

SYNTHESIS AND CHARACTERIZATION OF ORGANIC ELECTROLUMINESCENT MATERIALS FOR OLEDs APPLICATION

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University of Delhi

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The Award of the degree of**

**Master of Engineering
In
Polymer Technology**

Submitted by

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CERTIFICATE

This is to certified that Mr Reetesh Kumar student of Final year of Master of Engineering (polymer Technology), College Roll No.06/poly/o3, from Delhi College of Engineering, (University of Delhi), Delhi 110042 has individually completed a project titled **“Synthesis and Characterisation of Organic Electroluminescent Materials for OLEDs application”** is a bonafied record of his work carried out under our joint supervision in the division of Engineering Materials, OLEDs Labs (Polymeric and Soft Materials Section) at National Physical Laboratory, K.S. Krishnan Road. New Delhi-110012.

Further it is also certified that this dissertation has not been submitted for any other degree or diploma in any other college or university to best of our knowledge.

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ABSTRACT

The rapid growth of Organic Light Emitting devices due to their potential application in large screen flat panel displays is expected in the coming year. So, there has been much effort into the development of organic electroluminescent materials for use in OLED applications. The report on "*synthesis and characterisation of organic electroluminescent materials for OLED applications*" contains description of emissive device structure, physics of organic layer structure in an OLED and general description of characterisation technique for materials. The experimental section consists of synthesis of two materials *Tris (8-hydroxyquinoline) Aluminium (Alq₃)* and *Tris (2-phenylpyridine) Iridium (III) complex Ir(ppy)₃* and fabrication of light emitting diodes applying these materials as emitting layers. The materials were characterised by UV-Vis absorption spectra, photoluminescence spectra, Fourier transform Infra-red spectra and thermogravimetric analysis (TGA). The EL and I-V characteristics have also been measured.

INTRODUCTION

Electroluminescence has been a subject of interest for several decades because of its many applications in areas such as telecommunications or information displays. Light-emitting diodes using p-n junctions of inorganic semiconductors have dominated the field in the last twenty years; however, efficient blue emission has only recently been achieved and inorganic semiconductors are difficult to form over large areas, making the process uneconomic.

During the last decade, an explosive growth of activity in the area of organic electroluminescence has occurred in both academia and industry, stimulated by the promise of light-emitting plastics for the fabrication of large, flexible, inexpensive and efficient screens to be used in different applications. Thus, a substantial amount of research is presently directed towards color control and improvement of manufacturability and reliability of devices in order to make their commercialization viable.

Organic materials are preferred over inorganic materials in electroluminescence (EL), because of the high photoluminescence. There has been long interest in the possibility of light emission by fluorescent organic materials through charge injection under an applied field. However, the promise offered by the high fluorescence quantum yield was for a long time countered by the large voltages required for generating electroluminescence.

In the present report, two organic materials Tris-(8-hydroxyquinoline)aluminium (Alq_3) and Tris-(2-phenylpyridine)iridium (III) complex $\text{Ir}(\text{ppy})_3$ were synthesized and characterized by taking different optical and thermal methods like UV-Vis spectra, Photoluminescence spectra, Fourier Transform FT-IR spectra and Thermo-gravimetric Analysis (TGA). The synthesized materials sublimed under vacuum and used for device fabrications. The fabricated devices of the following configuration ITO/TPD/ Alq_3 /LiF/Al and ITO/TPD/ $\text{Ir}(\text{ppy})_3$ /LiF/Al were studied and characterized by there electroluminescence (EL) spectra and current voltage (I-V) characteristics. On applying bias voltage (more than 6V) to the device with configuration ITO/TPD/ Alq_3 /LiF/Al produced green electroluminescence (EL) and life time of device was very short. While in the case of device structure ITO/ TPD $\text{Ir}(\text{ppy})_3$ /LiF/Al needs higher voltage in the range 12-20V which produced green electroluminescence (EL).

CHAPTER 1. OLEDs: AN INTRODUCTION

1.1 HISTROY AND DEVELOPMENT OF OLEDs

Electroluminescence is one of the scientific discoveries in the last century that changed the life of mankind immensely. Now the electroluminescence from polymeric materials will certainly change not only the way we illuminate our home but our life style too.

In contrast to photoluminescence (PL), the light emission from an active material as a consequence of optical absorption and relaxation by radiative decay of an excited state, electroluminescence (EL) is a non-thermal generation of light resulting from the application of an electric field to a substrate^{1,2}. In the latter case, excitation is accomplished by recombination of charge carriers of opposite sign (electron and hole) injected into an inorganic or organic semiconductor in the presence of an external electric field.^{3,4}

This phenomenon was first discovered for inorganic materials in 1936, when Destriau et al. observed high field electroluminescence from a ZnS phosphor powder dispersed in an isolator and sandwiched between two electrodes³⁻⁵. General Electric introduced first LED based on inorganic emitter GaAsP in market in early 1960s. Later it was found that the materials that were generally used for inorganic LEDs are compounds of elements from group 13, 14 and 15 of the periodic table such as GaAs, GaP, AlGaAs, InGaP, GaAsP, GaAsInP and more recently AlInGaP. Semiconductors with large band gaps are difficult to obtain blue LEDs. Nevertheless, blue inorganic LEDs based on SiC, ZnSe, or GaN were developed, but exhibited distinctly lower efficiencies in comparison

to others³⁻⁶. Since last few decades a lot of development is seen in the field of inorganic LEDs. Light emitting diodes (LEDs) of various colours with good quantum efficiencies have been fabricated and its economic benefit was exploited worldwide.

Destriau's discovery of electroluminescence (EL) in inorganic compounds (ZnS, phosphors) in 1936 and the discovery in 1947 that a transparent anode could be constructed by depositing a layer of Indium Tin Oxide (ITO) onto a glass surface opened the possibility of obtaining light emitting planar surfaces⁷.

The fact that many aromatic organic molecules are photoluminescent suggested their use as electroluminescent materials. In 1963, Pope et al. reported electroluminescence (EL) from an organic semiconductor. They observed emission from single crystals of anthracene, a few tens of micrometers in thickness, using silver paste electrodes and required large voltages to get emission typically 400V⁸. Helfrich and Schneider made similar studies in 1965 using liquid electrodes. Considerable effort has been taken to understand the basic mechanism as well as to provide stable electroluminescent devices. Development of organic thin film electroluminescence (EL) advanced with the study of thin film devices. In 1982, Vincett et al. reported blue electroluminescence (EL) from anthracene sublimed onto oxidised aluminium as one electrode, and were able to reduce voltage considerably, for example, to 12 V^{7,8}.

In 1983, the discovery of electroluminescence (EL) in poly(vinylcarbazole) led to a search for other electroluminescent materials covering other ranges of the visual spectrum. However, the development of electroluminescent organic devices was not successful at that point due to the relatively poor lifetimes and relatively low efficiencies.

Organic electroluminescent devices proved not to be competitive with incandescent light sources, and essentially all research was focused on traditional inorganic electroluminescent materials, since light-emitting devices (LEDs) based on these materials have been commercially available since 1960s^{7,9}.

In 1987, the group of Tang and Van Slyke at Eastman-Kodak demonstrated efficient electroluminescence (EL) in two layer sublimed molecular film devices comprised of a hole transporting layer of an aromatic diamine and emissive layer of 8-hydroxyquinoline aluminium (Alq3)⁹⁻¹³. This result provided a basic design for light emitting diode architecture, which was applicable to systems employing low molecular weight electroluminescent materials. The technique they used to emit light was to vacuum deposit small molecules to form a layered structure. The layered device structure was produced on an ITO (anode acts as hole injection layer) coated glass substrate over that electroluminescent material and a magnesium-silver alloy (cathode acts as electron injection layer) were vacuum evaporated one by one. The thin film layered structure permits a high electrical field at low voltage. Thus, light from thin film organic materials is usually produced at low voltage. High quality thin molecular layers were an important condition for the development of OLEDs^{7,8}.

In 1990, Burroughes et al. at the Cavendish Laboratories at Cambridge University presented the first LED using polymers as active material¹⁴. The active material used was a conjugated polymer^{3,13}. In comparison to the traditional solid state LED, the new organic approaches were believed to be much more efficient. In nature organic materials are in some cases able to perform in a chemical way a 100% relationship of energy

consumption versus emission of light, e.g. the fireflies. Unfortunately such high efficiency is unrealistic in fabricated electroluminescent devices^{7-9,12}.

Conjugated polymers, and small molecules (oligomers and metal complexes) are considered as the two classes for OLEDs⁷. Despite of the fact that the two approaches only emitted a small amount of light that lasted only a few minutes, it caused a major interest among other researchers and companies. Much because of the predicted features of the organic displays would overcome the advantages for other display techniques, e.g. low voltage, low weight and wide viewing angle.

The above classifications of light emitting organic layers in the organic light emitting devices both possess luminescent and conductive properties. To achieve accurate functions of the material, a modification of the specific characteristics of the material are often done. Oligomers and small molecules have molecular structures of relatively short characteristics and consequently low molecular weights. The most commonly used material with the most explored properties among the small molecules are hydroxyquinoline aluminium (Alq3) and oligomer p-hexaphenyl.

Conjugated polymers are composed of a long repeating chain of similar smaller molecules, called monomers. They possess consequently, compared to small molecules, a molecular weight twenty to fifty times higher. A frequently used conjugated polymer is the poly paraphenylene vinylene (PPV).

1.2 ELECTROLUMINESCENT MATERIALS USED FOR OLED

Materials used for the fabrication organic light emitting diodes are of organic origin and semi conducting in nature, during the fabrication of the OLED it's important to select an appropriate electoluminescent material for proper function and best performance.

The materials for OLED is broadly divide into two divisions.

- a. Polymers.
- b. Small Molecules.

a. POLYMERS

Besides their roles as inert binders, polymers have been used in OLEDs as electroluminescent materials since the late 1980s, when emission was observed in poly (1,4-phenylene vinylene).¹⁵ The major advantage of using polymers over small organic molecules is that polymers can be solution processed. The simplicity of solution processing equates to a low manufacturing cost, which can lead to techniques known as roll-to-roll processing and ink-jet printing¹⁶. Roll-to-roll processing is a technique in which a polymer solution is sprayed onto a large flexible substrate which already contains the anode. After deposition of the cathode, the substrate can then be cut into smaller sections depending on the final application of the OLED. Ink-jet printing is a high-resolution patterning of red, green, and blue light-emitting polymers using the same

technology found in an ink-jet printer. Based on a drop diameter of 20 μm and a 100 nm thick layer, ink-jet printing can use polymer solutions with concentrations as low as 1%¹⁶. Polymers in OLEDs are used as emissive as well as hole transport layer and electron transport layer.

ELECTRON-TRANSPORT POLYMERS

Many polymers have been designed and synthesized for application in OLEDs, but one of the most popular polymer for use in OLEDs is poly (*p*-phenylene vinylene) (PPV) and its derivatives as shown in Figure 1.1.^{17,18, 15-19} A readily soluble version of PPV can be made by the addition of alkyl chains (poly[2,3-bis(2-ethylhexyloxy-1,4-phenylene vinylene)] (BEH-PPV), however this results in the disruption of planarity of the polymer, decreasing the efficiency and brightness of the device.²⁰ Schmidt and coworkers were able to achieve brightness as high as 146 cd/m^2 (equivalent to an LCD monitor) at 9.5 V by blending a 2,5-dialkoxy-substituted poly(*p*-phenylene ethynylene) (EHO-OPPE) derivative with a polymeric triphenyldiamine²¹. One of the brightest device was prepared by using a distyrylbenzene derivative (Distyrylbenzene-blocksexi (ethylene oxide) (DSB-block-EO)), shown in Figure 1.1, reaching a brightness of 2000 cd/m^2 at 19 V.²² Besides brightness, another desirable quality is color tunability. By copolymerizing 2,5-didodecyloxy-*p*-phenylenebutadiynylene with a fluorine derivative and a thiophene derivative (PPPBs), as shown in Figure 1.1, the emission color can be tuned from blue to red²³. A variety of colors were also seen using poly (thiophene) derivative, with efficiencies ranging between 0.1-1%.²⁴

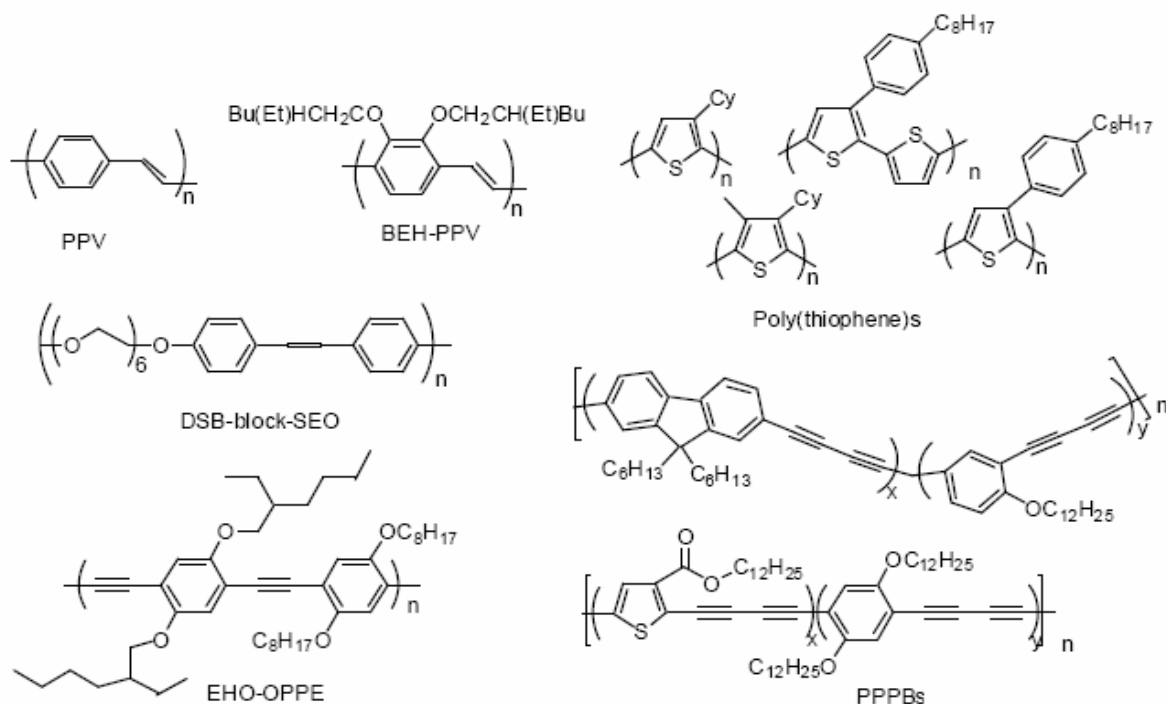


Figure 1.1 Structures of electron-transport polymers.

