxygen and water. This leads to oxidation and delamination of the metal cathode (Liew et al 2000, Kolosov et al 2001) as well as potential chemical reactions within the organic layers. The device acts like an electrochemical cell producing H2 and O2 at the electrodes there by, degrading the device. As most of the OLED work, to date, has been focused on the development and manufacture of glass-based displays, the degradation problem is a meliorated by sealing the display in an inert atmosphere, e.g., in a nitrogen or argon glove box (< 1 ppm water and oxygen), using a glass or metal lid attached by a bead of UV cured epoxy resin (Burrows et al 1994). A desiccant such as CaO or BaO is often located in the package to react with any residual water incorporated in the package or diffusing through the epoxy seal. In addition to encapsulation techniques using a lid, thin-film encapsulation techniques are also possible. Wong et al have done effective thin film encapsulation of OLED by altering and repeating deposition of multilayers of CFx and Si3N4 films (Wong et al 2008).

4. Generation of White Light
As discussed earlier for generation of white light, all the three primary colors have to be produced simultaneously and for illumination purpose should have good colour rendering index (>75) and good position close to (0.33, 0.33) on the CIE-1931 diagram. Since it is difficult to obtain all primary emissions from a single molecule, excitation of more than one organic species are often necessary. Generally two methods are used to generate white light from OLEDs i.e (a) Colour mixing and (b) Wavelength conversion.

4.1 Colour mixing
In the colour mixing technique, no phosphors are used, and therefore the losses associated with the wavelength conversion do not occur and this approach has the potential for the highest efficiency. This method uses multiple emitters in a single device and mixing of
different lights from different emitters produces white light. White light can be obtained by mixing two complementary colours (blue and orange) or three primary colours (red, green and blue). The typical techniques used for the production of white light by colour mixing are (a) Multilayer structure consisting of red, green and blue emissive layers, (b) Single emissive layer structure (c) exciplex/excimer structure and (d) microcavity structure.

### 4.1 Multilayer device structure

Most widely used approach to achieve white light is a multilayer structure where simultaneous emission of light from two or more separate emitting layers with different emission colours results in white light. This technique is based on the consecutive deposition or co-evaporation of different emitting materials and control of the exciton recombination zone. This structure consists of many organic–organic interfaces leading to interface barriers, which may result in the inhibition of carrier injection and joule heating. Therefore to minimize the charge injection barriers and joule heating at the organic/organic interfaces the emissive materials are chosen in such a way that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of different adjacent emissive materials closely match with each other. The emission from the device depends on the thickness and composition of each layer, and is to be precisely controlled to achieve color balance. The exciton recombination zone is controlled by inserting blocking layers that block only one type of carrier between the hole transporting layers (HTL) and electron transporting layers (ETL), so that the recombination takes place in two or three different layers (Deshpande et al 1999, Li and Shinar 2003, Ko and Tao 2001, Tokito et al 2003, Yang et al 2002, Kim et al 2004, Zugang and Nazar’ e 2000, Lee et al 2002, Xie et al 2003, Cheng et al 2004, Zhang et al 2005, Guo et al 2005). This results in emission from different layers (Fig. 7). By controlling the recombination current within individual organic layers, emission from red, green and blue light emitting layers is balanced to obtain white light of the desired colour purity.

Deshpande et al (1999) achieved white light emission by the sequential energy transfer between different layers. The device was fabricated in the configuration ITO/α-NPD/α-NPD:DCM2(0.6–8 wt%)/BCP/Alq3/Mg:Ag (20:1)/Ag. Here 4,4’ bis (N-(1-naphthyl-N-phenyl-amino)) biphenyl (α-NPD) was used as a hole injection layer, α-NPD: DCM2 (2, 4- (dicyanomethylene)-2-methyl-6-(2- (2, 3, 6, 7-tetrahydro-1H, 5H benzol[l, j]quinolinizin-8-yl)vinyl)- 4H-pyran) layer was used as a hole transport layer (HTL) as well as an emitting layer, 2,9-dimethyl-4,7-diphenyl-1,10- phenanthonline (BCP) layer was deposited for the purpose of hole blocking, Alq3 was used as a green emitting electron transporting layer (ETL) and Mg:Ag alloy followed by a thick layer of Ag was deposited as the cathode.
A maximum luminance of 13500 cd/m$^2$, a maximum external quantum efficiency $>0.5\%$ and an average power efficiency of 0.3 lm/W were reported for the above configuration. Recently Wu et al. (2005) reported white light emission from a dual emitting layer OLED with and without blocking layers. The device with a blocking layer exhibited better performance with an external quantum efficiency of 3.86%. The emission colour of these devices strongly depends upon the thickness of the emissive layer and the applied voltage. The drawback of this technique is that it requires complex processing and a large amount of wasted organic materials resulting in relatively high fabrication cost. The CIE coordinates are often dependent upon the driving current due to shift of the exciton recombination zone. Brian et al. (2002) have demonstrated that multi- emissive layer fully electrophosphorescent WOLEDs can take advantage of the diffusion of triplets to produce bright white devices with high power and quantum efficiencies. The device color can be tuned by varying the thickness and the dopant concentrations in each layer, and by introducing exciton blocking layers between emissive layers.

Gong et al. (2005) have reported that high performance multilayer white light emitting PLEDs can be fabricated by using a blend of luminescent semiconducting polymers and organometallic complexes as the emission layer and water soluble (or ethanol soluble)PVK-SO$_3$Li as the hole injection/transport layer (HIL/HTL) and t-Bu-PBD-SO$_3$Na as the electron injection/electron transport layer (EIL/ETL). Each layer is spin-cost sequentially from solution. Illumination quality white light is emitted with stable CIE coordinates, stable colour temperature and stable clour rendering indices.

Tayagi et al. (2010) have demonstrated a WOLED by double layers of blue Zn(hpb)$_2$ and yellow Zn(hpb)mq emitting materials. Broad electroluminescence spectrum has been observed and as the thickness of Zn(hpb)mq layer increases the dominant wavelength shifts from bluish region to yellowish region. Three peaks have been observed in the EL spectrum at wavelengths 450 nm, 485 nm and 550 nm. The peak at 450 nm and 485 nm are due to the recombination of electrons and holes in Zn(hpb)$_2$ layer and the peak at 550 nm is due to the recombination in Zn(hpb)mq layer. The peak at 485 nm has been attributed to the excimer formation in Zn(hpb)$_2$. The EL spectrum of double layer was found to be an overlap of the EL spectrum of Zn(hpb)$_2$ and Zn(hpb)mq layers. CIE coordinates (0.29, 0.38) were well
recently Wu et al (2005) reported white light emission from a dual emitting layer OLED with and without blocking layers. The device with a blocking layer exhibited better performance with an external quantum efficiency of 3.86%. The emission colour of these devices strongly depends upon the thickness of the emissive layer and the applied voltage. The drawback of this technique is that it requires complex processing and a large amount of wasted organic materials resulting in relatively high fabrication cost. The CIE coordinates are often dependent upon the driving current due to shift of the exciton recombination zone. Brian et al (2002) have demonstrated that multi-emissive layer fully electrophosphorescent WOLEDs can take advantage of the diffusion of triplets to produce bright white devices with high power and quantum efficiencies. The device color can be tuned by varying the thickness and the dopant concentrations in each layer, and by introducing exciton blocking layers between emissive layers. Gong et al (2005) have reported that high performance multilayer white light emitting PLEDs can be fabricated by using a blend of luminescent semiconducting polymers and organometallic complexes as the emission layer and water soluble (or ethanol soluable) PVK-\text{SO}_3\text{Li} as the hole injection/transport layer (HIL/HTL) and t-Bu-PBD-\text{SO}_3\text{Na} as the electron injection/electron transport layer (EIL/ETL). Each layer is spin-coated sequentially from solution. Illumination quality white light is emitted with stable CIE coordinates, stable colour temperature and stable color rendering indices. Tayagi et al (2010) have demonstrated a WOLED by double layers of blue Zn(hpb)$_2$ and yellow Zn(hpb)mq emitting materials. Broad electroluminescence spectrum has been observed and as the thickness of Zn(hpb)mq layer increases the dominant wavelength shifts from bluish region to yellowish region. Three peaks have been observed in the EL spectrum at wavelengths 450 nm, 485 nm and 550 nm. The peak at 450 nm and 485 nm are due to the recombination of electrons and holes in Zn(hpb)$_2$ layer and the peak at 550 nm is due to the recombination in Zn(hpb)mq layer. The peak at 485 nm has been attributed to the excimer formation in Zn(hpb)$_2$. The EL spectrum of double layer was found to be an overlap of the EL spectrum of Zn(hpb)$_2$ and Zn(hpb)mq layers. CIE coordinates (0.29, 0.38) were well within the white region and have low turn on voltage (5V). The highest brightness obtained was 8390 Cd/m$^2$ at a current density of 518 mA/cm$^2$. White OLEDs which comprised of separate emitters having independent electrodes stacked one over the other in which separate voltage source control the emission from each device is known as stacked OLED. Stacking is advantageous due to better luminous efficiency, better color contrast and good color rendering over a wide range. Furthermore, this tuning strategy can delay the onset of differential aging of the several emitting layer. It has been shown that by layering several devices in this manner, a high total brightness OLED can be achieved without driving any particular element in the stack at such a high intensity that its operational lifetime is reduced (Lu and Sturm 2002, Brian et al 2002).

