

# **Synthesis and Characterization of Cadmium Metal Complex Based Materials for OLED Applications**

Thesis submitted in partial fulfillment  
of the requirements for award of degree of

**MASTER OF TECHNOLOGY**  
in  
**MATERIALS SCIENCE AND ENGINEERING**

By:

**RAHUL KUMAR**  
(Roll No: 60702014)

Under the Guidance of

**Dr.M.N.KAMLASANAN**  
Scientist 'G'  
Center for Organic Electronics  
National Physical Laboratory  
New Delhi-110012

**Dr.KULVIR SINGH**  
Assistant Professor  
School of Physics & Material  
Science  
Thapar University,  
Patiala-147004



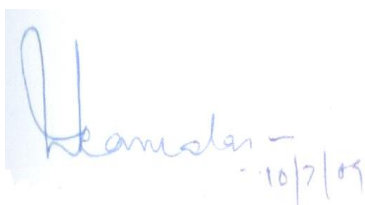
**SCHOOL OF PHYSICS AND MATERIAL SCIENCE**  
**THAPAR UNIVERSITY PATIALA-147004, INDIA**

**JULY, 2009**

**CERTIFICATE**

This is certify that the thesis entitled “**Synthesis and Characterization of Cadmium Metal Complex Based Materials for OLED Applications**” submitted by **Mr. Rahul Kumar** is in partial fulfillment for degree of Master of Technology in Material Science and Engineering of this University. This work has been done under our supervision . The work presented in this thesis is original to the best of our knowledge and has not been submitted to any other degree of this or any other university. The work has been carried out from 10-01-09 to 10-07-09.

### Supervisors



**Dr.M. N. Kamlasanan**  
Scientist ‘G’  
Center for Organic Electronics  
National Physical Laboratory  
New Delhi 110012



**Dr. Kulvir Singh**  
Assistant Professor  
School of Physics & Material Science  
Thapar University  
Patiala 147004

### Countersigned by:



**Dr. O. P. Panday**  
Prof. & Head  
School of Physics & Material Science  
Thapar University, Patiala



**Dr. R. K. Sharma**  
Dean, Academic Affairs  
Thapar University  
Patiala 147004

## ACKNOWLEDGEMENT

I express my deep sense of gratitude to Dr. M. N. Kamlasanan for providing me an opportunity to work in Centre for Organic Electronics, NPL. His astonishing language skills and his clear vision of scientific content help me in tremendous manner.

Words can hardly express my sense of gratitude to Dr. Ritu Srivastava for her invaluable supervision during the course of my thesis work. Dr. Srivastava was always available and helpful. Her great knowledge and wonderful attitude help in my training tremendously; her kindness, patience are much appreciable.

I want to express my deep sense of gratitude to my supervisor Dr. Kulveer Singh. His wide knowledge and logical way of thinking have been of great value for me. I express my gratitude to Dr. O. P Pandey, Head, School of Physics and Material Science, Thapar University Patiala for his invaluable support and encouragement.

I wish to express my sincere thanks to Dr. Vikram Kumar (Director NPL), for permitting and providing the facilities necessary for carrying out thesis work at NPL.

Dr. A. K. Gupta, Dr. S. S. Bawa, Dr. A. K. Aggarwal Head HRD group, NPL, for their support and encouragement during the course of thesis work. I am extremely thankful to Dr. Suresh Chand, Dr. S. K. Dhawan, for their invaluable help.

I also want to thanks Mr. Dharamveer Siani, from HRD group for his kind help.

I am deeply indebted to my teachers, Dr. K. K. Raina, Dr. N. K. Verma, Dr D.P Singh, Dr. Sunil Kumar, Dr. Manoj Kumar, Dr. Puneet Sharma, Dr. Lavleen Kaur, Dr. Alka, Dr .Sanjeev and Dr. S. D. Tiwari. Their ideals and concepts have had a remarkable influence on my understanding in the field of Material Science and Engineering.

I would like to give my special thanks to Miss Gayatri Chauhan, Mr. Arunandan Kumar, Miss Manisha Bajpayi, Miss Priyanka Tyagi, Mr. Amit kumar yadav, Miss Rakhi, Mr. Anzar Gani, Mr. Razi Ahmed, Miss Omvati and all members of Centre for Organic Electronics for their kind support in my work. Miss Gayatri and Mr. Arunandan helped me in all possible ways. Their timely discussions are very much appreciable. I also want to thanks my classmates Mr. Arjun singh & Miss Namita Gandhi. I wish to express my sincere thanks to my friends Akash Katoch, Ranveer Singh Pawar, Rajiv Sherawat, Satyendra, Arun Kumar & Amit Sharma.