HOLE-TRANSPORTING POLYMERS

Research on hole-transport polymers, some of which are shown in Figure 1.2, have also led to improved efficiency.^{20,25-26} By copolymerizing both the hole- and electron-transporting derivatives of fluorenes, Morteani et al., have shown devices with a brightness of 100 cd/m^2 at 2.1 V that range in color from blue to red.²⁷ By using poly-(N-vinylcarbazole) (PVK) as the hole-transporting layer, Kido and co-workers reached a brightness of 3400 cd/m^2 at 14 V.²⁰ However, Jen and co-workers have obtained brightness as high as $59,000 \text{ cd/m}^2$ with their perfluorocyclobutane-based arylamine hole transporting materials (PFCBs).²⁶

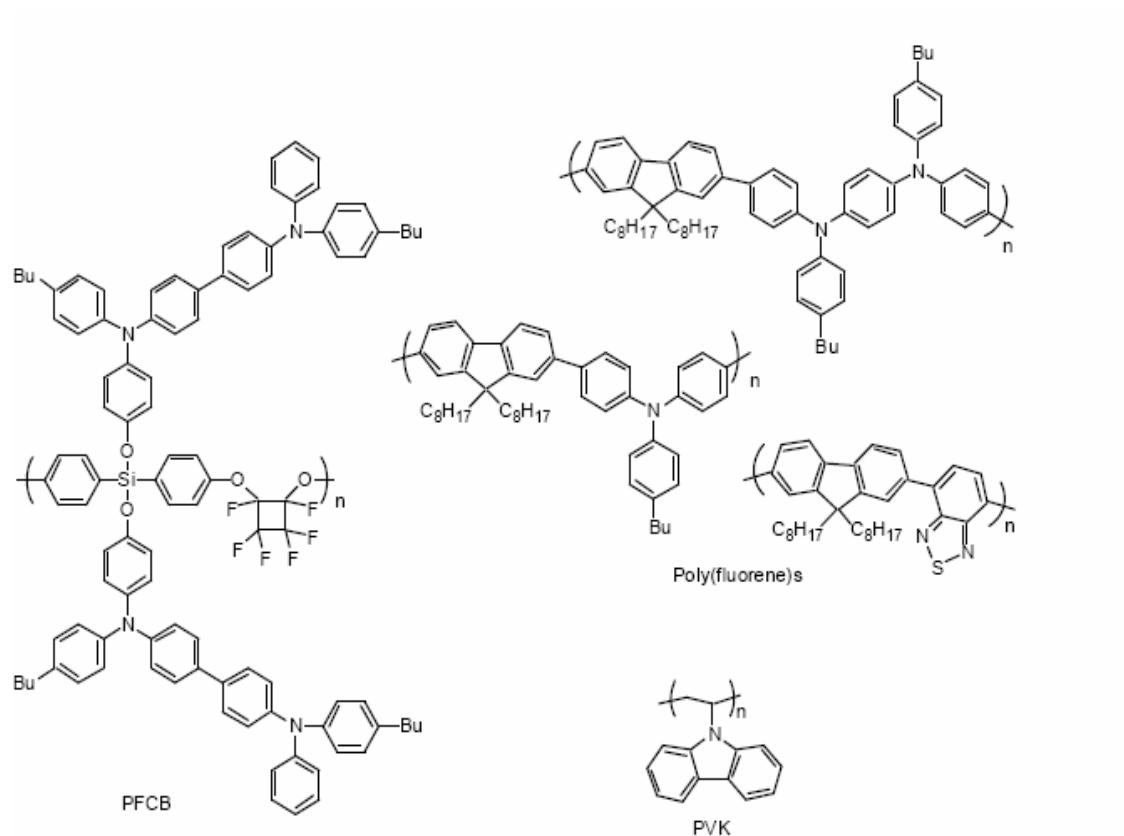


Figure 1.2 Structures of hole-transport polymers.

Even though much improvement of these polymeric systems has been seen over the past twenty years, the optimization of polymers can be very tedious. Polymers do have the advantage over small organic molecules of being solution processable; they are at a disadvantage when it comes to optimization. Small organic molecules can easily be modified in order to tune the properties of the OLED, whereas the monomers of the electroluminescent polymers must first be re-synthesized, then polymerized, and finally the polymers are re-tested in order to optimize the device.¹⁶ A more efficient method would be to attach the small organic molecules onto a polymeric backbone, thereby maintaining the ease of optimization associated with the small molecule while gaining the processability of a polymer.

b. SMALL MOLECULES

Small molecule materials for OLEDs are generally low molecular weight organic molecules or complexes of organic molecules. These are generally coated onto the suitable substrates by the process of vacuum deposition to yield thin amorphous films. However, they can be blended into a polymer matrix or grafted into a polymer backbone so that they can be applied easily by spin coating. The requirements for an organic small molecule or complex to be used in the form of an emission layer in the device are that it should be thermally stable to enable vacuum deposition, highly luminescent in the solid-state and should be thin-film forming. Also, it should be able to transport electrons with the desired efficiency. Although wide ranges of metal chelates are highly luminescent in solution, few are able to satisfy all the above criteria. The discovery of the highly successful tris (8-hydroxyquinoline) aluminum as an efficient electron transport and electroluminescent material lead to further research and development in this field, and now there are a wide variety of small molecule emitters with varied emission wavelengths to chose from. Because light emission from the Alq_3 complexes originates from the electronic transitions located on the quinolinolate ligands (ligand-centered excited states). The HOMOs are located on the phenoxide side of the ligand, while the LUMOs are located on the pyridine ring. Thus the attachment of electron-donating substituents to the phenolate ring results in a red-shifted emission, while the attachment of electron-donating substituents to the pyridine ring results in a blue-shifted emission from the complex. Additionally, the nature of the metal ion has been shown to have a profound effect on the quinolinolate photoluminescence and electroluminescence. With increased covalent nature of the metal-ligand bonding (primarily metal-nitrogen bond), the emission is red-

shifted, while the more ionic bond in strongly electropositive metal ions results in a blue shift.

Structures of some small molecule used in OLEDs are as below-

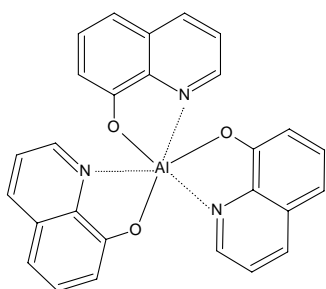


Fig 1.3 Tris (8-hydroxyquinoline) aluminum (Alq3)

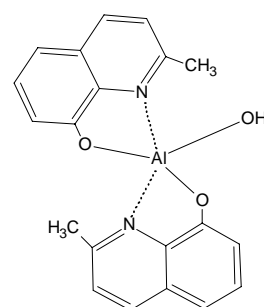


Fig1.4 Bis (8-hydroxy quinoline) Aluminum hydroxide

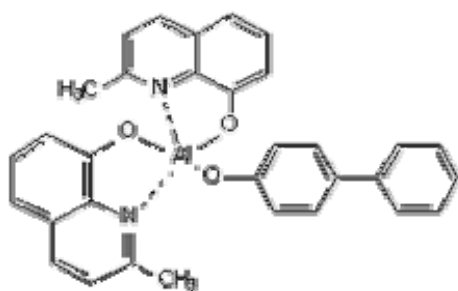


Fig1.5 Bis- (2-methyl-8-quinolinolato) aluminium

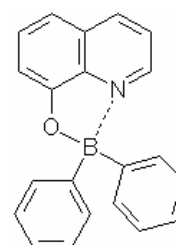


Fig.1.6. Diphenylborane-8-hydroxyquinolate

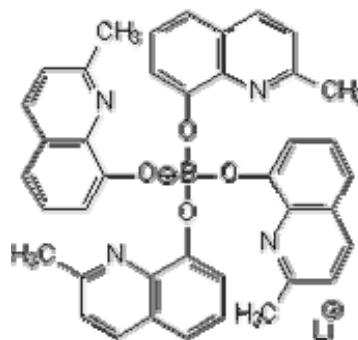
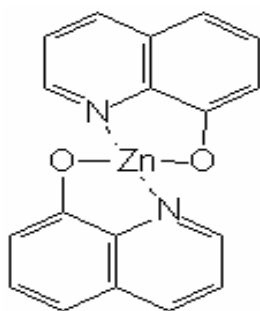


Fig.1.7 Bis (8-hydroxy quinolate)zinc Fig.1.8 Tetra (2-methyl-hydroxyquinolato)boron

PHOSPHORESCENT MATERIALS

The new developments in the modern OLED sciences and technology is the discovery of electro phosphorescence which overcome the limit, since phosphorescent material can generate emission from both triplet and singlet excitons. This lifts the upper limit of the internal quantum efficiency of the usual fluorescent dopant-based devices from 25% to nearly 100%. Phosphorescence is inherently a slower and less efficient process, but triplet states constitute the majority of electro generated excited states (~75%), so the successful utilization of the triplet manifold to produce light should undoubtedly increase the overall luminance. Utilization of triplet excitons in OLED was proposed several years ago lanthanide chelates have been examine for the devices.²⁹⁻³⁰ The design and synthesis of triplet emitting materials containing heavy-metal complexes, where strong spin-orbit coupling leads to singlet–triplet state mixing which removes the spin-forbidden nature of the radiative relaxation of triplet state, are therefore particularly important in achieving high-efficiency electro phosphorescence in OLEDs. Most of the efficient phosphorescent LEDs were fabricated using organic materials.^{31,32} Several examples are shown in Fig. 1.9.

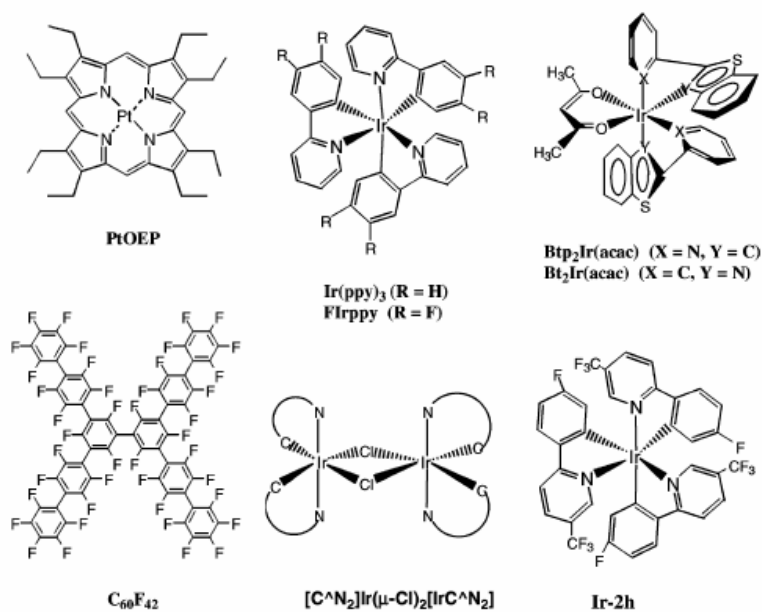


Fig. 1.9. Triplet emitting materials and related intermediates

The first triplet emitting device is based on the red 2,3,7,8,12,13,17,18-octaethyl-12H,23H-porphine platinum(II) (PtOEP) doped in CBP [82 ,85] having an external quantum yield of 5.6%. But, the relatively long phosphorescence lifetime (~50 ms) of PtOEP tends to result in triplet–triplet annihilation at high current [7]. As compared to PtOEP it was found that the red triplet phosphor, bis(2-(20-benzo[4,5-a]thienyl)pyridinato-N,C30) iridium(acetylacetonate) (Btp₂Ir(acac))³³ with a shorter phosphorescence lifetime (~4 ms) leads to a significant improvement in Z_{ext} reaching 2.5% at high current density of 100 mA/cm². The red EL spectrum of Btp₂Ir (acac) has a maximum at λ_{max} ¼ 616 nm with additional intensity peaks at 670 and 745 nm and the CIE coordinates are x ¼ 0:68; y ¼ 0:32. An even shorter lifetime (~1.8 ms) has recently been reported for Os complexes which were used as red electrophosphorescent dopants blended in poly (N-vinylcarbazole) and 2-t-butylphenyl-5- biphenyl-1,3,4-oxadiazole as the emitting layer in a polymer LED.³⁴ Because the emission originates from triplet metal-to-ligand charge-transfer excited state, the emission peaks of the reported Os

complexes, ranging from 620 to 650 nm, can be tuned by changing the structures of the ligands.

The osmium complexes trap both electrons and holes, which facilitates the direct recombination of holes and electrons on the dopant sites. The peak external quantum efficiency and brightness achieved from the complexes were 0.82% and 970 cd/m² with CIE_{x;y} = 0.65, 0.33. A tris-ortho-cyclometalated iridium complex based on pinene-substituted 2-phenylpyridine (Ir(mppy)₃) has recently been found to reduce concentration quenching because the sterically hindered pinene spacer in the phosphor molecule minimizes molecular aggregation or interaction.³⁵

One of the keys for highly efficient phosphorescent emission in OLEDs is to confine the triplet excitons generated within the emitting layer. Thus, by employing starburst perfluorinated phenylene (C₆₀F₄₂) as both hole and exciton blocking layer, and a starburst hole-transport material of 4,4',4''-tris(N-carbazolyl)triphenylamine as a host matrix for the Ir(ppy)₃ dopant in the emitter, a maximum external quantum efficiency reaches to 19.2%, and the efficiency is sustained over 15% even at high current densities of 10–20 mA/cm² which is better than the brightness of fluorescent tubes for lighting. The onset voltage of the electroluminescence is as low as 2.4 V and the peak power efficiency reaches 72 lm/W which fulfills the promise of OLED as a potential low-power display device.³⁶ This performance can be attributed to the efficient transfer of both singlet and triplet excited states of the host to Ir(ppy)₃, leading to high internal efficiency. Further advantage of Ir(ppy)₃ is that it has a short phosphorescent decay time of <1 ms which reduces saturation of the phosphor at high drive current conditions. In addition to emission from the iridium dopant, it is possible to transfer the exciton energy also to a

fluorescent dye by Förster energy transfer. The Ir dopant in this case acts as a sensitizer, utilizing both singlet and triplet excitons to efficiently pump a fluorescent dye³² and thus avoiding the quenching of phosphorescence by triplet–triplet annihilation.

The further improvement of operational lifetime of the red Btp₂ Ir(acac)₃ to ~10,000 h is possible by optimizing the architecture of a mixed-layer comprising a hole transporter, an electron transporter and a phosphorescent dopant as the emissive layer.³⁶ All of the iridium chelates can be synthesized by cyclometalation using IrCl₃·nH₂O onto an appropriate ligand such as 2-phenylbenzoxazole, 2-phenylbenzothiazole, 2-phenylpyridine and 2-phenylquinoline.³⁷ These reactions produce chloride-bridged dimers, [C^NN₂]Ir(m-Cl)₂[Ir C^NN₂] which can be transformed into a variety of different octahedral iridium(III) complexes [C^NN₂]Ir(LX). Judicious choice of the cyclometalating ligand [C^N] can lead to a variety of colors of emission that range from green to red. Recently, Du-Pont researchers have developed a new synthesis of organometallic iridium complexes that can be prepared in one step by heating IrCl₃·nH₂O in excess [CN] ligand in the presence of a catalytic amount of silver trifluoroacetate as promoter.³⁸ By this method, they have synthesized a variety of fluorinated and trifluoromethylated derivatives with emissions ranging from λ_{max} 506 to 595 nm. It was claimed that by replacing C–H bonds to C–F bonds by fluorination, there are several potential benefits: (1) the C–H bond is an effective promoter for radiationless decay of an excited state. Replacing it with a C–F bond of lower vibrational frequency can reduce the rate of radiationless deactivation and enhance the PL efficiency; (2) fluorinated compound usually can be sublimed better for thin film deposition; (3) introduction of C–F bond or CF₃ group can alter the molecular packing and minimize the self-quenching behavior; (4) fluorination can

enhance the electron mobility; (5) HOMO/LUMO levels can be modified by fluorination and thus allow the optimization of carrier injection and the tuning of EL color.