![Schematic diagram of horizontally and vertically stacked OLED.](image-url)
In a similar concept to the stacked OLED, tunable emitters of different colours (red-, green-, and blue) are placed side by side in strips. If spaced sufficiently very closely the colors will merge, as in full color display, producing bright and efficient white light similar to SOLED emitter with less complexity (Brian et al. 2002). This technology is similar to liquid crystal flat panel displays. Here the pixels of the three principal colours are patterned separately either horizontally or vertically and addressing them independently (Burrows et al. 1997, Forrest et al. 1997, Burrows et al. 1998) (see Fig. 8). In the horizontally stacked pattern the individual colour emitting pixels are deposited either in the form of dots, squares, circles, thin lines or very thin strips. As a result of mixing of these colours any desired range of colours can be produced in the same pane. As each colour component is addressed individually, the differential colour ageing can be mitigated by changing the current through the components. Each pixel can be optimized to operate at a minimum operating voltage and for highest efficiency. Also by reducing the size of the pixels the lifetime of the device can be controlled to the maximum.

Stacked white OLEDs usually produce higher brightness and efficiency than those of conventional WOLED and can be a good candidate as a light source because double or even triple current efficiency can be obtained in such devices as compared to the single emitter device. Recently Sun et al. (2005) reported an efficient stacked WOLED using a novel anode cathode layer (ACL) for connecting a blue phosphorescent and red phosphorescent emissive unit. This ACL layer was used as a middle electrode and EL characteristics of two individual emissive units were also studied. By biasing the two emissive units in a proper ratio white emission was obtained. They reported a maximum luminescence of 40000 cd/ m² at 26 V with CIE coordinates of (0.32, 0.38). The luminescence efficiency was 11.6 cd /A at 28 mA/cm².

Liao et al. (2004) and Kido et al. (2003) have demonstrated a variant of the SOLED that allows the contacts between intermediate OLED in the stack to electrically “float” and performs as a series of independent OLEDs, with a single electron exciting the multiple OLEDs as it passes through the circuit.

Chang et al. (2005) fabricated two types of stacked/tandem WOLEDs containing an interconnecting layer of Mg:Alq/WO and one control white emitting device for comparison. In these devices white emission was obtained by mixing complementary blue and yellow colours. Device 1 was obtained by connecting blue and yellow devices in series, while device 2 stacked two white emitting devices with the same blue and yellow dopants as used in device 1. Device 2 shows better performance compared to device 1 and the control device. An interesting amplification effect was observed in device 2 such that it exhibited the highest efficiency of 22 cd /A, which was almost three times that of the control device. This was due to the microcavity effect, which enhances the amount of light emitted in the forward direction. This shows that by just connecting two devices higher efficiency can be achieved. It was found that the driving voltage increases with increasing number of active units. Device 2 was the least stable, while the control device showed the longest half-life. This was due to the fact that device 2 suffered more driving power than the control and device 1. The thermal breakdown process may be present in these stacked devices due to non-ohmic contact of the interconnecting layers. However the half-life of device 2 at 100 cd/m² was projected to be greater than 80000 h. In these stacked devices the emissive intensity and colour were dependent on the viewing angle. This viewing angle dependence of emissive intensity and colour was attributed to the microcavity effect. Therefore it is
important to have a good optical design for the stacked devices. Such device structures had disadvantages of having complex layer structure and lack of known methods for damage free post deposition patterning of organic layers at resolution required for color displays.

Another approach for white light emission from multilayer OLEDs is the multiple quantum well structure (Liu et al 2000) (Fig. 9), which includes two or more emissive layers separated by blocking layers. Electrons and holes tunnel through the potential barriers of the blocking layers and distribute uniformly in different wells and emit light. Matching of the energy levels of different organic materials is not so critical in this system. Excitons are formed in different wells and decay to produce different coloured lights in their own wells. The confinement of charge carriers inside the quantum well improves the probability of exciton formation and they do not move to other zones or transfer their energy to the next zone. But this approach is very complicated and requires the optimization of thicknesses of various light emitting and blocking layers. This multilayer architecture has relatively high operating voltage due to the combined thickness of many layers used.

Fig. 9. Schematic diagram of a multiple quantum well white OLED

4.1.2 Single emissive layer structure

The fabrication process and device operation of white OLEDs through multilayer structure is very complex and several parameters need to be optimized for good colour rendering and to have luminescence efficiency. Also, these devices have high operating voltage because of the thick profile due to the several stacked organic layers used to perform different functions for efficient WOLEDs. The device profile must be as thin as possible to ensure low voltage operation. Single layer white light emitting devices consist of only one active organic layer can emit in the entire visible range and can overcome all such complexities. In comparison to other structures single layer structure can achieve higher emission colour stability. White emission from a single layer consisting of a blue emitter doped with different dyes or blending two or more polymers has been reported by many authors (Mazzeo et al 2003, Lee et al 2002, Al Attar et al 2005, Tasch et al 1997, Ko et al 2003, Chuen and Tao 2002, Shao and Yang 2005, Yang et al 2000, Chang et al 2005, Tsai et al 2003).
4.1.2.1 Host Guest structure

One of the most widely used methods to generate white light is host-guest structure. In this structure often a higher energy-emitting host (donor) material is doped with lower energy emitting guest (dye, dopant or acceptor) materials to cause energy transfer from the host to the guests. The dopant site can be excited directly by capturing the charge carriers or by energy transfer from the host to guest, as a result light emission can come from both the host and guests, the combined effect of which produces white light and is called emission due to the incomplete energy transfer. There are many examples where blue and red/orange color emitting dyes are co-deposited to form the emission layer (Chuen and Tao 2002, Koo et al 2003, Zheng et al 2003, Jiang et al 2002).

An important aspect of host-guest systems is the choice of host and guest materials for both single and multidoped systems. The energy transfer from host to guest can be either Förster (Lakowicz 1999) type energy transfer or Dexter type (Turro 1991) charge transfer or due to the formation of excimer or exciplexes (the principles are discussed in section 5). The primary conditions for such energy transfers are overlap of the emission spectrum of the host and absorption spectrum of the guest (Fig. 10). Therefore, the host material is always one with emission at higher energies, generally a blue-emitting material.

Fig. 10. Spectral overlapping between emission of donor and absorption of acceptor.

The host-guest system for white light generation can be either a single-doped or a multi-doped system in a single layer (D’Andrade et al 2004) or a multilayer structure (Lim et al 2002). The simplest device structure with a single emitting layer is obtained by doping primary (Kido et al 1994, Hu and Karasz 2003,) or complementary (Kawamura 2002, Zhang et al 2003, 2003a) color emitting dyes in a conductive polymer/small molecule host. In these devices, the concentration of the dopants was so maintained that emission from the host was small or negligible.