I owe my most sincere gratitude to my late Father, Mother, Guru, & my sister whose honest support and obstinate love give me energy to complete this work successfully. Lastly I want to thank Mr. Raju and Mr. Hament for their help in arranging laboratory material during my experiment.

*Rahul Kumar*

**(RAHUL KUMAR)**

## ABSTRACT

Organic semiconductors have attracted lot of attention in academic and technological community due to its potential applications in organic light emitting diodes (OLEDs), organic photovoltaic cells etc. OLED is being considered as one of the most promising technology for flat-panel displays and in general lighting.

The most important part of OLED devices is the electroluminescence layer, for which polymer and small molecular weight metal chelates can be used. The small molecule based metal chelates are the appropriate candidates as these are processed by conventional vacuum deposition techniques. Small molecule based Cd metal complexes can be used in OLED devices as electron and hole transport layer. It can also be used an emissive layer because of their wide spectral response in the visible region. The materials which I have chosen have good emissive properties in visible (particularly green and yellowish green ) region.

My thesis work includes synthesis of three Cadmium complexes, cadmium {(2, 2' bipyridine) 8-hydroxyquinoline} [Cd(Bpy)q], bis(2-methyl 8-hydroxy quinolate) Cadmium [Cd(mq)<sub>2</sub>] and Cadmium {2-(2'-hydroxyphenyl) benzoxazole}(8-hydroxyquinoline) [Cd(HPB)q], and characterization by following techniques (FTIR, TGA, UV visible and Photoluminescence Spectroscopy).

# Table of Contents

<b>Chapter 1.....</b>	<b>1</b>
<b>Introduction.....</b>	<b>1</b>
1.1 History of organic electroluminescence.....	2
1.2 Limitations of Inorganic Light Emitting Diodes.....	3
1.3 Organic electroluminescent material used in OLEDs.....	4
1.3.1 Construction of an OLED.....	8
1.3.2 OLED Components.....	8
1.3.3 Working principle.....	9
1.3.4 Device Efficiency.....	9
1.3.5 Advantages & Disadvantages.....	10
1.3.6 Applications of OLEDs.....	11
1.3.7 Challenges and Critical Issues.....	12
1.4 Electroluminescent materials used in OLED.....	13
1.4.1 Polymers.....	14
1.4.2 Small molecules.....	15
1.5 Metal complexes and there selection criteria.....	17
1.6 Deposition Techniques for OLED fabrication.....	19
<b>Chapter 2 .....</b>	<b>22</b>
<b>Motivations and Scope of the work.....</b>	<b>22</b>
2.1 Motivations.....	23
2.2 Scope of the work.....	27
<b>Chapter 3.....</b>	<b>29</b>
<b>Experimental Details.....</b>	<b>29</b>
3.1 Synthesis.....	30
3.1.1 Synthesis of cadmium (2, 2' bipyridine) 8-Hydroxyquinoline (Cd(Bpy)q).....	30
3.1.2 Synthesis of bis(2-methyl- 8-Hydroxyquinlate)(cadmium) Cd(mq) <sub>2</sub> .....	31

3.1.3 Synthesis of Cadmium 2-(2-hydroxyphenyl) benzoxazole Cd(HPB)q.....	31
3.3 Material Characterization, device fabrication techniques.....	32
3.3.1 Materials characterization.....	32
3.3.1.1 UV-Visible Absorption Spectroscopy.....	32
3.3.1.2 Photoluminescence Spectroscopy.....	35
3.3.1.3 Fourier Transforms Infra-Red (FT-IR) Spectroscopy.....	36
3.3.1.4 Thermo gravimetric Analysis.....	37
3.3.2 Device Fabrication Techniques.....	38
3.4 Device Fabrication.....	40
3.4.1 Cd(Bpy)q and Cd(mq) <sub>2</sub> Cd(HPB)q based Organic Light Emitting Device.....	41
<b>Chapter 4.....</b>	<b>42</b>
<b>Result and Discussion.....</b>	<b>42</b>
4.1 Structural and thermal characterization.....	43
4.1.1 Structural and thermal characterization of Cd(Bpy)q.....	43
4.1.2 Structural and thermal characterization of Cdmq <sub>2</sub> .....	44
4.1.3 Structural and thermal characterization of Cd(HPB)q.....	46
4.2 Optical Characterization.....	48
4.2.1 Optical Characterization of Cd(Byp)q.....	48
4.2.2 Optical Characterization of Cdmq <sub>2</sub> .....	49
4.2.3 Optical Characterization of Cd(HPB)q.....	49
4.3 Device characterization.....	50
4.3.1 Device characterization of Cd(Bpy)q.....	50