One of the bluest emissive triplet complexes reported is fac-tris[2-(4,5-difluorophenyl)pyridine-C₂,N] iridium(III) known as Firppy³⁹ which has $\lambda_{\text{max}} \approx 500$ nm in polystyrene with a quantum yield of $\sim 22\%$ and a triplet lifetime of ~ 4.5 ms. Using Al as the cathode, Ir-2h as the luminescent layer, 4,7-diphenyl-1,10-phenanthroline (DPA) as the electrontransport layer and bis[4-(N,Ndiethylamino)-2-methylphenyl]-(4-methylphenyl)methane (MPMP) as hole-transport layer on top of ITO/glass, intense electroluminescence at 525 nm with an efficiency of 20 cd/A and a maximum radiance of 4800 cd/m² was achieved.

Now, the bluest phosphorescent iridium complex is Firpic⁴⁰ which was reported by Thompson and his associates at Universal Display Corp. in the ICEL-3 conference (Fig. 1.11). In their device of [ITO/NPB/CBP | Firpic/BAIq/Mg:Ag], the external quantum efficiency was reported to reach 5.5% with EL efficiencies of 5 lm/W and 12 cd/A at 100 cd/m². Its EL emission peaks at 470 nm with a CIE coordinates of $x \approx 0.14$; $y \approx 0.30$ which is still somewhat cyan in color, but definitely bluer than those of Firppy. In the poster, it was also disclosed that a t-butyl-isocyanide

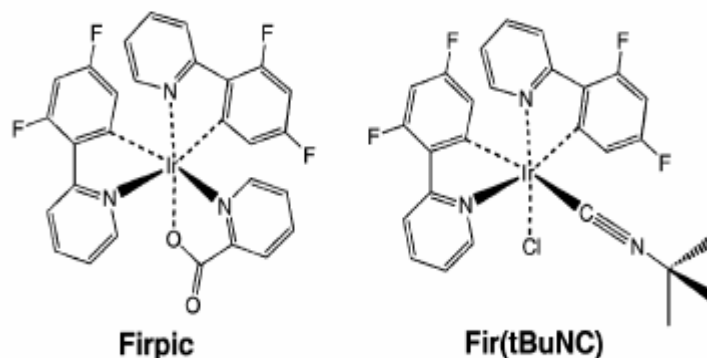


Fig. 1.10. Blue-emitting phosphorescent materials.

(t-BuNC) ligated iridium complex (Fir(tBuNC)Cl) actually had a triplet blue photoluminescence peak at 450 nm in methylene chloride. But, unfortunately it was too unstable to be fabricated into a device. Both of these new blue iridium complexes were isolated as a mixture of facial and meridional isomers. One of these white OLED devices which attained a maximum external quantum efficiency of $5.2 \pm 0.5\%$, maximum EL efficiency of 11 ± 1 cd/A, a maximum luminous efficiency of 6.4 ± 0.6 lm/W with CIEx;y $\frac{1}{4} \frac{1}{2} 0.37; 0.40$ at 10 mA/cm² and a maximum luminance of 31,000 cd/ m² at 14 V, is among the best ever reported to date.

Red electrophosphorescence from light-emitting devices based on ruthenium(II)-complex $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$ -doped wide-band-gap semiconductive polymers, i.e., poly(vinylcarbazole) (PVK), polydihexylfluorene (PDHF), and ladderlike polyphenylene (LPPP), as the emitting layers are reported.⁴¹ However, only highly efficient energy transfer was investigated in a PVK system, not only because of the relatively longer lifetime of its excited state compared with PDHF and LPPP, but also because of the good chemical compatibility of $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$ with PVK. The EL spectra show the characteristic spectrum of $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$, at a peak of 612 nm and Commission

Internationale del'Eclairage of (0.62, 0.37). The optimized device indium tin oxide/ PVK: 5 wt% [Ru(4,7-Ph₂-phen)₃]²⁺/PBD/Alq₃ /LiF/Al shows the maximum luminance efficiency and power efficiency as 8.6 cd/A and 2.1 lm/W, respectively.

Further high efficiency electrophosphorescence (EPH) in organic light-emitting devices was achieved employing a cyclometallated platinum [Pt(II)]-complexes-doped blend of *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4' diamine and bisphenol-A-polycarbonate as the emitting layer. Using bis-[2-(5-trimethylsilanyl-thiophen-2-yl)-pyridine] Pt(II) [Pt(thpy-SiMe₃)] as a phosphorescent dopant, a maximum EPH external quantum efficiency of 11.560.5% photons/ carrier was achieved with a three-fold lower roll-off factor at increasing current density, compared with commonly used Pt-based dye 2,3,7,8,12,13,17,18-octaethyl-21*H*, 23*H*-porphine platinum (II) (PtOEP). The emission spectrum of the device peaking at >590 nm shifts the chromaticity coordinates toward the orange relative to the PtOEP-based devices.⁴²

In the Similar work highly efficient red-emitting electro phosphorescent devices were fabricated by doping an iridium (Ir) complex containing trifluoromethyl (CF₃)-substituted pyrimidine ligand into a conjugated bipolar polyfluorene with triphenylamine and oxadiazole as side chains. The device efficiency can be enhanced through effective exciton confinement using a layer of 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene on the cathode side and a layer of in situ polymerized tetraphenyldiamine-perfluorocyclobutane on the anode side. For a blend with 5 wt % of the Ir complex, a maximum external quantum efficiency of 7.9 photon/electron % and a maximum brightness of 15800 cd/m² are reached with Commission Internationale de L'Eclairage chromaticity coordinates of $x=0.65$ and $y=0$.⁴³

In 2004 Hino et al⁴⁴ demonstrated high efficiency electro phosphorescence in organic light-emitting devices employing a phosphorescent dye doped into a low-molecule material. Methoxy-substituted 1,3,5-tris[4-(diphenylamino)phenyl]benzene (TDAPB) was selected as the host material for the phosphorescent dopant fac-tris(2-phenylpyridine) iridium(III) [Ir(ppy)₃], and organic films were fabricated by spin-coating. A peak external quantum efficiency of 8.2% (29cd/A), luminous power efficiency of 17.3 lm/W, and luminance of 33,000 cd/m² were achieved at 9.4 V with a 90 nm-thick emitting layer. Emission from the host TDAPB material was not observed in the electroluminescence (EL) and photoluminescence (PL) spectra. The decrease in efficiencies at a high current is analyzed using the triplet–triplet annihilation model. The high performance for the simple device structure in this study is attributed to excellent film forming properties of the material and efficient energy transfer from the host to dopants.

Recently Qin et al in 2005⁴⁵ studied a phosphorescent dye, triss1-phenylisoquinolined iridium (III) [Ir(piq)₃] doped interface of 4,48,49-trisscarbazol-9-yl-d-triphenylamine (TCTA) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) has been studied in organic light emitting diodes. Two devices with different emissive interfaces, TCTA+6% Irspiqd₃/BCP and TCTA+6% Ir(piq)₃/BCP+1% Ir(piq)₃, exhibited nearly the same red Irspiqd₃ emissions and (*I*–*V*) characteristics. However, the second device showed higher efficiency and luminance than the first device over the whole voltage range. The maximum efficiency of 6.0 cd/A reached at 0.026 mA/cm² in the second device was 30% higher than that of 4.6 cd/A reached at 0.032 mA/cm² in the first device. The improved performance of the second device is attributed to the fact that the

excitons can be formed on both sides of the TCTA/BCP interface and can be more efficiently collected with the additional 1% Ir(ppy)₃ doped in the BCP layer. Therefore, the exciton-collecting structure, doping phosphorescent dyes into both sides of the TCTA/BCP interface, is believed to be a very useful way to optimize the performance of phosphorescent organic light emitting diodes.

Zhang et al⁴⁶ reported white organic light-emitting devices (WOLEDs) based on 4,48-bis(2,28-diphenyl vinyl)-1,18-biphenyl (DPVBi) and phosphorescence sensitized 5,6,11,12-tetraphenylnaphthacene (rubrene). In the devices, DPVBi acts as a blue light-emitting layer, and rubrene sensitized by a phosphorescent material, fac tris (2-phenylpyridine) iridium [Ir(ppy)₃], acts as a yellow light-emitting layer. The devices have a maximum brightness of 8633cd/m² (at a driving voltage of 22 V). The maximum luminous efficiency is 9.22 cd/A (at a current density of 0.90mA/cm²). Commission international De L'Eclairage coordination of (0.30,0.37) is obtained for luminanceranging from 100 to 1000 cd/m².

Kawamura⁴⁷ demonstrate that three Ir(III) complexes used as principal dopants in organic electro phosphorescent diodes have very high photoluminescence quantum efficiency (η_{PL}) in a solid-state film. The green emitting complex, fac-triss2-phenylpyridinatodiridium(III) [Ir(ppy)₃], the red-emitting bis[2-(2'-benzothienyl)pyridinato-N,C^{3'}) (acetylacetonato)iridium(III) [Btp₂Ir(acac)], and the blue complex bis[(4,6-difluorophenyl)pyridinato-N,C^{2'}](picolinato)iridium(III) (FIrpic) were prepared as codeposited films of varying concentration with 4,4'-bis(*N*-carbazolyl)-2,2'-biphenyl, a commonly used host material. The maximum η_{PL} values for Ir(ppy)₃, Btp₂Ir(acac), and FIrpic were, respectively, 97%±2% (at 1.5 mol%), 51%±1% (at 1.4

mol%), and $78\% \pm 1\%$ (at 15 mol%). Furthermore, we also observed that the maximum η_{PL} of FIrpic reached $99\% \pm 1\%$ when doped into the high triplet energy host, *m*-biss*N*-carbazolyldbenzene, at an optimal concentration of 1.2 mol%.

1.3 BASIC PRINCIPLES OF OLED

The basic structure of an OLED is shown in Figure 1.11. The basic principles of an OLED include the injection of electrons from one electrode and injection of holes from the other electrode. The electrons move through the electron-transport layer (ETL), while the holes move through the hole-transport layer (HTL), until the capture of the oppositely charged carriers or recombination, followed by the radiative decay of the excited electron-hole state or exciton. The color of the light emitted during this process is determined by the band gap of the exciton.

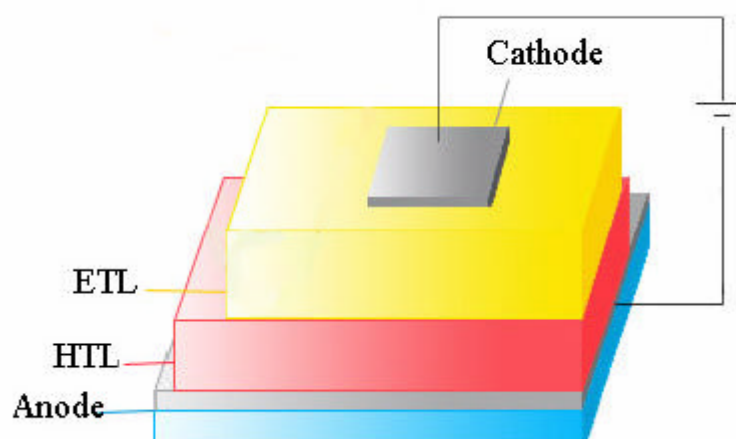


Figure 1.11. Structure of OLED Device

In order to obtain high efficiencies and a long lifetime, a device must contain the following features: low injection barriers at the interface between the metal electrodes and organic material, allowing for as many charges as possible into the system; a balance of electron and hole density and mobility, so that, for example, the majority of the holes do not reach the cathode before they are captured by an electron, decreasing the efficiency of the system; a recombination zone away from the metal cathode, again so that the holes are not annihilated by the cathode before recombination; and a high thermal stability of all of the organic material so that they can sustain fabrication conditions.¹⁶

PROPERTIES OF CATHODE AND ANODE

In order to obtain a balanced injection, where the rate of injection of positive charges is equal to the rate of injection of negative charges, a low work function metal, such as calcium, magnesium, or aluminum as well as alloys containing these metals, is employed as the cathode. The low work function is necessary to decrease the energy barrier for the electron injection (ϕ_{Ee}) into the organic material, as shown in Figure 1.13.¹⁶ The organic material that will act as the electron-transport layer should then have an electron affinity (E_a) close to the work function of the cathode (F_{cat}).¹⁶ If a close match between the electron affinity and the work function of the cathode cannot be found, then inserting a metal-insulating layer, such as lithium fluoride, between the metal cathode and the electron-transport material can provide an intermediate level between the cathode and the LUMO of the electron-transport material.⁴⁸ The work function of the anode (F_{an}), usually indium-tin-oxide (ITO) should closely match the ionization potential (I_p) of the hole-transport material and should contain a low energy barrier for hole injection

(Eh).6 Other properties of anodes currently being used in OLEDs include good transmittance in the visible and near infrared region, low electrical resistivity, and easy processability.⁴⁹

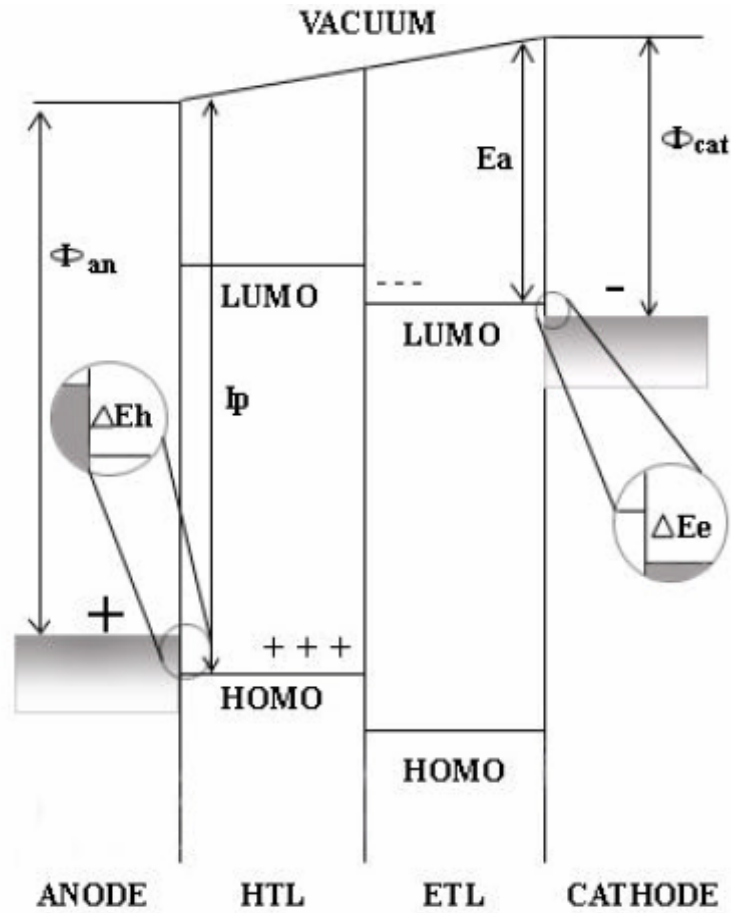
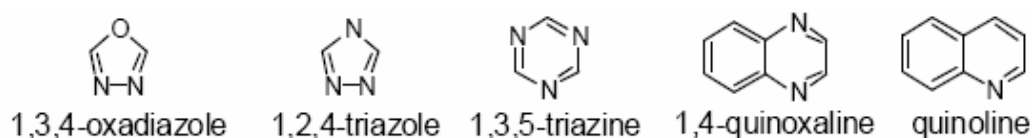


Figure 1.12 Schematic energy-level diagrams for a four-layer device containing an anode, Hole-transport layer (HTL), electron-transport layer (ETL), and a cathode.