It is not necessary to use only dyes to take advantage of the energy transfer; blends of two polymers can also be used as host-guest systems (Lee et al 2002). The guest molecules can be florescent or phosphorescent in nature. However, phosphorescent dyes based on Ir and Pt complexes have provided significantly higher efficiency of OLEDs because of their ability to emit from both singlet and triplet excitons of the host molecule (Kamata et al 2002),...
whereas a florescent dye can only utilize the singlet exciton. The devices based on phosorescent dyes are named as electrophosphorescent devices. Representative examples of various host materials, florescent and phosorescent dyes are listed in Table 2.

<table>
<thead>
<tr>
<th>Host materials</th>
<th>1. Poly(N-vinylcarbazole) (PVK)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2. 1,1,4,4-Tetraphenyl-1,3-butadiene (TPD)</td>
</tr>
<tr>
<td></td>
<td>3. 4,4′,N,N′-Dicarbazole-biphenyl (CBP)</td>
</tr>
<tr>
<td></td>
<td>4. 9,10-Bis(3′,5′-diaryl)phenyl anthracene (JBE)</td>
</tr>
<tr>
<td></td>
<td>5. 9,10-Bis(2′-naphthyl)anthracene (BNA)</td>
</tr>
<tr>
<td></td>
<td>6. Bis(2-methyl-8-quinolato) (triphenylsiloxy) aluminum (III) (SAIq)</td>
</tr>
<tr>
<td></td>
<td>7. 4-[(4-(1-Naphthyl)-N-phenylaminophenyl)-1,7-diphenyl-3,5-dimethyl-1,7-dihydro-dipyrazolo(3,4-b:4′,3′-e)pyridine (PAP-NPA)</td>
</tr>
<tr>
<td></td>
<td>8. Bis (2-(2-hydroxyphenyl)benzothiazolato)zinc (Zn(BTZ))</td>
</tr>
<tr>
<td></td>
<td>9. 4,4′Bis(N-(1-naphthyl)-N-phenyl-amino)-biphenyl (α-NPD)</td>
</tr>
</tbody>
</table>

| Florescent dyes | Red 1. 4-(Dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM1) |
|                | 2. 4-(Dicyanomethylene)-2-methyl-6-(2-(2,3,6,7-tetrahydro-1H,5H-benzo[1,3]quinolin-8-yl)vinylyl)-4H-pyran (DCM2) |
|                | 3.4-(Dicyanomethylene)-2,6-di-(4-dimethylaminobenzaldehyde)-γ-pyran (DCDM) |
|                | 4.4-(Dicyanomethylene)-2-tert-butyl-6(1,1,7,tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) |
|                | 5. 5,6,11,12-Tetraphenyl-naphthacene (Rubrene) (orange) |
|                | 6. Zinc tetraphenylporphyrin (ZnTPP) |

| Green 1. Coumarin6 |
|                | 2. 9-Cyananthracene (CNA) |
|                | 3. Tris(8-quinolato)aluminum (III) (Alq3) |

| Blue 1. (perylene) |
|                   | 2. 4,4′-Bis(2,2′-diphenylvinyl)-1,1′-biphenyl(DPDB) |
|                   | 3. 9,10-Bis(3′,5′-diaryl)phenyl anthracene(JBE) |

| Phosphorescent dyes | Red 1. Fac-tris(2-phenyl)-bis(2-(2′-benzothiényl)-pyridinato-N,C')(acetylacetone)Ir(III) (Bt2Ir (acac)) |
|                    | 2. Bis(2-(2′-benzothiényl)-pyridinato-N,C')(acetylacetone)Ir(III)(Btp2Ir (acac)) |
|                    | 3. Bis(2-phenylbenzothiozolato-N,C)(acetylacetone)Ir(III)(Bt2Ir (acac)) |
| Green  Fac-tris(2-phenylpyridyl)iridium(III)(Ir(ppy)) |
| Blue   1. Bis((4,6-difluorophenyl)-pyridinato-N,C)(picolinate)Ir(III)(Flrpic) |
|        2. Bis[2(3,5-bis(trifluoromethyl)phenyl)-pyridinato-N,C][iridium(III)picolinate (CF3ppy)Ir(pic)] (greenish-blue) |

Table 2. List of various host materials and florescent and phosorescent dyes used for fabrication of WOLED
In most of the electrophosphorescence based OLEDs the device quantum efficiencies drop rapidly with increasing current density and consequently with the brightness due to triplet-triplet annihilation at high current densities. WOLED based on phosphorescent material had a maximum forward viewing power efficiency of $26 \pm 3 \text{ lm W}^{-1}$ at low luminosity, decreasing to $11 \pm 1 \text{ lm W}^{-1}$ at 1000 cd m$^{-2}$ (Kamata et al 2002, D’Andrade et al 2004).

The color tenability and spectral characteristics in host–guest systems is achieved by changing the concentration of the dopants and the energy transfer rate to each dopant and energy transfer between the dopants in multi-doped systems respectively (Kido et al 1994, Kamata et al 2002, Kawamura et al 2002). The range in which the dopant concentration can be varied is limited, usually less than 1 wt.% and 10 wt.% for fluorescent and phosphorescent dyes, respectively and the upper limit for dopant concentration is due to aggregate formation at higher concentration or quenching of luminescence due to non-radiative processes. For example, in a single dopant system, energy transfer from host to guest can be fast enough to saturate all the guest sites leading to change in spectral characteristics for higher current densities in a device or higher excitation intensity in PL measurements (Cheun and Tao 2002, Zheng et al 2003). Similarly, in case of multi-doped systems the emission from the higher energy dopant increases due to the filled lower energy states (Kamata et al 2002). Therefore, the concentration ratio of the dopants has to be carefully balanced in order to have stable white emission over the entire operating conditions of the device.

Theoretically, for single layer white OLEDs, the organic material should have chromophores that emit in different visible regions but most of the single molecule used as emitting material show the photoluminescence (PL) peak in the high-energy blue region (Tsai et al 2003, Paik et al 2002). It is their electroluminescence (EL) that is white or near white, which implies that some other emitting species like aggregates (Tsai et al 2003) or intramolecular charge transfer complex (Paik et al 2002) form in the solid state of the film during operation of the device, which is responsible for the additional peaks in the longer wavelength regions. Also, the formation of red-shifted peaks and their relative intensity is highly dependent on the applied bias and thus the emission spectrum is again voltage dependent (Tsai et al 2003, Paik et al 2002). In the case of emission through aggregates, the relative intensity of the peaks becomes further dependent on the solvent used for spin coating and the morphology of the film (Tsai et al 2003). Various molecules that are reported to give white or near-white emission are listed in Table 3.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene fused norbornadiene derivatives</td>
<td>(Tsai et al 2003)</td>
</tr>
<tr>
<td>Silicon-based alternating copolymers</td>
<td>(Paik et al 2002)</td>
</tr>
<tr>
<td>containing carbazole and oxadiazole moieties</td>
<td></td>
</tr>
<tr>
<td>1,4-Bis-(9-anthrylvinyl)-benzene polymer</td>
<td>(Romdhane et al 2003)</td>
</tr>
</tbody>
</table>

Table 3. List of organic molecules that are reported to give white or near-white electroluminescence
Rai et al (2009) reported the fabrication of a WOLED by using Zn(hpb)$_2$ doped with an orange fluorescent dye DCM in the configuration ITO/$\alpha$-NPD/ Zn(hpb)$_2$:DCM/BCP/Alq$_3$/LiF/Al and obtained white light emission with broad spectrum for very low concentration of the dye (0.01%). Since Förster type energy transfer (Rai et al 2008a, Shoustikov et al 1998) was improbable at such low dye concentration, the reason for emission from such low concentration was ascribed as due to trapping of carrier on to dye molecule followed by recombination. The white EL spectrum (Fig11) of device with suitable color coordinates was independent of the applied voltage.