4.3.2 Device Characterization of Cd(HPB)q.....	53
4.3.3 Device Characterization of Cdmq <sub>2</sub> .....	56
<b>Chapter-5.....</b>	<b>59</b>
<b>Conclusion and Future Scope.....</b>	<b>59</b>
5.1 Conclusion.....	60
5.2 Future Scope.....	60
<b>References .....</b>	<b>62</b>

## List of Figures

Figure 1.1: Luminescent Aluminum chelates.....	5
Figure: 1.2 Beryllium metal chelates.....	5
Figure 1.3: Luminescent Boron chelates.....	6
Figure 1.4: Luminescent Zinc chelates.....	7
Figure 1.5: OLED components.....	8
Figure 1.6: Charge transport and light generation in OLED's.....	9
Figure 1.7: P type polymers.....	14
Figure 1.8: N-type polymer.....	15
Figure 1.9 (a): Principle of Luminescent metal chelate.....	17
Figure 1.9(b): Luminescent chelate.....	17
Figure 1.10: Thermal Vapour evaporation Technique.....	20
Figure 1.11: Spin Coating.....	21
Figure 3.1: Scheme- Synthesis of Cd(Bpy) <sub>2</sub> .....	30
Figure 3.2: Scheme- Synthesis of Cd(mq) <sub>2</sub> .....	31
Figure 3.3: Scheme- Synthesis of Cd(HPB) <sub>2</sub> .....	32
Figure.3.4 Block digram of UV-Vis Spectrometer.....	33
Figure: 3.5 Energy level diagram.....	34
Figure: 3.6 Schematic diagram of luminescence experiment.....	36
Figure 3.7 Set-up of FT-IR (modle510p).....	37
Figure 3.8(a): Device structure of OLED ( Cd(mq) <sub>2</sub> / Cd(HPB) <sub>2</sub> as an emitter).....	41
Figure 3.8(b): Device structure of OLED (Cd(Bpy) <sub>2</sub> as an emitter).....	41
Figure 4.1 Shows the FTIR of Cd(Bpy) <sub>2</sub> .....	43
Figure 4.2. Thermo Gravimetric analysis of Cd(Bpy) <sub>2</sub> .....	44
Figure: 4.3 FTIR of Cdmq <sub>2</sub> .....	45
Figure: 4.4 Thermo gravimetric analysis of Cdmq <sub>2</sub> .....	46
Figure 4.5 FTIR of Cd(HPB) <sub>2</sub> .....	47
Figure: 4.6 Thermo gravimetric analysis of Cd(HPB) <sub>2</sub> .....	47
Figure: 4.7 UV-Vis and Photoluminescence spectra of Cd(Bpy) <sub>2</sub> .....	48
Figure: 4.8 UV-Vis and Photoluminescence spectra of Cdmq <sub>2</sub> .....	49
Figure: 4.9 UV-Vis and Photoluminescence spectra of Cd(HPB) <sub>2</sub> .....	50
Figure: 4.10 EL Vs Wavelength at different voltages of Cd(Bpy) <sub>2</sub> .....	51
Figure: 4.11 Current density-Voltage-Luminescence curve of Cd(Bpy) <sub>2</sub> .....	52
Figure 4.12 Luminescence –current density curve of Cd(Bpy) <sub>2</sub> .....	52
Figure: 4.13 Current Efficiency – Voltage- Power Efficiency curve of Cd(Bpy) <sub>2</sub> .....	53

Figure 4.14 electroluminescence spectra at different voltages for Cd(HPB)q.....	54
Figure: 4.15 Current density-voltage- luminescence curve for Cd(HPB)q .....	54
Figure: 4.16 Luminescence-Current density curve for Cd(HPB)q.....	55
Figure: 4.17 Current efficiency-voltage- Power efficiency curve for Cd(HPB)q.....	55
Figure: 4.18 Electroluminescence spectra for Cdmq <sub>2</sub> at different voltages.....	56
Figure 4.19 Current Density- Voltage- Luminescence curve for Cdmq <sub>2</sub> .....	57
Figure 4.20 Luminescence- current density curve for Cdmq <sub>2</sub> .....	57
Figure 4.21 Current Efficiency-Voltage-Power efficiency curve for Cdmq <sub>2</sub> .....	58