PROPERTIES OF ELECTRON TRANSPORT AND HOLE-TRANSPORT MATERIALS

Electron-transport materials usually consist of Electron deficient heterocycles containing imine nitrogen atoms in an aromatic ring.⁵⁰ Some examples are shown in Figure 1.13. heterocyclic moieties with high reduction potentials reduce the interface barriers between the organic material and the cathode.⁵⁰ They also have high ionization potential or low HOMO, which blocks holes from traveling through the material, and large electron affinities or low LUMO, which assists in the injection of electrons.⁵⁰ The oxadiazoles and triazoles, which both have high thermal stability, are generally used as hole-blocking layers between the emitting layer and the cathode in a multilayer device.^{51,52} Both quinoxalines and quinolines are electroluminescent materials,

ELECTRON TRANSPORT MATERIALS



HOLE TRANSPORT MATERIALS

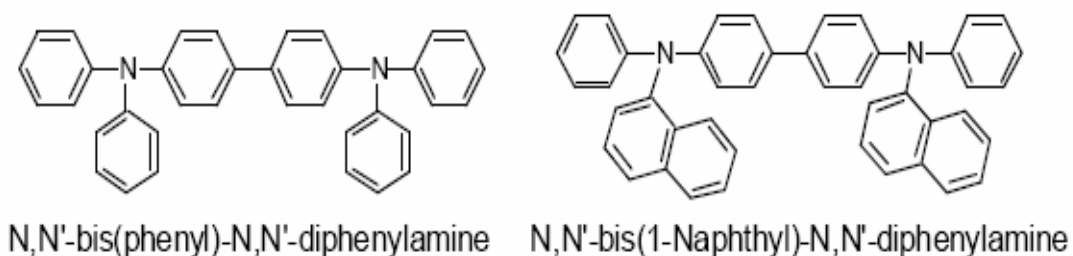


Figure 1.13 Structures of Electron- and Hole-Transport Materials.

These compounds to be used as the electron-transport and emitting layers in devices.^{53,54} The biggest drawback with all of these heterocycles is their processability. These small molecules must be vacuum deposited, while their polymer analogs have limited solubility, making them difficult to process.⁵⁰

Compared to the electron-transport materials, the hole-transport materials such as triarylaminines, also shown in Figure 1.14, have small ionization potentials or high HOMO and small electron affinities or high LUMO which assist in hole injection and in electron blocking, respectively.⁵⁰ The properties of these compounds, such as the glass transition temperature and the ionization potential, can be improved by the addition of electron withdrawing groups to the phenyl ring or by replacing the biphenyl moiety with a fluorene derivative.^{55,56} In contrast to the polymeric electron-transport materials, the polymer analogs of the hole-transport materials are readily soluble.^{57,58}

An optional emission layer (EML) can be used in OLEDs, which would be the location of recombination and the radiative decay. The electronic excitation energy (E^*) or band gap energy of the HTL and the ETL should be higher than that of the EML.¹³ Efficient OLED can be fabricated by following these conditions:⁵⁰

$$I_p(\text{ITO}) = I_p(\text{HTL}) \sim I_p(\text{EML}) \sim I_p(\text{ETL}) \quad (1)$$

$$E_a(\text{HTL}) \sim E_a(\text{EML}) \sim E_a(\text{ETL}) = I_p(\text{cathode}) \quad (2)$$

$$E^*(\text{HTL}) > E^*(\text{EML}) < E^*(\text{ETL}) \quad (3)$$

1.4 PATHWAY OF RADIATIVE DECAY

Charge carrier recombination is a bimolecular reaction between an electron and a positive charge. Electrons enter the system at the cathode and migrate towards the anode. During the migration, the electron can encounter a positive charge and recombine to form an excited state or the electron can transverse through the entire sample and discharge at the anode. One requirement for recombination is low mobility of one of the charges. This will create a high local charge density which will ensure the other charge will pass within a collision capture radius.¹⁷ The neutral bound excited state of an electron and a hole, called an exciton, is formed from two spin $\frac{1}{2}$ charges. Assuming that the recombination process is spin-independent, excitons are formed in a 3:1 ratio of triplet to singlet state, where only 25% of all recombination form a singlet state. Fluorescence is the spin-allowed radiative decay of excitons from the singlet state.¹⁷ Triplet excitons do not produce light except when triplet-triplet annihilation occurs, which is known as phosphorescence.¹⁷

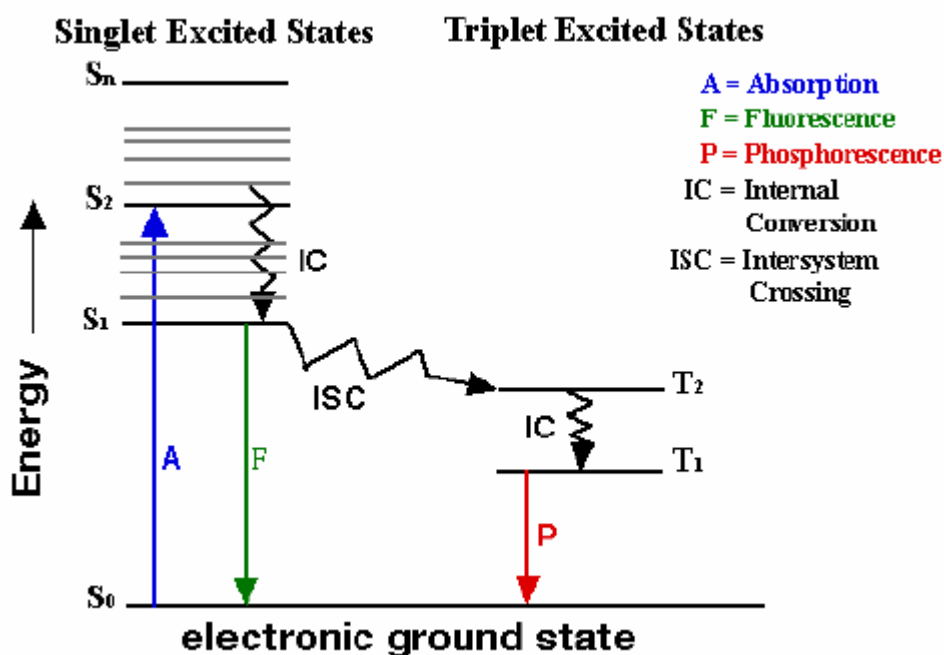


Figure 1.14 Jablonski diagram showing pathway of absorption, fluorescence, and phosphorescence.

While phosphorescent devices are highly desirable, fluorescence is the emission process used in the majority of the devices fabricated, thereby quantum efficiencies of 25% are the highest achievable efficiency for these devices. The main source for nonradiative decay or loss of efficiency in solid state materials is the quenching of the excited state due to either impurities or energy transfer. Diluting the active chromophore in an inert binder (such as an electrically- inert polymer) will cause energy transfer to decrease, but brightness will also decrease due to the lower injection rate.

1.5 ADVANTAGES

Organic light emitting diodes are now came out of laboratory trials and since last few years they have been applied in the microelectronic gadgets to enhance efficiency and lifespan of the gadget. The miniaturization of the electronic gadgets in future will be possible. The most advantageous thing going to happen that the shape and size of illumination system will change dramatically. Some of the most important advantages that will lead the development of the OLEDs as one of the feasible technologies are

- Enhanced brightness, contrast and low glare,
- Improved colour variation and resolution,
- Reduced cost on manufacturing and power consumption,
- Ultra-light weight and ultra-thin devices are possible,
- Wide viewing angle nearly 160° ,
- Wide operating temperature range,
- Inherent ruggedness,
- Large area coatings,
- Device can be fabricated in any shape,
- Variable pixel size from displays to large area illumination,
- Low operating voltage (2 V) and fast switching speed,
- Almost two-dimensional light source is possible,
- No back light required for video display,
- Can be spin coated on the substrate and
- Ink-jet printing technology possibly will reduce the cost of OLEDs so effectively that it could be affordable to general public.

1.6 INHIBITING FACTORS

Some of the inhibiting factors that are the concern of the general applications of OLEDs are short operational and shelf life, stability at high brightness levels, low device efficiency. Complex device structure may affect the cost of manufacturing. Uniformity of the coating for large area lighting sources is the main concern.

1.7 ADVANCES AND APPLICATIONS

We have only begun to imagine what OLED technology can create in the way of products, applications, job creation and new markets. The technology will not only improve existing methods of illumination but will create entirely new lighting product possibilities. OLEDs will create new markets where distributed sources of light can be applied, or are even desirable.

The focus of the OLED industry is now on the application in displays. The first application other than in display will probably be backlighting (such as LC displays), and, on a large scale, for location maps in shopping malls, advertising signs etc. Lightweight, thinness and flexibility will allow different mounting options, which in turn will motivate a shift from the conventional light bulbs. One can envision that ceiling or wall panels made of OLEDs can light commercial buildings in future. The desired luminescence will vary according to the applications.

Some recent applications that have been realized during last few years are-

- Pioneer introduced the first commercially available OLED based display in 1997.

- It was a passive matrix display used for car radio faceplates.

-Small molecules based displays were also found in Motorola cellular phones by 2000.

-More recently, the first commercially available polymer based LEDs have been sold in a simple passive matrix scheme as displays in MP3 players made by Delta Optoelectronics.

-In a well published Phillips electric razor displayed as prominently as James Bond's newest gadget in the movie "Die Another Day".

Some future applications of OLEDs are- large scale displays, "smart panels", ultra-light weight wall hanging TV monitors, large screen computer monitors, light panels for residential and commercial buildings, lighting for advertising sign boards, office windows, walls and partitions that could be used as the computer screens, colour changing lighting panels, and walls for home and office etc.

CHAPTER 2 MATERIAL CHARACTERIZATION AND DEVICE FABRICATION TECHNIQUE

2.1. MATERIALS CHARACTERIZATION

Characterizing the material by various characterization techniques as listed below basically constitute characterization of organic light emitting diodes. In material characterization basically we try to characterize the synthesized material by variety of techniques to assure that the appropriate materials with suitable properties are synthesized. Some of the characterization techniques used for the characterization of materials is listed below.

2.1. a. ULTRAVOILET & VISIBLE SPECRTOSCOPY.

2.2. b. FOURIER TRANSFORMS INFRARED SPECTROSCOPY (FT-IR).

2.3. THERMAL ANALYSIS.

- a. DIFFERENTIAL SCANNING CALORIMETRY (D.S.C).
- b. THERMOGRAVIMETRIC ANALYSIS (T.G.A).

2.1. A. UV-VISIBLE SPECTROSCOPY

A diagram of the components of a typical spectrometer is shown in the following diagram. The functioning of this instrument is relatively straightforward. A beam of light from a visible and/or UV light source (colored red) is separated into its component

wavelengths by a prism or diffraction grating. Each monochromatic (single wavelength) beam in turn is split into two equal intensity beams by a half-mirrored device. One beam, the sample beam (colored magenta), passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The other beam, the reference (colored blue), passes through an identical cuvette containing only the solvent. The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as I_0 . The intensity of the sample beam is defined as I . Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm.

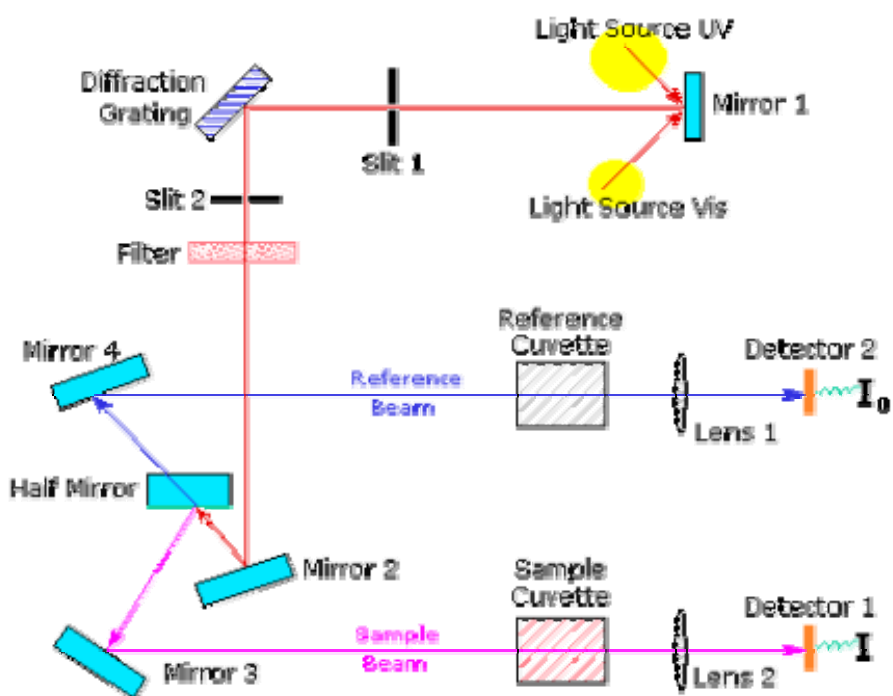


Fig 2.1. Block diagram of UV-Vis spectrometer

If the sample compound does not absorb light of a given wavelength, $I = I_0$. However, if the sample compound absorbs light then I is less than I_0 , and this difference may be

plotted on a graph versus wavelength, as shown on the right. Absorption may be presented as transmittance ($T = I/I_0$) or absorbance ($A = \log I_0/I$). If no absorption has occurred, $T = 1.0$ and $A = 0$. Most spectrometers display absorbance on the vertical axis, and the commonly observed range is from 0 (100% transmittance) to 2 (1% transmittance). The wavelength of maximum absorbance is a characteristic value, designated as λ_{\max}

Different compounds may have very different absorption maxima and absorbances. Intensely absorbing compounds must be examined in dilute solution, so that significant light energy is received by the detector, and this requires the use of completely transparent (non-absorbing) solvents. The most commonly used solvents are water, ethanol, hexane and cyclohexane.

2.1.b. FOURIER TRANSFORMS INFRA-RED (FT-IR) SPECTROSCOPY

A molecule absorbs radiation only when the natural frequency of vibration of some part of molecule (i.e. atoms or group of atoms comprising it) is the same as the frequency of the incident radiation. After absorbing the correct wavelength of radiation, the molecule vibrates at increased amplitude. This occurs at the expense of the energy of the IR radiation, which has been absorbed.