![Fig. 11. Electroluminescence spectrum of WOLED at 6–10 V.](image)

The most important benefit of OLEDs with only one emission zone over the others is the fact that high emission colour stability can be achieved. But the approach of white emission by two or three different light emitting dopants in a single layer has its own problem that different rates of energy transfer between dopants may lead to colour imbalance. Some fraction of the highest energy (blue) will readily transfer energy to the green and red emitters and the green emitter can transfer energy to the red emitter. If the three emitters are at equal concentrations the red emitter will dominate the spectrum. So the doping ratio must be blue > green > red at a very carefully balanced ratio. Shao et al (2005) demonstrated the achievement of highly colour stable WOLED using a single emissive layer containing a uniformly doped host. To avoid the difficulties in the precise control of dopants by thermal co-evaporation, the host $\alpha$-naphthylphenylbiphenyl diamine ($\alpha$-NPD) was uniformly doped by the fused organic solid solution method prior to the deposition with 4,4’-bis(2,2-diphenylethen-1-yl) biphenyl (DPVBi) for the blue emission, and 10-(2-benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7,-tetra methyl-1H, 5H,11H benzopyrano(6,7,8-ij) quinolizin-11-one (C545T) for the green emission, 5,6,11,12 tetrphenylnaphthacene (rubrene) for the yellow emission and 4-(dicyanomethylene)- 2-tertbutyl-6-(1,1,7,7 -teramethyljulolidyl -9 -enyl)-4H-pyan (DCJTB) for the red emission. The correct weight ratio of $\alpha$-NPD, DPVBi, rubrene, DCJTB and C545T for stable white light emission was 100:5.8:1:0.342:0.304:0.394. The excitons generated from the blue dopant easily transferred their energy to other dopants. But the energy transfer from host to guest exhibits...
energy losses which has been avoided by the process of direct triplet exciton formation in the phosphorescent dyes. This leads to reduction in the operating voltage and hence increases the power efficiency.

D’Andrade et al (2004) reported white light emission from a single emissive layer WOLED. The emissive layer contained three organometallic phosphorescent dopants: tris(2-phenylpyridine) iridium(III) (Ir(ppy)$_3$) for green light emission, iridium (III)bis(2-phenylquinolyl-N, C$^2'$) (acetylacetonate) (PQIr) for red light emission and iridium(III)bis(4', 6'-difluorophenylpyridinate) tetrakis(1-pyrazolyl) borate (FIr6) providing blue light emission. The materials were simultaneously codoped into wide energy gap p-bis(triphenylsilyly)benzene (UGH2) host. The triplet doped WOLED exhibited a peak power efficiency of 42 lm /W with a colour rendering index 80 and a maximum external quantum efficiency of 12%.

Srivastava et al (2009) used single emission layer device structure in which two phosphorescent materials were co-doped in suitable ratio and fabricated organic LEDs to get the white light emission from the devices. The greenish blue and red emission came from the single emitting layer by an incomplete energy transfer process in which a mixture of highly efficient phosphorescent materials (FIrPic) (Bis(2-(4,6-difluorophenyl)pyridinato-N,C$^2'$) iridium(III)) (greenish blue) and (Ir-BTPA) (bis(2-(2'-benzothienyl) pyridinato-N,C$^3'$) (acetyl-acetonate) iridium(III)) (red) were used as guest molecules and 4,4' bis 9 carbozyl (biphenyl) (CBP) as host. BCP (2, 9 dimethyl 4, 7 diphenyl 1, 1' phenanthrolene) was used as hole blocking material. A suitable combination of charge carrier transport material and electrode materials were used to fabricate white light emitting diodes. Varying dopant concentrations controls the color of the device (Fig. 12). The maximum luminance of the device is 4450 cd/m$^2$. The CIE coordinates of the device are (0.27, 0.32) which is well within the white region.

Further, Rai et al (2010) fabricated an efficient WOLED using a blue light emitting material namely Zn(hpb)$_2$ and tuning its spectral response for white light emission by optimally doping it with bis(2-(2'-benzothiényl) pyridinato-N,C30) iridium(acetylacetonate) (Ir(btp)$_2$acac) that results in emission from both the host and the guest. The blue component for the white emission has been obtained from the singlet state of the host material Zn(hpb)$_2$
and red component from the triplet energy transfer from the triplet state of the host to the triplet state of the guest as shown in Fig. 13. The color coordinates of the white emission spectrum was controlled by optimizing the concentration of red dopant in the blue fluorescent emissive layer. Organic light-emitting diodes were fabricated in the configuration ITO/α-NPD/Zn(hpb)$_2$:0.01 wt%Ir(btp)$_2$acac/BCP/Alq3/LiF/Al. The J-V-L characteristic of the device shows a turn on voltage of 5 V. The electroluminescence (EL) spectra of the device cover a wide range of visible region of the electromagnetic spectrum with three peaks around 450, 485 and 610 nm. A maximum white luminance of 3500 cd/m$^2$ with CIE coordinates of (x, y=0.34, 0.27) at 15 V has been achieved. The maximum current efficiency and power efficiency of the device was 5.2 cd/A and 1.43 lm/W respectively at 11.5 V.

EL spectrum of the white emitting device (0.01wt% Ir(btp)$_2$acac) at various voltages i.e. 6 to 12V is shown in Fig.14 which consist of emission in red, green and blue of the electromagnetic spectra.

![Energy transfer mechanism for Zn(hpb)$_2$ doped with phosphorescent dopant Ir(btp)$_2$acac in electroluminescence process.](image)

**Fig. 13.** Energy transfer mechanism for Zn(hpb)$_2$ doped with phosphorescent dopant Ir(btp)$_2$acac in electroluminescence process.

![EL spectrum of WOLED at different bias voltage (6 to 12 V).](image)

**Fig. 14** EL spectrum of WOLED at different bias voltage (6 to 12 V).

### 4.1.2.2 Solution processed WOLED

One of the ways to get white light emission from conjugated polymers is by using blends of two polymers to extend their emission spectrum (Lee et al 2002, Gong et al 2005, Granstrom...
and Inganas 1996). Gong et al (2005) achieved WOLED by using a blend of conjugated polymers (PFO-ETM and PFO-F (1%)) and organometallic complex (Ir(HFP))<sub>3</sub> as an emissive layer. The device exhibited a maximum brightness of 10 000 cd/m<sup>2</sup> at 25 V. The emission of white light can be understood as the electrons and holes are recombined by two processes: direct recombination on the main chain (PFO-ETM) to produce blue and green emission in parallel with electron and hole trapping on the fluorenone units and on the Ir(HFP)<sub>3</sub> followed by radiative recombination with green light from PFO-F (1%) and red light from the triplet excited states of Ir(HFP)<sub>3</sub>. As a result the mixture of these primary colours gives white light. The devices had a CCT value of ~4500 K, which is very close to that of sunlight (~4700 K) at a solar altitude of 22° and a CRI value of 86. Both CCT and CRI values were insensitive to applied voltage and current density. It has been seen that the quality of emission colour in doped/blend devices is very sensitive to doping/blending concentration and a minor shift in the dopant or polymer ratio will significantly affect the quality of colour. This problem can be solved if a single material is used as an emissive layer and the material has chromophores emitting in the different visible regions. Research is in progress on the development of white OLEDs based on a single molecule as emissive material (Tsai et al 2003, Bai et al 2004, Tu et al 2004). Mazzeo et al (2005) reported a bright single layer white OLED by spin coating a single emitting molecule 3,5 dimethyl 2,6-bis (dimesitylboryl)-dithieno(3,2'-b:2',3'-d)thiophene. White emission was achieved by the superposition of intrinsic blue-green light emission of the single molecule with red shifted emission from cross-linked dimers. Bright white electroluminescence was obtained with a maximum luminance of 3800 cd/ m<sup>2</sup> at 18 V and an external quantum efficiency of 0.35%. Tu et al (2006) reported a successful development of a WOLED by using a single polymer: polyfluorene derivatives with 1,8-naphthalimide chromophores chemically attached on to the polyfluorene backbones. Optimization of the relative content of 1,8-naphthalimide derivatives in the polymer resulted in pure white-light electroluminescence from a single polymer. The external quantum efficiency of the single emissive WOLEDs is significantly affected by the thickness of emissive and transport layers. Better device efficiency requires the optimization of these layers for balanced charge recombination within the emissive layer.