## List of Tables

Table (1) Inorganic vs. Organic material.....	3
Table (2) PL emission (nm) of different Zinc metal complexes.....	19
Table (3) Summary.....	26

CHAPTER 1  
**INTRODUCTION**

## 1.0 Introduction

OLEDs constitute a new and exciting emissive display technology. In general, the basic OLED structure consists of a stack of fluorescent organic layers sandwiched between a transparent conducting anode and metallic cathode [1, 2]. When an appropriate bias is applied to the device, holes are injected from the anode and electrons from the cathode; some of the recombination events between the holes and electrons result in electroluminescence (EL).

### 1.1 History of Organic Electroluminescence

The first EL from an organic molecule, anthracene, was reported by Pope and coworkers in 1963 [3]. They reported EL from a thick anthracene crystal (10 $\mu$ m-5mm), when a bias of several hundred volts was applied across it. The achievement did not stimulate much interest as the applied bias was very high. However, P. S. Vincent et al [4] achieved bright blue EL from vacuum-deposited 0.6 mm thick anthracene crystal films with an applied bias of less than 100V. The breakthrough was achieved by Tang and VanSlyke in 1987 [1], who made a bilayer structure by thermally evaporating the small molecular weight organic materials, N,N'-iphenyl-N, N'-bis(3-methylphenyl) 1, 1'-biphenyl-4, 4'diamine (TPD) and tris(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>) to achieve a total thickness of ~100 nm. They achieved a very bright green emitting OLED with brightness higher than 1000 cd/m<sup>2</sup> and an external quantum efficiency of ~1% when a low bias of 10V was applied across the structure [1]. Following this achievement Adachi et al [5] succeeded in fabricating stable multilayer devices by inserting hole and electron transport layers between the two electrodes.

In 1989, Tang et al [2] developed a laser-dye doped Alq<sub>3</sub> multi layer structure, in which the fluorescent efficiency was improved and the emission color varied from the original green to the dopant emission color. Following the success of fabricating small molecular OLEDs, Burroughs et al [6] discovered the first polymer LED (PLEDs) by spin coating a precursor polymer of the luminescent poly-(para-phenylene vinylene) (PPV) onto an indium tin oxide (ITO) coated glass. Compared to small molecular devices, polymer light emitting devices (PLEDs) have several potential advantages, e.g., fabrication by spin coating [6,7] or inkjet printing [8] from solutions and subsequent thermal treatment. Fluorescent emission of singlet excitons is the main mechanism of OLED light emission. As the probability of forming spin singlet states and spin triplet states are 25% and 75% respectively, the ideal maximum fluorescent

yield is, therefore, limited to 25% by spin statistics. To overcome this theoretical limit M. A. Baldo et al [9] fabricated and demonstrated phosphorescent OLEDs, by doping phosphorescent molecules, where the EL is due to triplet emission, into a fluorescent host layer

## 1.2 Limitations of Inorganic Light Emitting Diodes

- Single Crystalline- limitation of area
- Epitaxial films - lattice matching problems
- Large processing and material cost
- Non flexible

Following table (1) shows a brief comparison between Inorganic and Organic materials used for LED applications.