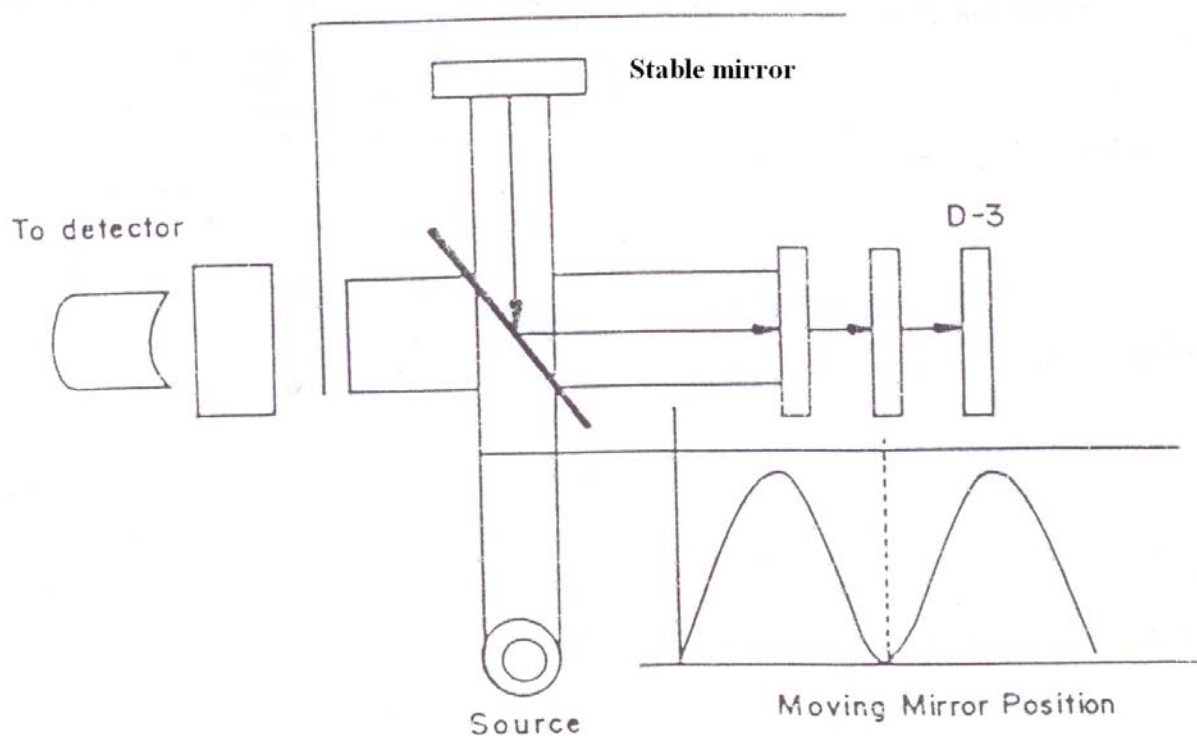


Fig 2.2. Basic principle of optical detection

Infrared spectroscopy is one of the most powerful analytical technique, which offers the possibility over the other usual method of structural analysis (X-ray diffraction, electron spin resonance, etc) is that its provides useful information about the structure of the molecules and bonding quickly, without tore-some evaluation method. Moreover, FT-IR provides a very faster of identifying chemical structures especially those of the organic ones.

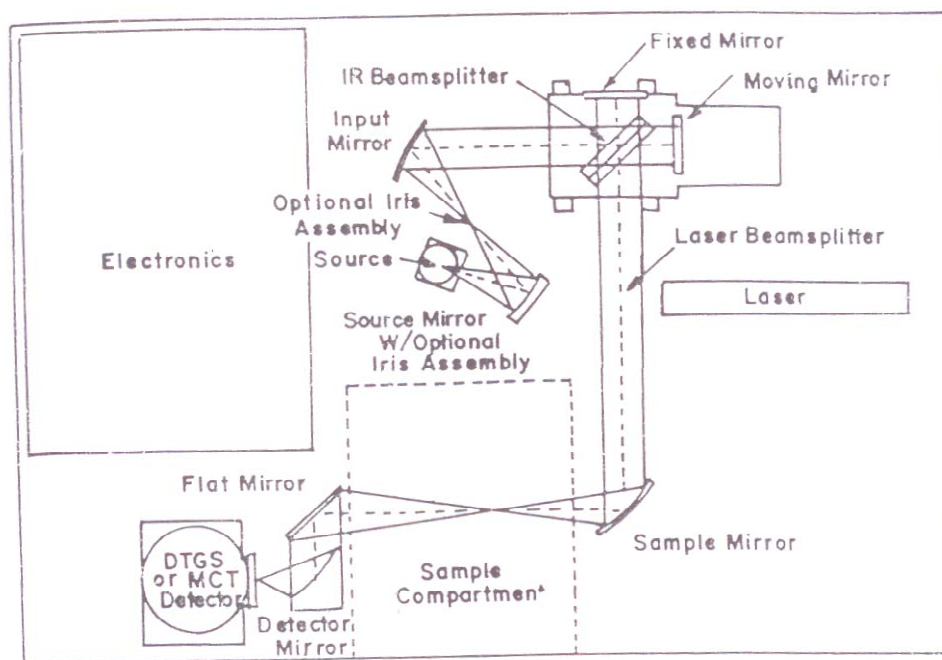


Fig 2.3. Set up of FT-IR(modle510p)

FT-IR spectroscopy employs an interferometer in place of monochromatic (fig). This device generates the Fourier transform of the infra-red spectrum, which is converted to spectrum itself by a computer. This approach has the advantageous of providing much higher source radiation throughput, incrsed signals-to-noise (S/N) ratio and higher wave number accuracy than is possible with a conventional light dispersive spectrometer.

The technique is based upon the simple fact that a chemical substance shows marked selective absorption in infrared region giving rise to close- packed absorption bands, called an IR absorption spectrum, which may extend over a wide wavelength range. Various bands in an IR spectrum correspond to characteristic functional groups and bonds

present in the chemical substance. IR spectrum of a chemical substance is thus a fingerprint for its identification. Band position in infrared spectrum may be expressed conveniently by wave number $\tilde{\nu}$, whose unit is cm^{-1} . The relation between velocity c , wavelength λ and frequency $\tilde{\nu}$ is as follows;

$$\tilde{\nu} = c/\lambda \text{ or } \tilde{\nu}/\text{cm}^{-1} = 1/\lambda$$

Band intensities in IR spectrum may be expressed either as transmittance (T) or absorbance (A). Transmittance is defined as the ratio of the radiant power transmitted by a sample to the radiant power incident on the sample. In most spectrums transmittance (T) versus wave number (cm^{-1}) has been plotted.

2.2. THERMAL CHARACTERIZATION

Thermal characterization encompasses various analytical methods such as thermogravimetric analysis (TGA), Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC) and Thermomechanical Analysis (TMA etc). IN the present work, DSC and TGA were used for the thermal studies of the chemically synthesized electroluminescent materials.

2.2. A. DIFFERENTIAL SCANNING CALORIMETRY

In DSC one estimates the heat flow thereby obtaining information about the nature of the reaction viz: exothermic or endothermic of given material at different temperatures. It measures the difference in the heat flow between the sample to be tested and known standard. In other words, in DSC the heat flow into or from a sample chamber is compared to a reference chamber and is measured as a function of time and temperature.

A Differential Scanning Calorimeter (DSC 7) of Perkin –Elmer was used in the temperature range -170°C to 200°C , with liquid nitrogen subambient accessory. For operation at or below room temperature (up to -50°C), the DSC 7 is equipped with an insulated reservoir, which allow the use of an ice water coolant. The block diagram of the DSC is given in Fig.2.4

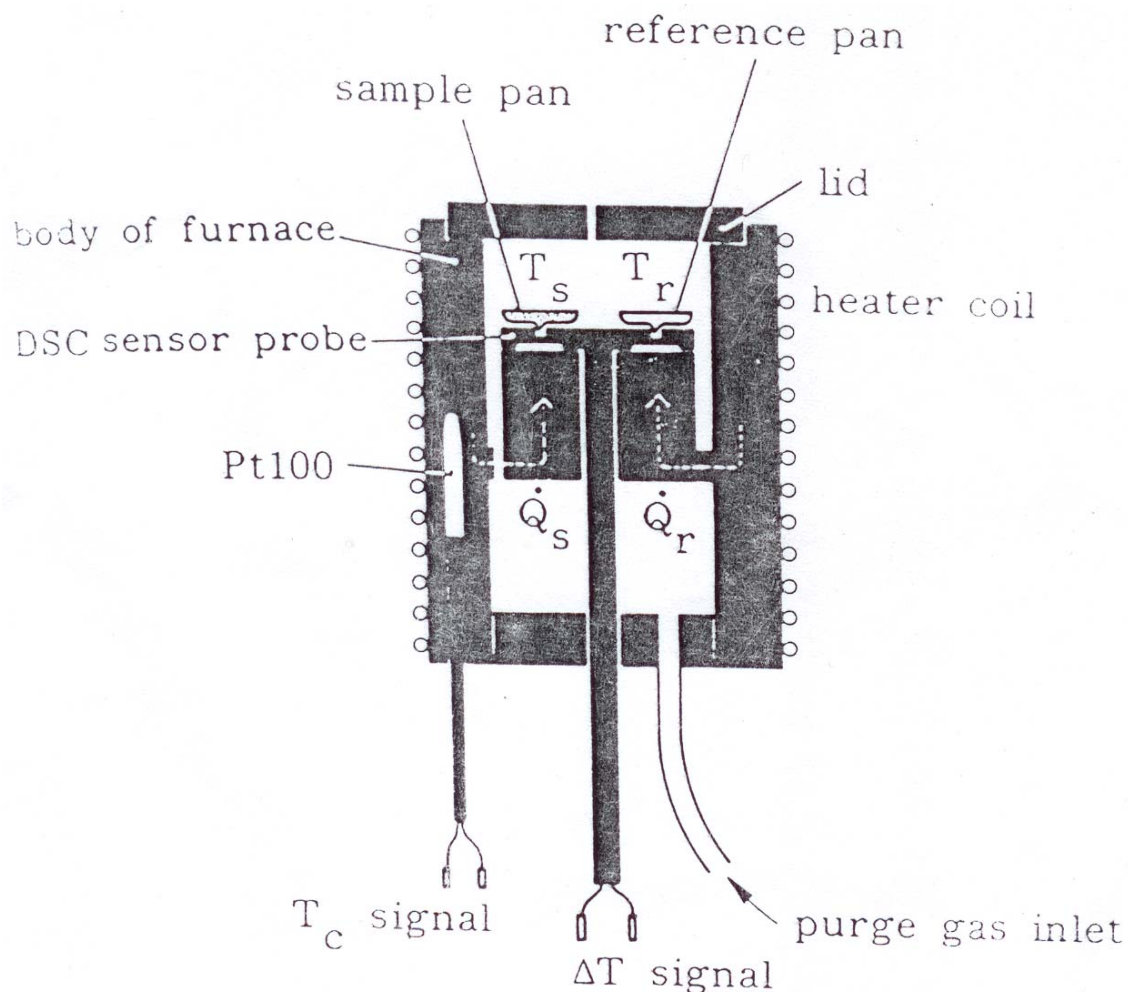


Fig 2.4 Block diagram of DSC

In Fig.2.4. T_s and T_r are the sample and reference pans respectively which are made of platinum. Aluminium pans are used as the sample holder .6-14 mg of the known sample in form of powder is taken in aluminium pans and covered it with the aluminium lid provided. The aluminium pan containing the sample is placed in sample pan and empty al

pan is placed in reference pan. Nitrogen gas is purged continuously in the chamber during the experiment to minimize heat dissipation. The difference in quantity of the heat is measured as function of temperature. For all the measurements the temperature is varied from room temperature to 500⁰C.

The DSC was calibrated with indium and zinc whose melting temperatures are 158⁰C and 425⁰C respectively. The base line was performed by keeping two empty aluminium pans in both the sample and the reference chambers. The base line was subtracted for each thermogram, 10 mg of sample is kept in aluminium sample holder at the same temperature through the use of an automatic compensator that senses any difference in temperature and makes appropriate adjustment. The heat compensation value is recorded as a function of heat flow rate. A cooling device is used to cool down the temperature of the system.

The other analysis, like determination of glass transition temperature, melting temperature and degradation temperature was performed by using the same equipment.

2.2. b. THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) gives information about the thermal stability including degradation kinetics of materials. In TGA, unlike DSC, the loss of weight of material as a function of temperature is measured. This loss is analyzed to look for the decomposition of materials. This technique is used to measure only reaction involving mass changes. The weight change are measured using a highly sensitive deflection type thermobalance capable of reproducing mass changes as small as $\pm 1.0 \mu\text{g}$ and depending

on the objective of experiment, the sample can be bathed in an inert atmosphere using gases such as Nitrogen or Argon.

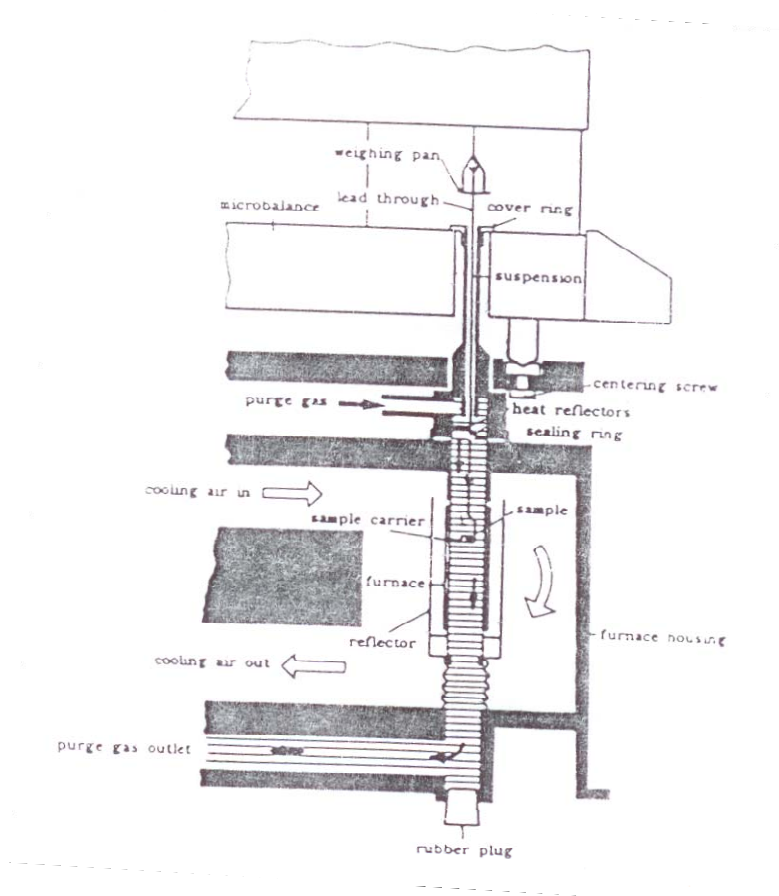


Fig 2.5. Construction of furnace and suspension led to TGA

In present studies, the samples were analyzed by using a microprocessor controlled mettler 3000 model using N₂ gas as a carrier at flow rate of (60-65 ml./min.) within a temperature range from 50⁰ C to 600⁰ C at a heating rate of 20⁰C/min. It comprises of a TC 10A TA microprocessor and TG-50 thermobalance. Figure 2.5. gives the construction of the thermobalance (TG-50) used in mettler TA 3000, used for the present investigation. Thermobalance consists of a furnace which can be heated at a controlled rate up to 1000⁰C in a desired atmosphere using a controlled flow of gases.

2.3. DEVICE FABRICATION TECHNIQUES

Fabrications of a OLED includes the deposition of a thin film (polymer or small molecules) over a glass substrate which is already coated with Indium tin Oxide (ITO) which is the anode and a low work function metal is the cathode. Typically organic layer thickness is nearly 100 nm.