### 4.1.3 Exciplex –Excimer structure

OLED characteristics are largely affected by the chemical and physical interaction at organic/organic interfaces. An interaction of organic materials at interface forms a charge-transfer excited-state complex which is known as exciplex/excimer (Li et al 2006, Su et al 2007). An exciplex/excimer is a transient charge transfer complex formed due to the interaction between the excited states of one molecule with the ground state of neighbouring molecule. The resulting electron-hole pair complex decays radiatively, the emission of which is considerably red shifted and broadened as compared to the individual molecules. When the two molecules are same, the transient complex is known as excimer on the other hand if they are different, they are termed as exciplex. The schematic diagram of the emission from the exciplex/excimer is shown below (Fig. 15).
Organic Light Emitting Diode for White Light Emission

and Inganas 1996). Gong et al (2005) achieved WOLED by using a blend of conjugated polymers (PFO-ETM and PFO-F (1%)) and organometallic complex (Ir(HFP)$_3$) as an emissive layer. The device exhibited a maximum brightness of 10 000 cd/m$^2$ at 25 V. The emission of white light can be understood as the electrons and holes are recombined by two processes: direct recombination on the main chain (PFO-ETM) to produce blue and green emission in parallel with electron and hole trapping on the fluorenone units and on the Ir(HFP)$_3$ followed by radiative recombination with green light from PFO-F (1%) and red light from the triplet excited states of Ir(HFP)$_3$. As a result the mixture of these primary colours gives white light. The devices had a CCT value of ~4500 K, which is very close to that of sunlight (~4700 K) at a solar altitude of 22° and a CRI value of 86. Both CCT and CRI values were insensitive to applied voltage and current density. It has been seen that the quality of emission colour in doped/blend devices is very sensitive to doping/blending concentration and a minor shift in the dopant or polymer ratio will significantly affect the quality of colour. This problem can be solved if a single material is used as an emissive layer and the material has chromophores emitting in the different visible regions. Research is in progress on the development of white OLEDs based on a single molecule as emissive material (Tsai et al 2003, Bai et al 2004, Tu et al 2004). Mazzeo et al (2005) reported a bright single layer white OLED by spin coating a single emitting molecule 3,5 dimethyl 2,6-bis (dimesitylboryl)-dithieno(3,2' b:2',3'-d)thiophene. White emission was achieved by the superposition of intrinsic blue-green light emission of the single molecule with red shifted emission from cross-linked dimers. Bright white electroluminescence was obtained with a maximum luminance of 3800 cd/m$^2$ at 18 V and an external quantum efficiency of 0.35%. Tu et al (2006) reported a successful development of a WOLED by using a single polymer: polyfluorene derivatives with 1,8-naphthalimide chromophores chemically attached onto the polyfluorene backbones. Optimization of the relative content of 1,8-naphthalimide derivatives in the polymer resulted in pure white-light electroluminescence from a single polymer. The external quantum efficiency of the single emissive WOLEDs is significantly affected by the thickness of emissive and transport layers. Better device efficiency requires the optimization of these layers for balanced charge recombination within the emissive layer.

4.1.3 Exciplex – Excimer structure

OLED characteristics are largely affected by the chemical and physical interaction at organic/organic interfaces. An interaction of organic materials at interface forms a charge-transfer excited-state complex which is known as exciplex/excimer (Li et al 2006, Su et al 2007). An exciplex/excimer is a transient charge transfer complex formed due to the interaction between the excited states of one molecule with the ground state of neighbouring molecule. The resulting electron–hole pair complex decays radiatively, the emission of which is considerably red shifted and broadened as compared to the individual molecules. When the two molecules are same, the transient complex is known as excimer on the other hand if they are different, they are termed as exciplex. The schematic diagram of the emission from the exciplex/excimer is shown below (Fig. 15).

![Fig. 15. Schematic diagram showing the formation of excimer/exciplex in organic molecule and light emission from excimer/exciplex molecule is red shifted from the excited monomer emission.](https://example.com)

Depending upon the spin multiplicity, excimer and exciplexes can be fluorescent or phosphorescent. When singlet excited state of the donor molecule interact with the singlet ground state of acceptor molecule, fluorescence excimer/exciplex are formed whereas interaction of triplet excited state of donor and triplet state of acceptor gives phosphorescence excimer/exciplex (Fig. 16).

![Fig. 16. Formation of excimer and exciplexes](https://example.com)

Donor and acceptors, from same molecule excimer are formed
Donor and acceptor, from different molecules exciplex are formed

![Fig. 16. Formation of excimer and exciplexes](https://example.com)
In the OLEDs there is a high possibility that exciplex formation occurs at the ETL/EML interfaces because HTL and electron transport layer (ETL) usually have an electron-donating and an electron-accepting nature, respectively. There have been some researches on the application of exciplexes for the tuning of emission colors (Li et al 2006, Liang and Choy 2006) and white emitting OLEDs (Tong et al 2007). Extensive studies on exited bi-molecular complexes and their application in electrophosphorescent devices have been done by Kalinowskii et al (2007) and Cocchi et al (2006).

Mazzeo et al. (2002, 2003, 2003a, Blyth et al 2003) obtained white-light emission by spin coating the blend of two different blue-emitting molecules having significant spatial overlap between their LUMOs. The green-red emission from the exciplex combined with the blue emission from the individual molecules gives white- or near-white-light emission. A host material can also be doped with two blue emitting and a red emitting material resulting in green emission from the exciplex, blue and red emission of guests through the energy transfer from host (Kim et al 2003). The concept of exciplex formation between two blue-emitting molecules can be extended to multi-layer device design in which these layers are placed adjacent to each other and the exciplex formation occurs at their interface (Cha and Jin 2003, Cocchi et al 2002 Liu et al 2002, Fang et al 2004). The exciplex emission is more favored if the difference between the HOMOs and LUMOs of the two molecules is large. This will tend to accumulate the charge carriers at the interface, causing increase in the probability of recombination near the interface. The emission color of these devices is highly dependent upon the thickness of the layers (Feng et al 2003) and the applied electric field (Cha and Jin 2003). The layer emitting in the red (Feng et al 2003, 2003a) or green/blue (Liang et al 2003) region can also be placed adjacent to the cathode if the white light is weak in intensity for red or green/blue emission.

WOLEDs can also be fabricated based on phosphorescence excimers. A high energy host organic material is doped with two blue-emitting phosphorescent dyes, namely iridium-bis(4,6-difluorophenyl-pyridinato- N, C)-picolinate (FIrpic) and platinum(II)(2-(4',6'-difluorophenyl)pyridinato-N, C')(2,4-pentanedionato) (FPt1) (D’ Andrade et al 2002). The white emission is obtained by combining the blue monomer emission from FIrpic through energy transfer from the host and excimer emission from the square planar complex of FPt1. Another simplification in the device structure is made using a single dopant only and coupling the monomer and excimer emission of the same molecule (D’ Andrade et al 2002, Adamovich et al 2002). The monomer to excimer ratio in these devices is very important to achieve balanced white-light emission and, therefore, the concentration of the dopants becomes crucial (Adamovich et al 2002, D’ Andrade and Forrest 2003).

Kumar et al (2010) has demonstrated the formation of exciplexes at the α-NPD/2-methyl 8-hydroxy quinolinolato lithium (LiMeq) interface using an ultra thin layer of DCM dye as a probe. They have placed the thin layer of DCM dye layer (1nm) at different distance from the interface. The exciplexes formed at the interface transferred their energy to the DCM dye by a Förster type energy transfer. Excitons were formed at the dye molecule and was detected which gave its characteristics emission. As the dye layer is moved away from the interface the intensity of emission from DCM decreased and emission from the exciplex increased indicating that the exciplexes are generated at the interface only. The maximum energy transfer was observed when the dye layer was placed at the interface which was limited by the number of dye molecules. At an optimum distance from the interface the emission from the exciplexes together with that from the dye gave white light emission. The
origin of exciplex formation was explained as due to a mismatch of the HOMO and LUMO (Fig17) energies and accumulation of charges at the α-NPD/LiMeq interface.