A deposited thin film is a layer on a surface having properties that differ from those of the bulk material (substrate) that has been formed by the addition of solid materials to the surface. Generally, the substrate material cannot be detected in the film, which can be an organic or inorganic material. This surface layer differs from surface conversion where the surface is chemically converted to another material, e.g., anodization of aluminium. The term thin film is generally applied to layers that have thicknesses on the order of several micrometers or less. These films may be as thin as a few atomic layers. In many cases, adding atoms or molecules to a substrate surface one at a time forms thin films. Thicker layers are generally called coatings. Although the same processes that are used to form thin films can often form coatings, there are some coating processes that are not applicable to forming thin films. For example, thermal spray coating processes, which melt small particles, accelerate them to high velocities, and splat-cool them on the surfaces, are not applicable to forming thin films.

The properties of thin films generally differ from the values for the materials in the bulk form. In many cases, the growth and properties of thin films are affected by the

properties of the underlying substrate material. The properties of the film can also be affected by the high surface to volume ratio of the film. Many techniques are used for device fabrication, one of them we used for device fabrication was vacuum evaporation technique.

2.3.a. VACUUM EVAPORATION TECHNIQUE

Vacuum deposition, sometimes called vacuum evaporation technique, is a major physical deposition technique that is extensively used for depositing thin films on the surface of a substrate. The vacuum thermal evaporation deposition technique consists in heating until evaporation of the material to be deposited. The material vapor finally condenses in form of thin film on the cold substrate surface and on the vacuum chamber walls. Usually low pressures are used, about 10^{-6} or 10^{-5} Torr, to avoid reaction between the vapor and atmosphere. At these low pressures, the mean free path of vapor atoms is the same order as the vacuum chamber dimensions, so these particles travel in straight lines from the evaporation source towards the substrate. This originates 'shadowing' phenomena with 3D objects, especially in those regions not directly accessible from the evaporation source (crucible). Besides, in thermal evaporation techniques the average energy of vapor atoms reaching the substrate surface is generally low (order of kT , i.e. tenths of eV). This affects seriously the morphology of the films, often resulting in a porous and little adherent material. In thermal evaporation techniques, different methods can be applied to heat the material. The equipments available in the laboratory use either resistance heating (Joule effect) or bombardment with a high-energy electron beam, usually several KeV, from an electron beam gun (electron beam heating). The principal processing variables in vacuum deposition are deposition geometry, deposition rate, and

substrate temperature during deposition and the level of gaseous and vapor (e.g., water vapor) contamination in the deposition environment. Deposition rates and amounts can be monitored in situ and in real-time by oscillation frequency to change. Calibration allows the change in frequency to be related to deposited film mass and by assuming a film density, the film thickness. In many applications the amount of material deposited is controlled by the evaporation-to-completion of a specific amount of material and using specific deposition geometry. In many cases a property of thin film, such as optical transmittance, is monitored during deposition and is controlled the amount of material deposit

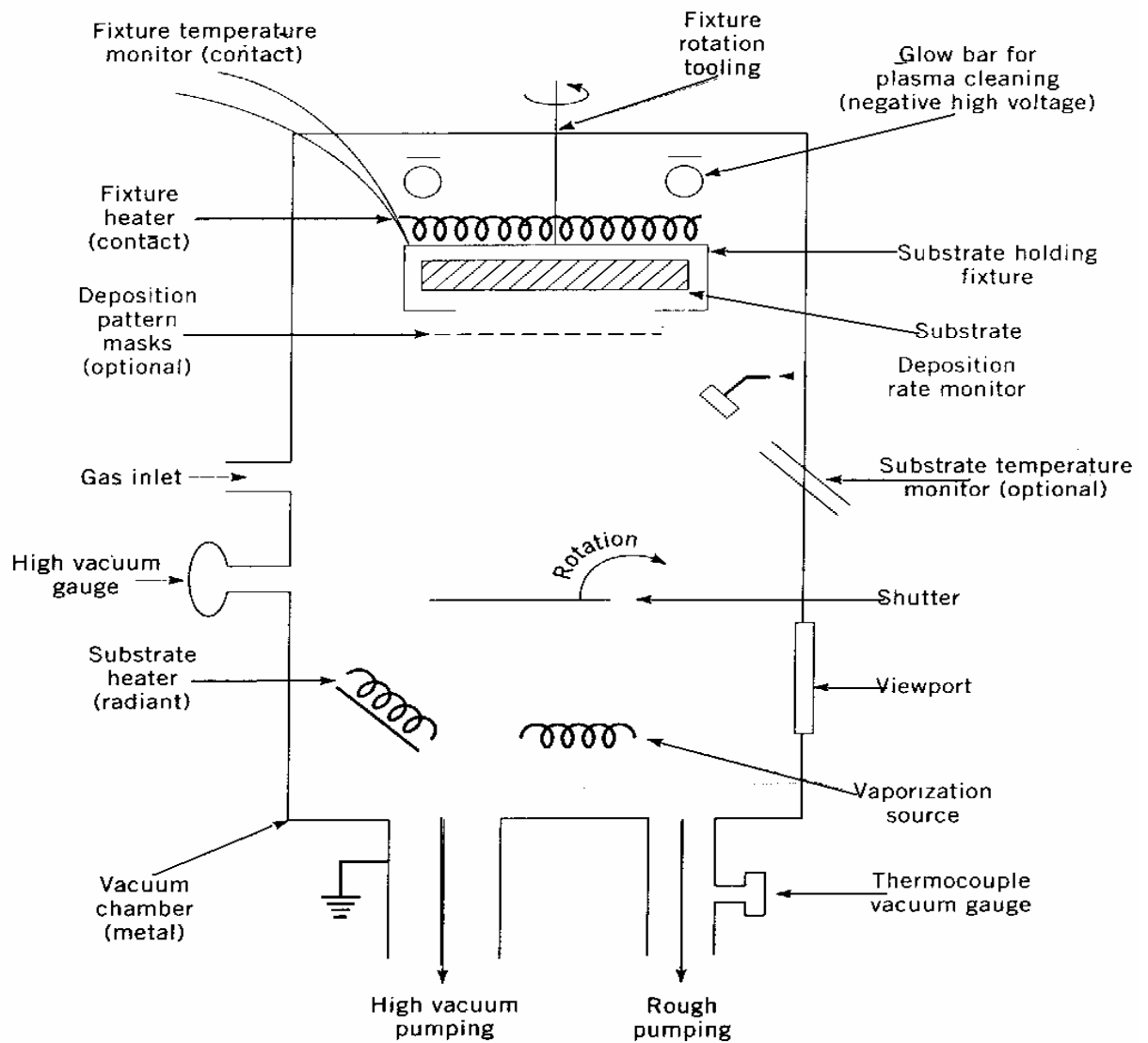


Figure 2.6 Principal Components of a vacuum deposition system

ADVANTAGES: -

There are several advantages of vacuum deposition:

- High purity films can be deposited from high purity source material.
- Vacuum premelting (with shutter closed) can be used to remove volatile contaminations from the source materials.
- The source of vaporized material can be of solid in any form and purity.
- High vaporization (deposition) rates can be attained.
- The line-of-sight trajectory and limited-area sources allow the use of shutters and masks to define deposition patterns.
- Deposition monitoring and control are relatively easy.
- Deposition system can be pumped at a high rate (high throughput) during the deposition to remove gaseous contaminants.
- Residual gases and vapors in the vacuum environment are easily monitored.

DISADVANTAGES: -

There also disadvantages of vacuum deposition:

- Many alloy compositions and compounds can only be deposited with difficulty.
- Line of sight and limited-area sources result in not only poor surface coverage on complex surfaces, but also poor film thickness uniformity over large areas, without proper fixturing and fixtures movement.

- The source geometry can change during the deposition thus changing deposition rate.
- For vaporizing large amounts of material, material often must be added to the source during the deposition run.
- Few processing variables are available for film property control.
- Source material utilization is poor.
- High radiant heat loads can exist in the deposition chamber.

CHAPTER 3: EXPERIMENTAL WORK

3.1. Synthesis of Electroluminescent Materials

3.1. a. SYNTHESIS OF TRIS (8-HYDROXYQUINOLINE) ALUMINIUM (Alq₃)

The fundamental principle of the synthesis of Alq₃ is to combine 8-hydroxy quinoline (HQ) anion with Al⁺³ in its aqueous solution. Alq₃ is precipitated under the optimum condition by adjusting pH value of solution. The aqueous solution of aluminum nitrate was chosen as Al⁺³ ion. Sodium hydroxide (NaOH) was used to adjust the pH value of solution. The degree of chemical reaction depends on the acidity and alkalinity of reactive materials. The pH value of Alq₃ when it is precipitated out completely ranged from 3 to 5. The chemical reaction during the synthesis of Alq₃ is:



The concrete processes of synthesis are shown as follows:

Solution (A): prepared by stirring 6.97 g HQ powder into 100 ml absolute ethanol and heating it up properly.

Solution (B): prepared by dissolving 15 g 9-H₂O/ Aluminum nitrate into 200 ml deionized water and mixing completely.

Solution (C): prepared by dissolving 5.3 g NaOH into 60ml deionized water.

Add solution (A) into (B) with full stirring until it dissolved completely and wait for about 15 min. The pH value of the mixed solution is 4. The Alq_3 is precipitated by adding solution (C) drop wise into the mixed solution. The pH was adjusted to give a final value of 5. At last, we carried out the vacuum adsorptive percolation process after 24 h. The Alq_3 filter cake was rinsed with deionized water. After repeating the process four to five times then it is transferred into the vacuum chamber to dry at $150^{\circ}C$. The pure Alq_3 was obtained.

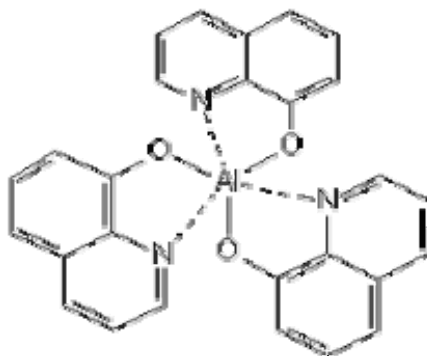


Fig 3.1. Tris-(8-hydroxyquinoline) aluminum

3.1. b. SYNTHESIS OF TRIS (2-PHENYLPYRIDINE) IRIIDIUM (III) COMPLEX

The $Ir(acac)_3$ (250mg) and 2-phenyl pyridine Hppy (0.45ml) were dissolve in glycerol (25.0ml) and the solution was refluxed under nitrogen atmosphere at $200^{\circ}C$ for 24 hrs. Addition of 1 M of HCl (150ml), after cooling results in ppt of the product, which was collected in a filter paper . This product was dissolved in hot dichlomethane DCM, and this mixture was filtered. This filtrate was flash chromatograph on a silica gel column.

The chromatographed solution was reprecipitated in methanol, to get the final product of yellow powder in 75% yield.

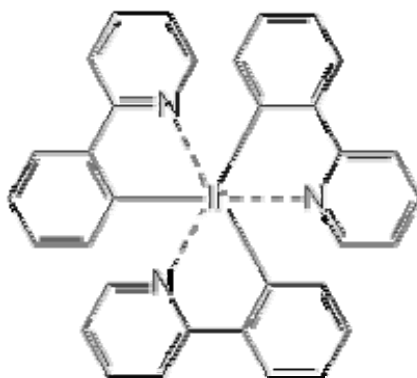


Fig 3.2. Structure of Tris-(2-phenylpyridine) iridium (III) complex

3.2. DEVICE FABRICATIONS

3.2.a. DEVICE FABRICATION USING ALQ₃ AS EMITTING LAYER

A double layer light emitting diode with device structure ITO/TPD/Alq₃/LiF/Al was fabricated using Alq₃ as emitting layer. The device was fabricated on a patterned indium tin oxide (ITO) coated glass substrate having a sheet resistance of 15 ohms/square. The substrate was cleaned in an ultrasonic bath using neutral Extran solution, distilled water, acetone, isopropyl alcohol and trichloroethylene. TPD & Alq₃ layers were thermally deposited on ITO by vacuum deposition technique, in which TPD & Alq₃ act as hole transport and emissive layer respectively. LiF & Al were also thermally deposited under vacuum and they acted as electron injection layer & cathode respectively. Finally, the device was hermetically sealed under pure nitrogen in a glove box with 150 μm thick glass slide using UV curable epoxy. The voltage was applied between these two electrodes using an Alpha Power Supply to get green emission under forward bias condition.

3.2.b. DEVICE FABRICATION OF IR(PPY)₃ USING AS DOPANT INTO HOST MATERIAL

Two layered light emitting diode with device structure ITO/TPD-Ir(ppy)₃/LiF/Al was fabricated using Ir(ppy)₃ as phosphorescent dopant in TPD. A patterned indium tin oxide (ITO) coated glass substrate was cleaned according to the process as explained in the above section. TPD-Ir(ppy)₃ was thermally deposited on the ITO coated glass in which TPD act an host and Ir(ppy)₃ act as dopant respectively. LiF and Al were also thermally deposited under vacuum which act as electron injection and cathode respectively. Finally, the device was hermetically sealed under pure nitrogen in a glove box with 150 μm thick glass slide using UV curable epoxy. The voltage was applied between these two electrodes using an Alpha Power Supply to get green emission under forward bias condition.

CHAPTER 4: RESULTS AND DISCUSSION

Two organic materials, tris(8-hydroxyquinoline) aluminium Alq₃ and tris(2-phenylpyridine) iridium complex were synthesized and light emitting diodes were fabricated using these materials as emitting and dopant layer. Materials and the devices were characterized by taking UV-Vis spectra, FTIR, Thermogravimetric Analysis (TGA), Photoluminescence (PL) Spectra and Current Voltage (I-V) Characteristics.

CHARACTERIZATION OF MATERIALS AND DEVICES

4.1. CHARACTERIZATION OF Alq₃

4.1.a. UV-VIS ABSORPTION SPECTRA OF Tris-(8-hydroxyquinoline) aluminium

UV-VIS absorption spectrum of the film was recorded on a Shimadzu UV-2401 spectrophotometer. The sample was prepared on fused silica substrate by thermal evaporation under vacuum. The absorption spectrum peak of the film found at 390 nm shown in figure

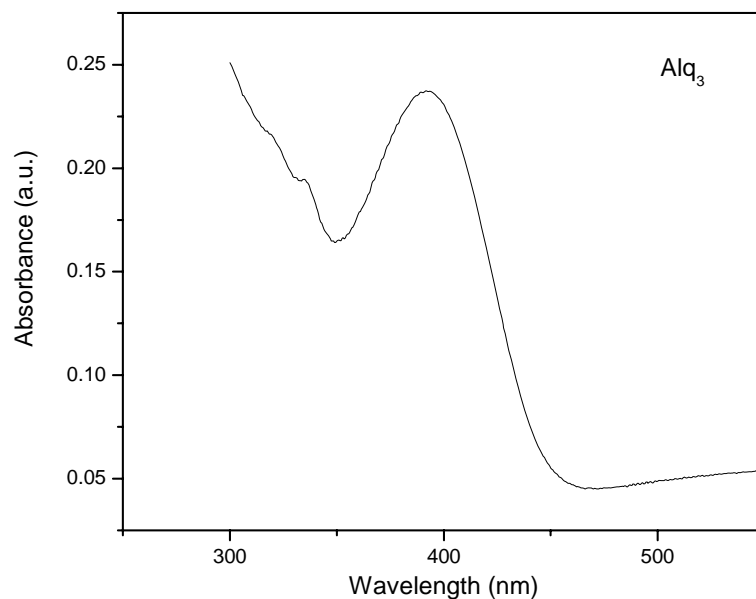


Fig 4.1 UV-Vis spectrum of Alq₃ vacuum evaporated on quartz

4.1. b. FTIR SPECTRA OF Alq₃

The IRA spectrum of Alq₃ shown in Fig. was collected using Nicolet-1705x infrared spectrophotometer. The powder specimen is compacted into pellet with KBr. The broad characteristic peak at 3417 cm⁻¹ corresponding to OH stretching vibration confirmed that the Al-O are coordinate not ionic bond. The peak centered at 3055 cm⁻¹ is attributed to the stretching vibration of C-H bond in aromatic ring. Another vibrational mode at 1670 and 1604 cm⁻¹ is assigned to the skeleton stretching vibration of C=C bond in aromatic ring. The prominent peaks which are the characteristic of the absorption vibration of the aromatic ring skeleton at 1588, 1550, 1467 and 1400 cm⁻¹ suggested that the conjugate action of aromatic rings in molecule is very strong and all electron orbits of quinolinic rings are p-bonding hybridizations. The peaks at 1390 and 1328 cm⁻¹ are attribute to the stretching vibration of C-N bond. The vibrational absorption peaks of C-O

at 1279 and 1251 cm^{-1} are weaker and narrower than the homologous peaks of HQ (comparing with standard Sadtler IR spectral set. The disagreement between IRA spectra of Alq₃ and HQ is excellent for indicating that there is a strong coordinate action which affect O bonding heavily between Al⁺³ and O ions. The characteristic peaks of quinolinic rings from 600 to 800 cm^{-1} labeled the existence of quinolinic rings. Intensity of peaks at 460, 416 and 710 cm^{-1} were decreased, increased and disappeared, respectively, due to the coupling effect on vibrational modes between Al⁺³ and ligands. However, the atomic coupling effect is not very strong because of the long bond distance. So that the Al-N vibrational mode can be regarded approximately as the vibration between Al⁺³ and whole HQ molecule. The peaks corresponding to Al- N stretching vibration should locate in low frequency range around 200 cm^{-1} which is out of the measuring range of spectrophotometer if the big mass, long bond distance and low coupling coefficient of the molecule

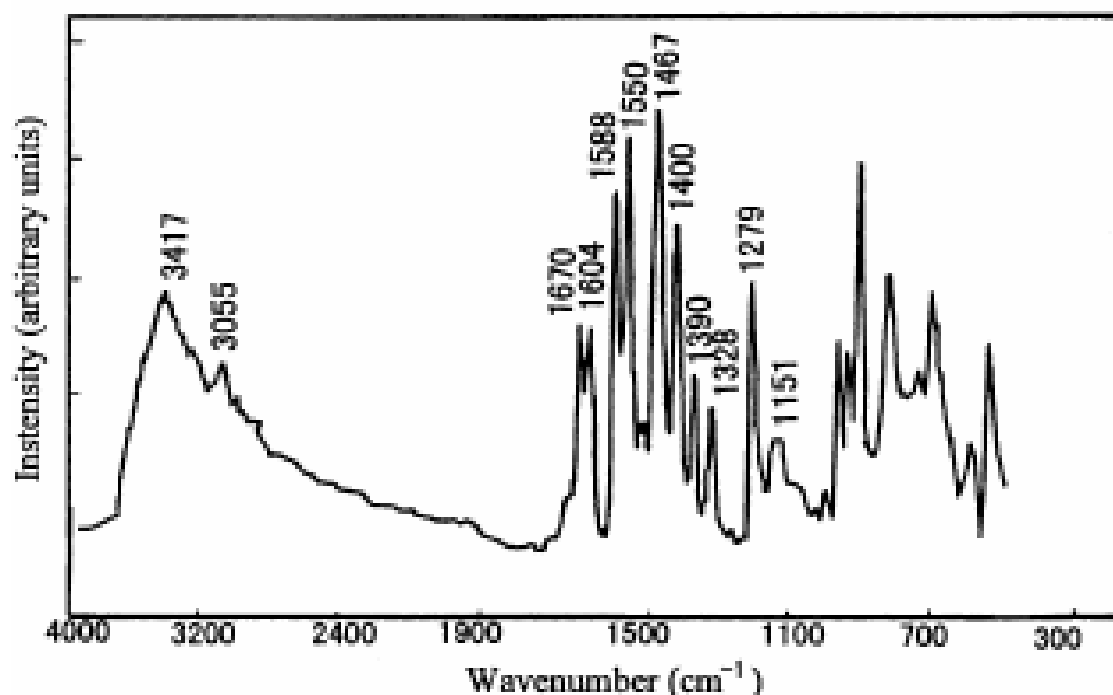


Fig 4.2 FT-IR spectrum of Alq₃ vacuum evaporated on quartz

4.1.c. THERMOGRAVIMETRIC ANALYSIS OF Alq₃

The TGA of synthesized Alq₃ was carried out on Mettler –Toledo –Star System shown in fig 4.3 The TGA plot of Alq₃ shows that a huge weight loss (83.88%) starts at 325⁰C and completes at 450⁰C this infers that the compound was stable up to 325⁰C after this temperature the compound starts decomposition.



Figure 4.3 Thermogravimetric Analysis of Alq₃

4.1.d. PHOTOLUMINESCENCE (PL) SPECTRA OF Tris(8-hydroxyquinoline) aluminium

Under UV illumination Alq₃ shows photoluminescence in the visible region. The sample absorbed at 390nm from UV source. Photoluminescence of Alq₃ was carried out

in solid state and a characteristic peak was observed at 525nm. This corresponds to 2.3 eV and have a full width at half maximum (FWHM) of 0.45 eV.

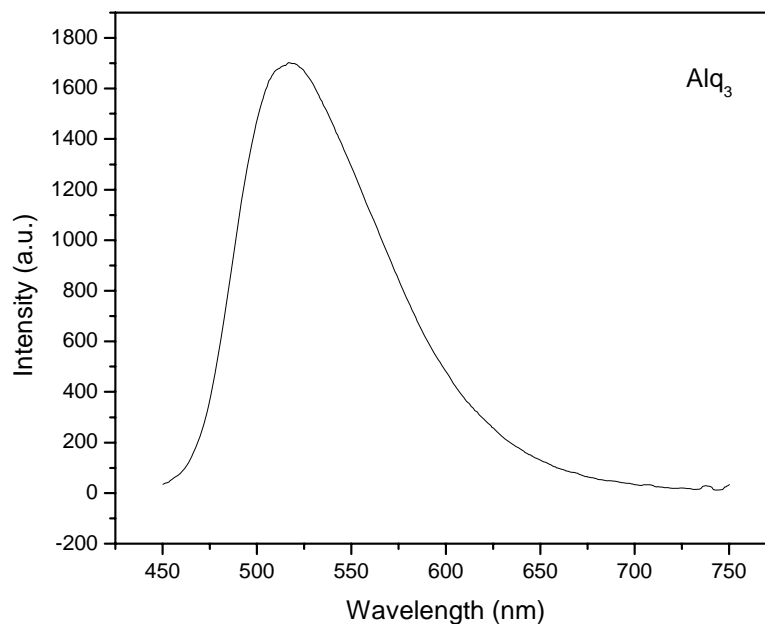


Fig 4.4 Photoluminescence spectrum of Alq₃

4.1. e. ELECTROLUMINESCENCE SPECTRUM OF Tris-(8-hydroxyquinoline) aluminium

The electroluminescence spectrum of ITO/TPD/Alq₃/LiF/Al at 10V is shown in the fig 4.5. The peak position is found at the same position as in the case of PL spectrum.

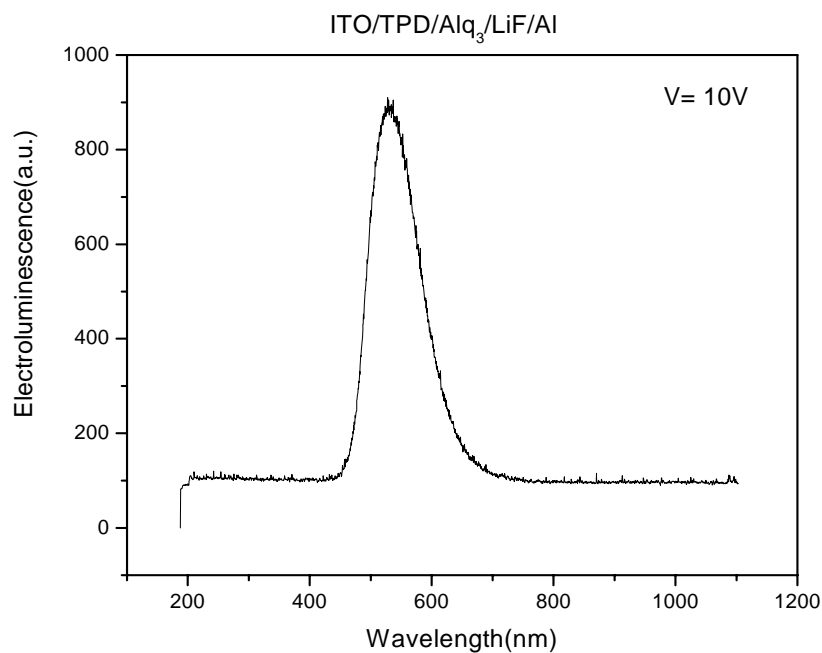


Fig 4.5 Electroluminescence Spectrum of Alq₃ based OLED

4.1.f. CURRENT VOLTAGE (I-V) CHARACTERISTIC OF Alq₃

The current voltage (I-V) characteristics of fabricated device were recorded by applying voltage across the device with ITO as anode and aluminium as cathode. The greenish light from the device was observed clearly at 6V. This is called the turn on voltage of the device. After this voltage an exponential increase in injection current was observed.

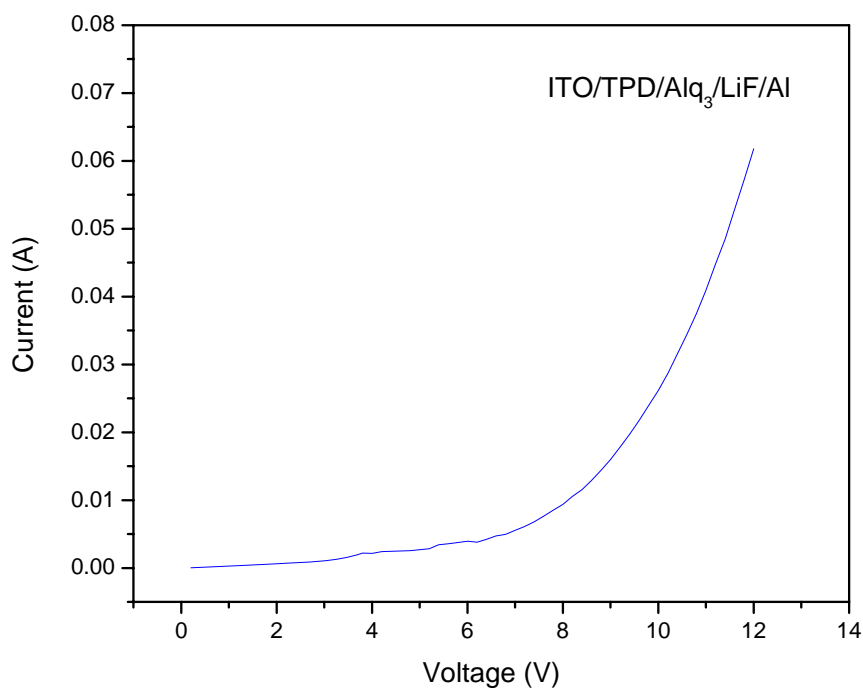


Fig 4.6 I-V Characteristics of Alq₃ based OLED

4.2. CHARACTERIZATION OF Tris-(2-phenylpyridine) iridium (III) COMPLEX

4.2.a. UV-VIS SPECTRUM OF Ir(ppy)₃

UV-Vis spectrum of Ir(ppy)₃ was recorded on Shimadzu UV-2042 spectrophotometer. The sample was prepared on fused silica substrate by thermal evaporation under vacuum. The absorption spectrum peak of Ir(ppy)₃ film display band in UV region due to π - π^* transition and in visible region due to MLCT spectra as shown in the Fig 4.7.

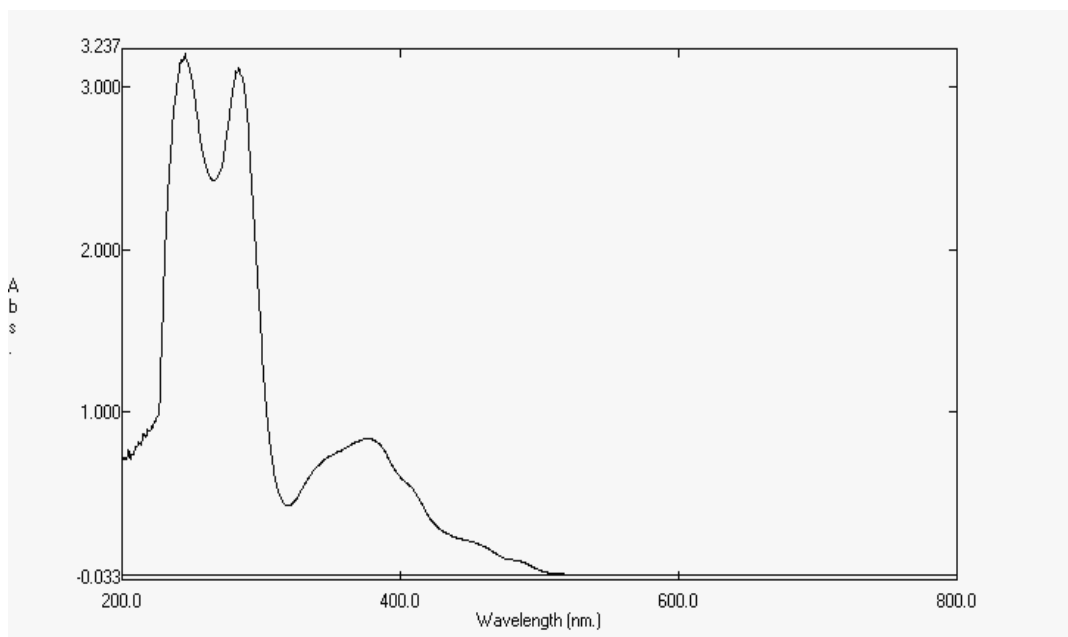


Fig 4.7 UV-Vis spectrum of Ir(ppy)₃

4.2.b. FT-IR SPECTRUM OF Ir(ppy)₃

Fourier Transform Infra-red spectroscopy (FT-IR) transmittance spectra of Ir(ppy)₃ shown in figure 4.8. The powder specimen is compacted into pellet with KBr. The peak centred at 3053 cm⁻¹ is attributed to stretching vibration of C-H bond in aromatic ring. Another vibration mode at 1598.45 cm⁻¹ is assigned to the skeleton stretching vibration of C=C bond in aromatic ring.

The prominent peak which is characteristic of transmittance of aromatic ring skeleton at 1579.74, 1460 & 1412 cm⁻¹ suggested that conjugation of aromatic ring is very strong. The peak at 1266.50 cm⁻¹ is due to aromatic C-N stretching. The peak at 1057.30 & 1030 cm⁻¹ is due to C-H in plane bending & peak 736.36 cm⁻¹ is due to C-H out of plane bending in aromatic ring.