![Energy level diagram showing the formation of exciplexes at the interface](image)

**Fig. 17.** Energy level diagram showing the formation of exciplexes at the interface

There are several issues involved in formation of exciplexes and excimers that limit the device performance. In the blended emissive layers, the formation of exciplex strongly depends on the concentration, structure and morphology of the film (Mazzeo et al 2002). In such cases fine-tuning of the emission spectrum can be done by concentration variation. However, there is a limit for concentration variation since phase separation or aggregation occurs above an optimum concentration, which in turn, will not allow spatial overlap of the LUMOs of the donor and the acceptor (Mazzeo et al 2002). Another difficulty in exciplex formation is the temperature dependence since at low temperatures the emission by exciton recombination will be predominant while at high temperatures, the exciplex emission will be predominant (Chao and Chen 1998).

The external quantum efficiencies of most of the exiplex emitting devices are usually low (~1%) (Noda et al 1999, Wang et al 1998, Kawabe and Abe 2002, Cocchi et al 2002). Indeed the appearance of exciplex is often considered as a major reason for the poor device performance but the dissociative property of the exiplex of the ground state imparts in to broad featureless emission band which is red shifted from the parent molecule emission spectrum. This is the reason that exiplex light emitting devices can be considered as promising technologies for manufacturing WOLEDs (Feng et al 2001).

### 4.1.4 Microcavity structure

WOLED fabricated by optical optimization through multimode resonant cavities have also getting some attention (Singha et al 2003, Dodabalapur 1994, 1994a). The microcavity is a system consisting of a pair of highly reflecting mirrors having separation of the order of a micron and utilizes the concept of Fabry-Perot resonant cavity. A resonant microcavity is formed when the emissive material is sandwiched between two metallic mirrors or a metallic mirror and semitransparent distributed Bragg reflector (DBR) (Peng et al 2003). During the operation of device, standing waves are generated, the wavelength of which depends upon the length and refractive index of the cavity. In conventional structures, light is wasted since it leaks in all directions. But in a microcavity light emerges only from one

www.intechopen.com
end of the cavity and the structure is more efficient. By varying the thickness of the layer, undesirable light can be filtered out and the emission of light can be obtained at any desired wavelength. Since a microcavity LED is more efficient and uses less current, it lasts longer. A microcavity resonator is one of the most effective ways of enhancing the luminance and brightness of monochromatic OLEDs (Hsu et al 2004, Neyts 2005). Spectral narrowing and intensity enhancement of spontaneous emission in OLEDs by microcavity has been reported (Juang et al 2005). Dodabalapur et al (1994) demonstrated the control of the emission of OLEDs by multimode resonant cavities such that the thickness of the cavity is greater than the single mode cavity devices so that it has several resonant modes within the emission spectrum of the material. White emission from the microcavity structures is obtained by a simple modification of the Fabry–Perot resonator (Singha et al 2003) in which combined emission from the two cavities of different lengths produces white light. Shiga et al (2003) employed a modified Fabry–Perot resonator cavity with different cavities of different lengths (see Fig.18, the terms MM, DM, EML and FL represent metallic mirror, dielectric mirror, emission layer and filter layer, respectively), and produced white light. One disadvantage of this approach is that the colour coordinates change with viewing angle and this angular dependence of the emission limits the microcavity applications for white OLEDs.

![Microcavity Diagram](image)

Fig. 18. Concept of (a) usual cavity and (b) multiwavelength resonant cavity (MWRC).

4.2 Wavelength conversion

Some blue or ultraviolet light from one OLED is used to excite several phosphors, each of which emits a different colour and these different colours are mixed to make a white light with the broadest and richest wavelength spectrum and is called down conversion by phosphors.

4.2.1 Down conversion by phosphor

A difficulty of colour stability due to differential ageing of various species occurs in several methods used for white emission from organic LEDs. White emission by down conversion phosphors may be an alternative method in which a blue emitting OLED is coupled with one or more down conversion phosphor layers. During the operation of the device a small portion of the blue light is scattered and goes through the phosphors without down conversion and the phosphor layers absorb emission from the blue OLED and emit according to their intrinsic property. The mixing of unabsorbed emission from the blue
OLED and the emission from the phosphors produces white light. A schematic diagram of white light emission by down conversion method is shown in Fig. 19. Here only the blue emitter conducts the charge and is the only site which is directly excited. Once the excitons are generated they excite other phosphors to produce balanced white emission. As the blue light emission decreases with age, light from other coupled phosphors should decrease proportionately because their relative intensities are directly related to those of the blue light emitter there for there is no differential colour ageing in the down conversion technique. The emission spectrum can be adjusted by varying the concentration and thickness of the phosphor layers (Misra et al. 2006, Gupta et al. 2006). These down conversion WOLEDs demonstrated the highest CRI value, 93 and efficiency 3.8 lm/W.

![Schematic diagram of white light emission by down conversion.](image)

Duggal et al. (2002) reported white light emission from a blue OLED coupled with down converting orange and the red organic phosphor, namely perylene orange and perylene red dispersed in poly(methacrylate) (PMMA) followed by a layer of inorganic light scattering phosphor, namely Y(Gd)AG:Ce dispersed in polydimethyl siloxane silicon. The quantum efficiency of photoluminescence of dyes in PMMA was found to be >98% and the quantum yield of Y(Gd)AG:Ce was 86%. These down conversion WOLEDs demonstrated the highest CRI value, 93 and efficiency 3.8 lm/W.

In Materials Research Society meeting 2005 (MRS Fall Meeting, 28 November–2 December 2005, Boston, MA, USA) one of the biggest changes pioneered by Junji Kido and Forrest’s groups has been the switching from fluorescent materials to phosphorescent materials. Phosphorescent dyes can convert both singlet and triplet excitons into light, making the devices potentially much more efficient. They reported a new blue OLED based on phosphorescent compound Flrpic, with a record breaking efficiency of 42 lm/W at 100 cd m⁻². They surrounded the Flrpic containing layer with layers of other compounds that allow triplet excitons to reside within the emissive layer. This creates an energetic well in the light emitting material so that excitons cannot get out and they decay in the presence of blue phosphor to give off blue light. To get white light they added a yellow phosphor to their blue light emitting layer, converting some of the emitted light to yellow, which combined with the blue to give off white light. The light photons emitted from OLEDs reflect off the glass-air interface and bounce back inside the device, where many of them are reabsorbed and generate heat instead of light. The efficiency of OLEDs has been boosted (36 lm/W to 57 lm/W) by adding a specialized antireflective coating to the outside of the glass.

White emission from down conversion can also be obtained by coupling UV light with red, green and blue phosphors which excites several phosphors, each of which emits a different colour, as a result of mixing these colours white light emission is obtained. The technique
has colour stability but the losses associated with wavelength conversion are the main drawbacks of this technique.

There is a lack of theoretical modelling of electroluminescence in OLEDs. Tyagi et al (2010) has developed a model based on Monte-Carlo simulation technique (Ries et al 1988, Ries and Bässler1987, Movaghar et al 1986, Houili et al 2006) to model the disordered semiconductor (assuming Gaussian density of states) to generate the electroluminescence spectrum of multilayer OLED for white light emission. The electroluminescence (EL) spectrum in an OLED was generated by the recombination of a positive charge carrier with a negative charge carrier in the emitting layer. The emitted photons have energy equal to the difference of energies of negative and positive charge carriers.

5. Photo physics of White OLEDs

Doping of wide band gap materials which emits in the blue region of the spectrum with lower band gap dopants can modify the emission properties of the host molecules. The modification of emission properties upon doping is due to efficient energy transfer process from the host molecules to the guest molecules (dopants) and with careful balancing of the doping it is possible to obtain white light emission. The dopants can be fluorescent or phosphorescent in nature. The dopant site can be excited directly or by energy/charge transfer from the host molecule.

The energy transfer in this matrix occurs in different ways. They are (i) Förster type energy transfer, (ii) Dexter transfer (iii) Exciplex - excimer charge transfer and (iv) Trap assisted recombination. The principles are discussed below.