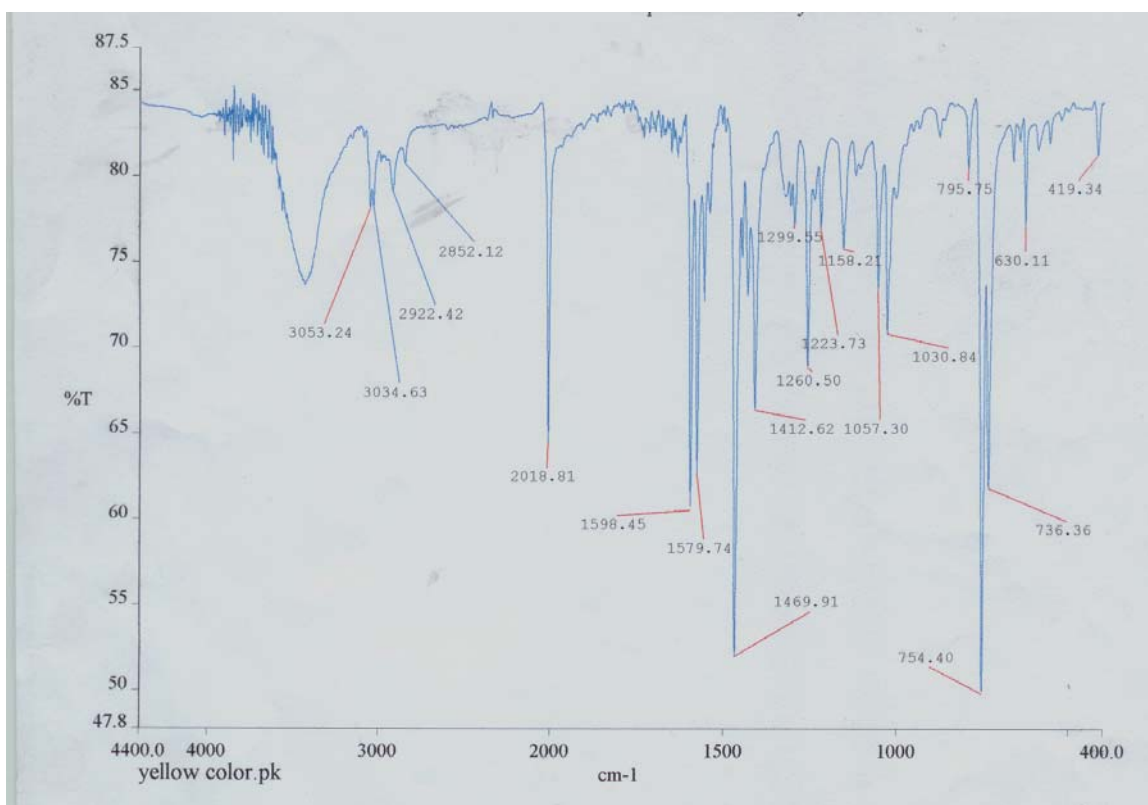


Fig 4.8 FT-IR spectrum of Ir(ppy)₃

4.2.c. THERMOGRAVIMETRIC ANALYSIS (TGA) OF Ir(ppy)₃

The Thermogravimetric Analysis (TGA) of synthesized Ir(ppy)₃ was carried out on Mettler Toledo Star System. The TGA of Ir(ppy)₃ the first step shows the very minute weight loss (3.1926%) that may due to some hydrated water. In the second step a huge weight loss of about 34.6% were taken place. The weight loss starts at 350⁰C and completed at 450⁰C. This weight loss suggests that the compound starts decomposing in this range; hence compound was stable up to this temperature.

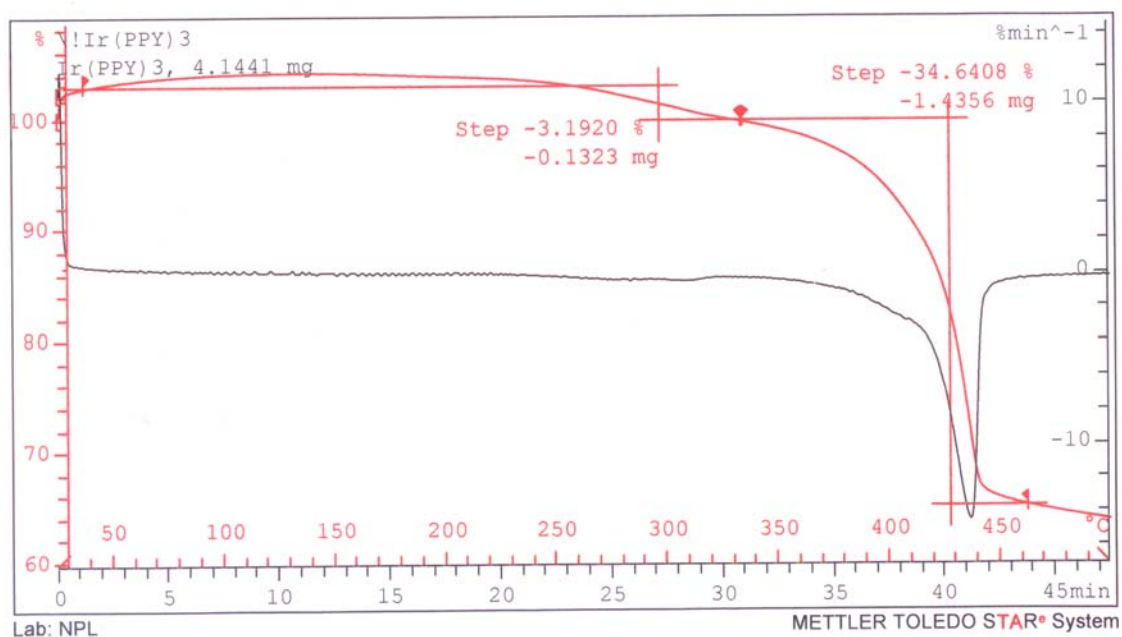


Fig 4.10 Thermogravimetric analysis (TGA) of Ir(ppy)₃

4.2.d. PHOTOLUMINESCENCE SPECTRUM OF Ir(ppy)₃

Under UV illumination, Ir(ppy)₃ shows an emission spectra, measured in dichloromethane solution at room temperature and we got the emission maxima at 520nm. This complex shows bright luminescence even in high illumination. Even the solid state complex is highly luminescent, but the solid state emission spectrum shows red shift compared to the solution spectrum.

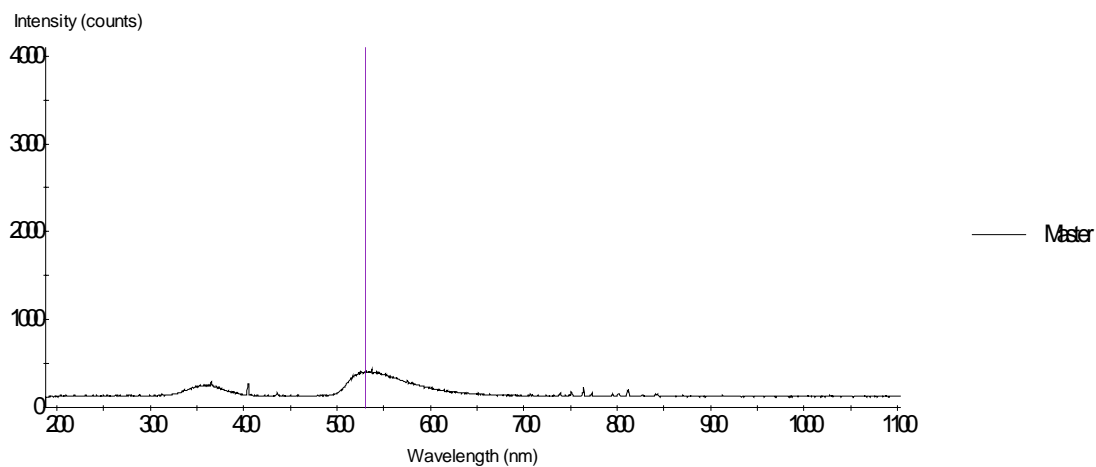


Fig 4.9 Photoluminescence Spectrum of Ir(ppy)₃

4.2.e. ELECTROLUMINESCENCE (EL) SPECTRA OF Ir(ppy)₃ DOPED IN TPD

The electroluminescent (EL) spectrum of the device ITO/TPD-Ir(ppy)₃/LiF/Al was taken at different potentials ranging from 10V to 20V. The peak maxima was obtained at 520nm. Peak intensity was increased as we increased the voltage as shown in the fig 4.11.

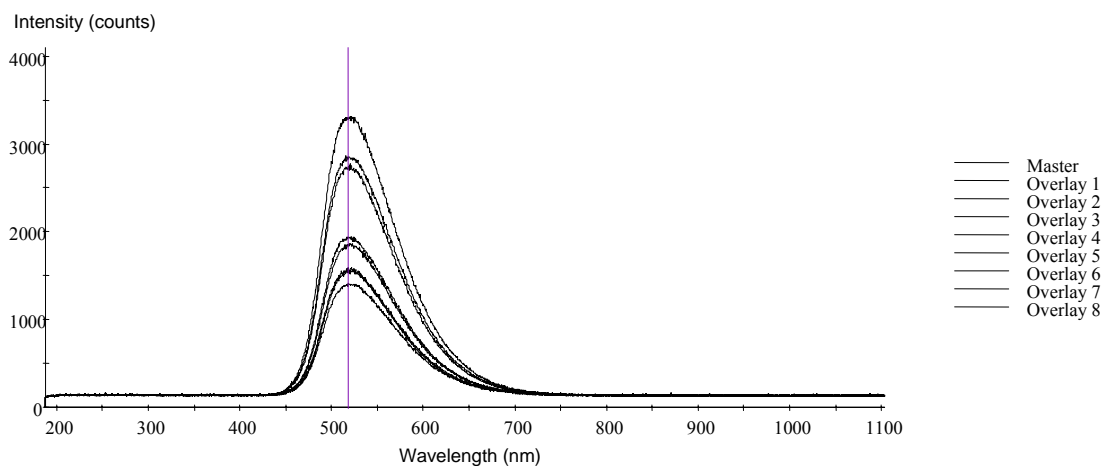


Fig 4.11 Electroluminescence (EL) Spectra of BCP-Ir(ppy)₃ device

4.2.f. CURRENT VOLTAGE (I-V) CHARACTERISTIC OF Ir(ppy)₃

The current voltage (I-V) characteristic of the fabricated device was recreated by applying a dc voltage across the device with ITO as anode and aluminium as cathode electrode (forward bias) as shown in fig (4.12). The current voltage (I-V) characteristic shows that the current starts rising above (5v) indicate the one set of light emission (threshold voltage). The (I-V) characteristic of device shows highly non linear nature with ohmic conduction at low voltage. An intense green emission was observed from the device on applying (15V) across it.

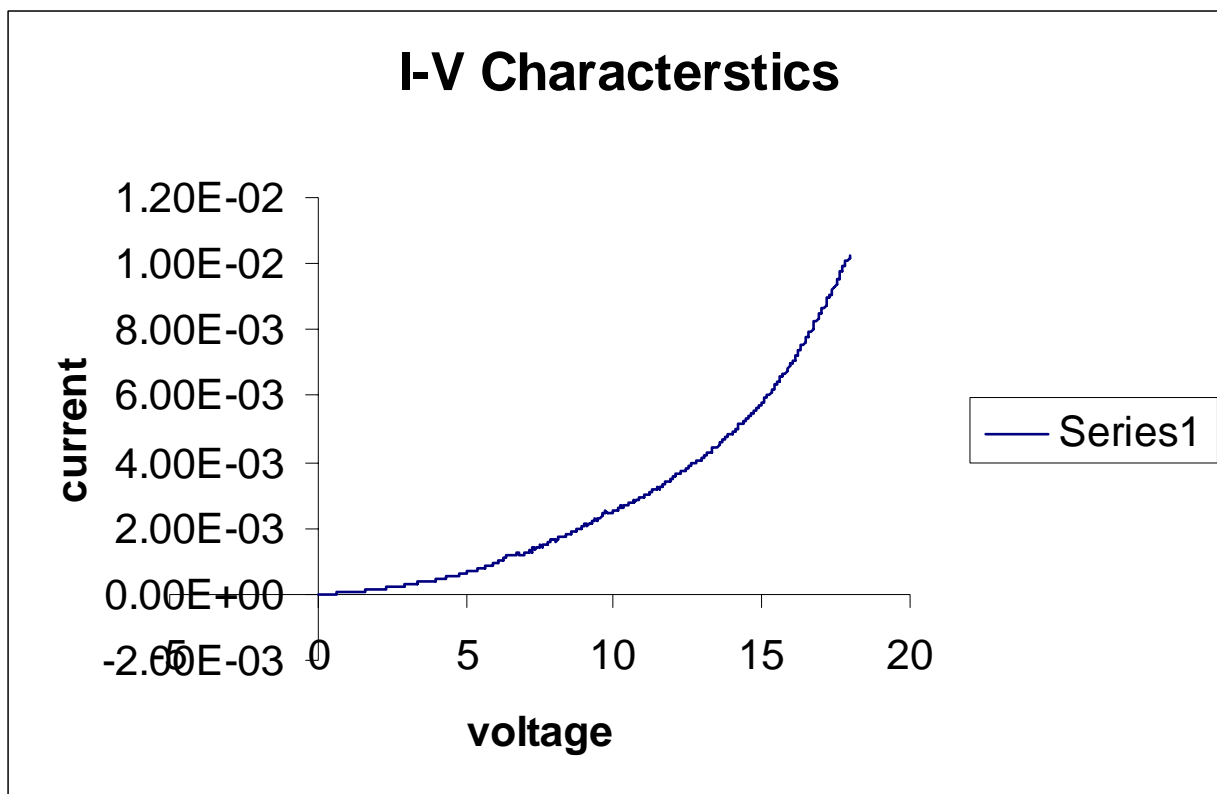


Fig 4.12 Current voltage (I-V) characteristic of Ir(ppy)₃

CONCLUSION

1. Tris-(8-hydroxyquiniline) aluminium and Tris-(2-phenylpyridine)iridium complex were synthesized and characterized by taking UV-Vis absorption spectra, Fourier Transform (FT-IR), Photoluminescence spectra and Thermogravimetric Analysis (TGA).
2. The results of UV-Vis absorption spectra (FT-IR) of these materials shows that materials synthesized were of good purity.
3. According to (TGA) of Alq₃ and Ir(ppy)₃, the thermal stability of these materials 300⁰C and 350⁰C respectively.
4. Two device of following configuration ITO/TPD/Alq₃/LiF/Al and ITO/TPD-Ir(ppy)₃/LiF/Al were fabricated and there electroluminescence (EL) spectra and current voltage (I-V) characteristic were measured.
5. From the electroluminescence spectra (EL) and current voltage (I-V) characteristic studies of the device the following result were obtained.
 - a. The device with configuration ITO/TPD/Alq₃/LiF/Al required low bias voltage of nearly 6V for device functioning and produce a green electroluminescence. The low voltage may be due to application of hole transport layer and electron injection layer.

- b. The device with configuration ITO/TPD- Ir(ppy)₃/LiF/Al required higher bias voltage of nearly 12V for device functioning and produce green electroluminescence. The large bias voltage required for device operation may be due to large triplet energy difference between host and dopant materials.
6. The materials synthesized have shown a very good results in applications of OLEDs therefore the synthesized materials have good prospect for industrial as well organic electroluminescent materials in coming days.

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