5.1 Förster Type energy transfer

A molecule that is in an excited singlet or triplet state (Donor) can transfer its energy to a molecule in the ground state (Acceptor) by electronic energy transfer (ET). Energy transfer always involves two molecules that are in close proximity to each other. It is the fundamental process of energy / exciton migration which consists of multiple energy transfer processes. Radiationless energy transfer can occur via a dipole-dipole interaction having a long range separation of about ~30-100Å known as Förster transfer or via exchange of electrons through overlapping orbitals termed as Dexter transfer. The Förster energy transfer requires spectral overlap of the emission spectrum of the donor with the absorption spectrum of the acceptor. The radiation field of the dipole transition of D is coupled with the dipole transition of A through space without the requirement of spatial overlap of wavefunctions and can be explained as

\[ D^* + A \rightarrow X \rightarrow D + A + h\nu \]

where \( D^* \), \( A \), \( X \), \( D \) and \( h\nu \) stand for excited donor, ground state of acceptor, intermediate excited system, ground state of donor and energy of emitted photon respectively. A scheme of Förster transfer is depicted in Fig. 20. The left side of Fig. 20 shows energy transfer between molecules of similar singlet energy. This is possible due to the weak overlap of absorption and emission spectra of identical molecules. The right side shows energy transfer to a molecule which is lower in its singlet energy (trap state). In both cases the ET occurs radiationless.
Furthermore the fluorescence lifetime of the donor molecules is significantly reduced as a consequence of efficient energy transfer to the lower energy trap. Since Förster energy transfer is mediated by dipole-dipole interaction without the need of direct overlap of orbitals, it can overcome distances up to 10 nm. It allows only singlet-singlet transition at low acceptor concentration and at a much faster rate of <10^-8 s.

5.2 Dexter transfer

The second possibility of energy transfer is known as exchange type or Dexter energy transfer. Dexter ET is based on quantum mechanical exchange interactions, therefore it needs strong spatial overlap of the involved wavefunctions of D and A. Since the overlap of electronic wavefunctions decays exponentially with distance, it is expected that the rate constant k<sub>DA</sub> decreases even more rapidly with distance R than observed in the case of singlet transfer. A schematic presentation of Dexter ET is shown in Fig. 21. Dexter ET occurs typically over distances which are similar to the van-der-Waals distance, i.e. R = 0.5 - 1nm. The rate constant drops exponentially with the distance R<sub>DA</sub> between D and A:

\[
E_{\text{D}}^* \rightleftharpoons E_{\text{A}}^* \rightleftharpoons E_{\text{D}} + E_{\text{A}} + \phi
\]
Organic Light Emitting Diode

Fig. 21. Schematic presentation of Dexture type ET

Dexter ET is a correlated two electron exchange process. Hence it allows triplet energy transfer without the additional need of intersystem crossing upon energy transfer of a triplet state unlike the Förster energy transfer which requires spin-forbidden ISC for triplet energy transfer. Due to this reason Förster ET is mostly used to describe singlet migration, whereas Dexter ET is used to describe the triplet migration in the solid state.

A lot of effort has been made to achieve white light emission from small molecules (Lim et al 2002, 2004, Kido et al 1995, Mazzeo 2003, Wang 2005, Niu et al 2005) as well as from polymers (Lee et al 2002, Park et al 2005, Al Attar et al 2005, Tasch et al 1997) using the Förster/Dexter energy transfer mechanism. Mazzeo et al (2003) have fabricated OLED from a blend of N, N’-diphenyl-N, N’-bis(3-methylphenyl)-1,1’-biphenyl- 4,4’-diamine (TPD) (PL in the blue region) with a thiophene based pentamer, (3,3’,4”,3’”,4’’)-tetracyclohexyl-3, 4-dimethyl- 2,2’:5’,2’’:5’’,2’’’:quinqethiophene-1,1-oxide (T5oCx) (PL in the red region). The incomplete Förster energy transfer occurred from host (TPD) to guest (T5oCx) and as a result, they got emission from both the molecules, which produced white light. This energy transfer was favoured by the overlapping of the strong emission spectra of TPD and absorption spectra of T5oCx. Wang et al (2005) achieved a highly efficient white organic LED using two blue emitters with similar structures 9,10-di-(2-naphthyl)-anthracene(ADN) and 9,10- di-(2-naphthyl)-2-terbutyl-anthracene (TADN) doped with (0.01–0.05%) yellow-orange emitting iridium (tri-fluorenyl) pyridine complex (Ir(Fl3Py)6am4) and doped with yellow-orange phosphor iridium (tri-fluorenyl) pyridine complex (Ir(Fl3Py)6am4). The white light emission from the system was attributed to a strong Dexter ET.

Fig. 21. Schematic presentation of Dexture type ET

The incomplete Förster energy transfer occurred from host (TPD) to guest (T5oCx) and as a result, they got emission from both the molecules, which produced white light. This energy transfer was favoured by the overlapping of the strong emission spectra of TPD and absorption spectra of T5oCx. Wang et al (2005) achieved a highly efficient white organic LED using two blue emitters with similar structures 9,10-di-(2-naphthyl)-anthracene(ADN) and 9,10- di-(2-naphthyl)-2-terbutyl-anthracene (TADN) doped with (0.01–0.05%) yellow-orange emitting rubrene. The device had a maximum external quantum efficiency of 2.41% (5.59 cd/A) and a maximum luminance of 20 100 cd/m² at 14.6 V. The advantage of the similar structure of ADN and TADN is that it depresses the molecular aggregation, which leads to better film morphology.

Park et al (2005) have demonstrated white emission from ITO/PVK/(PDHFPPV +MEHPPV)/Li:Al, ternary polymer blended LED. Here poly(N-vinylcarbazole) (PVK) acts as an energy donor as well as electron blocker while poly(9,9-dihexyl-2,7-fluorene phenylenevinylene) (PDHFPPV) + poly(2-methoxy-5-(2-ethylhexyloxy)-1,4- phenylene vinylene) (MEHPPV) blend acts as an emitting layer. In this bilayer system the spectral overlapping between the emission of PVK and absorption of PDHFPPV and between the emission of PDHFPPV and absorption of MEHPPV, meets the necessary condition for Förster energy transfer. The cascade energy transfer from PVK to PDHFPPV and then to MEHPPV and the emission from PDHFPPV and MEHPPV results in whitish light emission.
Al Attar et al (2005) fabricated an efficient white PLED based on a blue emitting poly(9,9-
bis(2-ethylhexyl)fluorine-2,7-diyl) endcapped with bis(4-methylphenyl)phenylamine (PF2/ 
am4) and doped with yellow-orange phosphor iridium (tri-fluorenyl) pyridine complex 
(Ir(Fl3Py)3). The white light emission from the system was attributed to a strong Dexter 
energy transfer from (PF2/6am4) to (Ir(Fl3Py)3). The devices have a with a peak external 
quanta efficiency of 2.8% and a luminance of 16 000 cd m⁻² at 5 V.

5.3 Exciplex - excimer charge transfer
The third possibility of energy transfer is known as Exciplex - excimer charge transfer. In the 
excimer formation the wavefunction of excited states extends over the molecules and the 
molecules are bound together only in the excited state but not in the ground state. This 
absence of the bound ground state provides a way for efficient charge transfer from higher 
energy host to lower energy guest. The charge transfer mechanism can also be explained as

\[ \text{D}^* + \text{A} \rightarrow \text{X} \rightarrow \text{D} + \text{A} + \text{hv}, \]

where D*, A, X, D and hv stand for excited donor, ground state of acceptor, intermediate 
excited system, ground state of donor and energy of emitted photon, respectively. Here X 
is the charge transfer exciplex/excimer complex. The charge transfer takes place at the 
interface of the charge transport layer and the emitting layer (Chao and Chen, 1998, 
mismatched electronic structure of the two molecules (exciplex) and wavefunction 
overlapping (excimer). The charge transfer excitations occur at energies close to those of 
excitations localized at the donor and acceptor molecules (Fang et al, 2004). The charge 
transfer occurs due to the interaction between the excited states of one molecule with the 
ground state of the other molecule (as discuss in section 4.1.3), resulting in a radiative 
electron–hole recombination pair. The exciplex formation is favoured by a large difference 
between the HOMOs and LUMOs of the emitter and the charge transport layer. Because of 
this large difference the injection of the charge carriers from transport layer to the emitter 
layer and from the emitter layer to the transport layer will be difficult and there will be 
accumulation of the carriers at the interface. Now the indirect recombination from LUMO of 
the transport layer to HOMO of the emitter layer is more favoured. The energy of the 
exciplex is always less than the energy of the excited single molecules and its emission is 
very broad.

5.4 Trap assisted charge transfer
The Fourth possibility of energy transfer is known as the charge trapping mechanism that 
requires the energy of the dopant to be in such a way that it is energetically favorable for 
charge transfer. In the trap assisted charge transfer mechanism the recombination process 
can be visualized as that the electron and hole gets trapped in the dye molecules which 
generates excitons which decays for the generation of light.
Fig. 22 shows the energy level diagram of the host and the dye molecules which is used to explain the charge trapping of dye molecules in the Zn(hpb)$_2$DCM system (Rai et al 2008). The host matrix and the dye have their highest occupied molecular orbital (HOMO) level at ~6.5 and ~5.07 eV respectively and their lowest unoccupied molecular orbital (LUMO) at ~2.8 and ~3.04 eV respectively. (Lee et al 2002) According to the energy level diagram, the dye molecules will be forming deep hole traps (1.43 eV) and shallow electron traps (0.24 eV) into the host forbidden energy gap. The hole traps being very deep will be above the Fermi level and will be always remain filled and will not alter hole transport properties. The electron traps being shallow and may lie on the same side of the LUMO compared to the Fermi level should contribute to the carrier trapping and the electrical properties of the guest-host system.

6. Problem to be solved

The main technical challenges that need to be met for OLED technology to displace fluorescent lighting for general illumination have been laid out in detail. The challenges are indeed formidable and will require a long-term investment in technology development. Because OLEDs possess potential features such as conformability to surfaces that are not possible with current lighting technology, it is likely that products will make it into the lighting market before all of the long-term challenges are met. Such shorter-term applications will help to fuel the necessary long-term development for general illumination. There are reasons to be optimistic that an OLED-based solid state light source will become a reality. One reason is simply that while the field has demonstrated incredible progress in the last decade, it has been largely constrained into pursuing certain types of device structures due to the needs of display applications. Once this constraint is lifted, new types of device structures and materials that have so far been ignored can be investigated. These extra
parallel approaches can only enhance progress. Another, related, reason for optimism has to do with the fact that OLED technology as a whole is still in a very early stage of development. OLEDs utilize organic molecules that are literally blended together into relatively simple device structures that then yield impressive performance. The number of possible organic molecules, each with tunable functions that can be utilized is virtually unlimited due to the capabilities of modern organic chemistry. In fact, the field is really still in its infancy with regard to understanding what types of molecules should be made. Although the device physics of an OLED is largely understood, the detailed physics of charge transport, exciton spin formation, and energy transfer is not. Similarly, the detailed material science required to understand how molecules interact and produce a characteristic morphology in the solid state is not well understood. These details are necessary to guide the development of new organic molecules/polymers and device structures that optimize performance. Thus, there is a good chance that as basic research in OLED technology continues, and as focused research on solid-state lighting accelerates, the exponential rate of progress seen in the last decade will continue into the next. If so, then by the end of the next decade OLEDs will have a good shot at surpassing fluorescents as the premier lighting technology.

7. Future prospects of WOLED

The prospects of organic LEDs are very good. In the R&D scenario, new efficient emitters are being reported everyday which are far more efficient than those which are in present use. On the technology side, new encapsulation strategies are being introduced particularly those based on of thin film encapsulation which has shown encouraging results. Similarly new ways to reduce the turn on voltage by doping of charge transport layers are also in progress. New organic deposition techniques as well as roll to roll processing of OLEDs are also showing encouraging results. Perhaps the new technologies based on all printed devices may revolutionaries the lighting industry. The efficiency of the best OLED has surpassed that of fluorescent discharge lamps and one can expect that in the coming years we see more efficient devices which replaces the existing lighting concepts.

8. Conclusion

White light sources based on OLEDs are efficient and clean and have the potential to replace the existing lighting system based on incandescent lamp and discharge tubes. Even though the technology has developed to a stage where it can be commercialized, there are many basic issues relating to material science which are not clearly understood and very intense research is required in this direction. Many government funded research agencies and commercial establishment are actively working to improve WOLED efficiency and life time to bring it to acceptable limits. These efforts have started showing results and in the near future we can expect a versatile organic based lighting system replacing the existing light sources.
Acknowledgements
The authors are grateful to Director, National Physical Laboratory, New Delhi, for his keen interest in this investigation. The authors gratefully recognize the financial support from the Department of Science and Technology (DST), Council of Scientific and Industrial Research (CSIR) New Delhi, for providing funds.

9. References
Blochwitz J, Pfeiffer M, Hofman M, and Leo K, Non-polymeric OLEDs with a doped amorphous hole transporting layer and operating voltages down to 3.2 V to achieve 100 cd/m², Synth. Met., 127 (2002)169–173


D’Androde B.W. and Brown J. J., Organic light-emitting device luminaire for illumination


Advanced Materials, 17, (September, 2005), 2053-2058


Gupta D., Katiyar M., Deepak, Various approaches to white organic light emitting diodes and their recent advancements. Optical Materials, 28, 4, (March 2006), 295-301


www.intechopen.com

Kamtekar K. T., Monkman A. P. and Bryce M. R., Recent advances in white organic light-emitting materials and devices (WOLEDs), *Advanced Materials*, 22 (2010), 572-582.


Li G and Shinar J, Combinatorial fabrication and studies of bright white organic light-emitting devices based on emission from rubrene-doped 4,4’-bis(2,2’-diphenylvinyl)-1,1’-biphenyl, Appl. Phys. Lett. 83 (2003) 5359


Optoelectronics Industry Development Association (OIDA) 2002 Organic light emitting diodes (OLEDs) for general illumination update 2002 Report August


Rai V. K., Srivastava R., Kamalasanan M. N. White organic electroluminescence from fluorescent bis (2-(2-hydroxyphenyl) benzoxazolate) zinc doped with phosphorescent material Journal of Luminescence, 130, 2, (February 2010), 249-253

Rai V. K., Srivastava R., Kamalasanan M.N. White organic light-emitting diodes based on blue fluorescent bis(2-(2hydroxyphenyl)benzoxazolate)zinc (Zn(hpb)) doped with DCM dye. Synthetic Metals, 159, 3-4, (February 2009), 234-237


Romdhane S., Marai F., Hassine L., Fave J.L., Roussel J., Majdoub M., Bouchriha H., UV and white electroluminescence in AVB polymer Synthetic Metals, Volume 139, Issue 2, 5 September 2003, Pages 245-249


UV and white electroluminescence in AVB polymer Synthetic Metals, Volume 139, Issue 2, 5 September 2003, Pages 245-249

www.intechopen.com

Wang L, Lei G and Qiu Y, “Bright white organic light-emitting diodes based on two blue emitters with similar molecular structures”, *J. Appl. Phys.* 97 2005 114503


Yang Y., Pei Q. Efficient blue-green and white light-emitting electrochemical cells based on poly(9,9-bis(3,6-dioxahexyl)-fluorene-2,7-diyl), *J. Appl. Phys.* 81 (1997) 3294


Organic light emitting diodes (OLEDs) have attracted enormous attention in the recent years because of their potential for flat panel displays and solid state lighting. This potential lies in the amazing flexibility offered by the synthesis of new organic compounds and by low-cost fabrication techniques, making these devices very promising for the market. The idea that flexible devices will replace standard objects such as television screens and lighting sources opens, indeed, a new scenario, where the research is very exciting and multidisciplinary. The aim of the present book is to give a comprehensive and up-to-date collection of contributions from leading experts in OLEDs. The subjects cover fields ranging from molecular and nanomaterials, used to increase the efficiency of the devices, to new technological perspectives in the realization of structures for high contrast organic displays and low-cost organic white light sources. The volume therefore presents a wide survey on the status and relevant trends in OLEDs research, thus being of interest to anyone active in this field. In addition, the present volume could also be used as a state-of-the-art introduction for young scientists.

How to reference
In order to correctly reference this scholarly work, feel free to copy and paste the following:


InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
Chinese Shanghai Dianji Daxue Da Han Di Ban She 405 Yuan
Phone: +86-21-62489820
Fax: +86-21-62489821
© 2010 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License, which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.