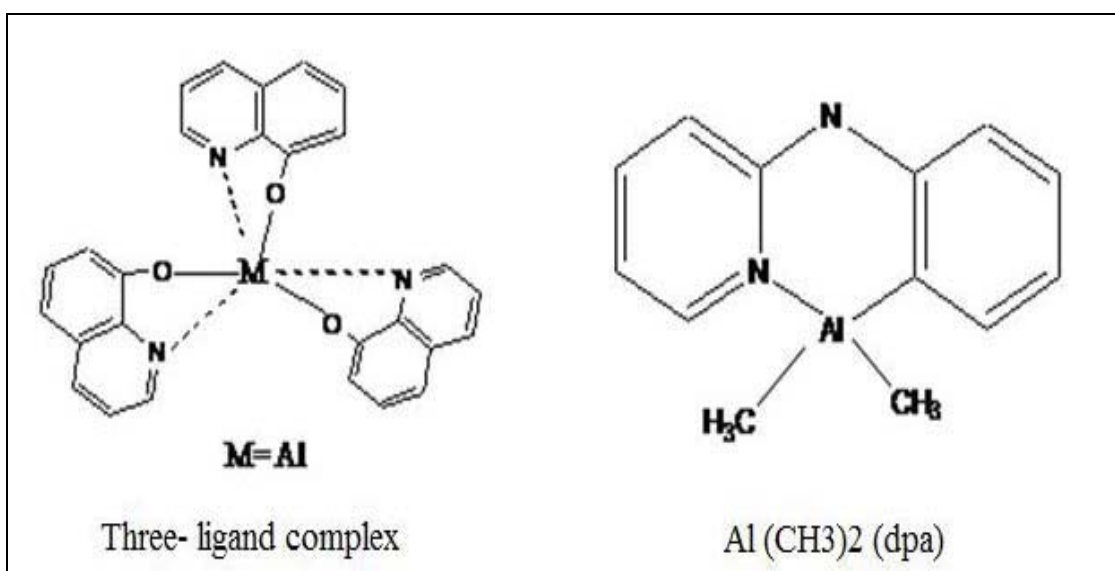
**Table (1): Inorganic vs. Organic material**

Characteristic	Organic	Inorganic
Structure (morphology)	Amorphous	Single crystalline
Charge Carrier Properties	Molecular	Lattice
Mobility (cm <sup>2</sup> /Vs)	10 <sup>-3</sup> to 10 <sup>-5</sup>	1 to 1500
Processing	Low temperature	High temperature
Synthetic flexibility	High	Low
<b>Construction</b>	<div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> <p><b><u>Organic LED</u></b></p> </div> <div style="text-align: center;"> <p><b><u>Inorganic LED</u></b></p> </div> </div>	

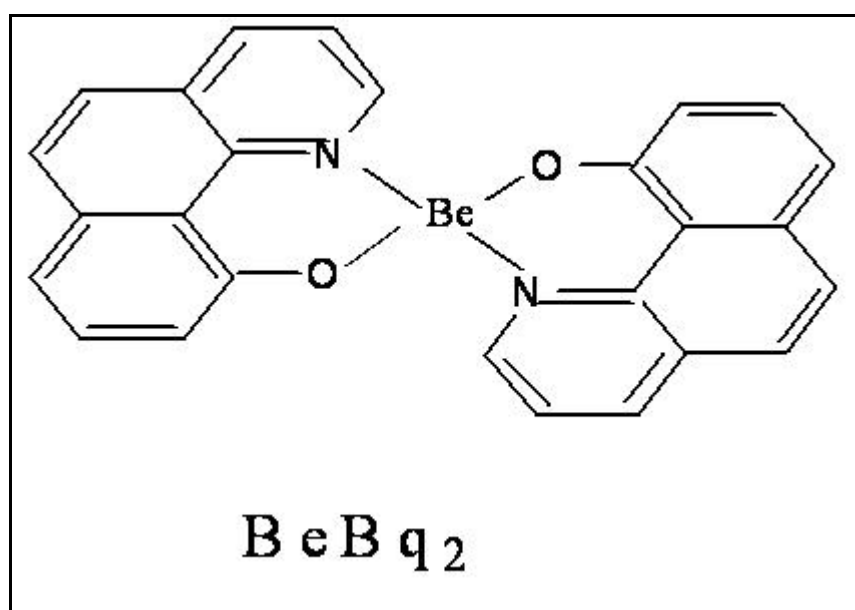
### 1.3 Organic Electroluminescent Material used in OLEDs

Organic electroluminescent (EL) materials and devices have attracted much attention and interest in recent years because of their potential application in flat panel displays [10-11]. These materials for EL devices can be classified into three categories according to their molecular structure: 1) organic dyes (no metal element), 2) chelate metal complexes, and 3) polymers [12]. The metal complexes are especially important because of the simplicity in synthesis procedures, ease of fabrication, high thermal stability and the wide spectral response [13, 14]. There are many factors affecting the photoluminescence efficiency of these metal complexes. The most common and important factor is the thermal vibration of the chromophore, which provides a path for the loss of energy via a radiation less pathway. One can reduce the loss of energy via thermal vibration by increasing the rigidity of the chromophore. For coordination compounds, this reduction can be achieved by chelating the appropriate chromophore to a suitable metal ion, which reduces the degree of freedom of thermal vibrations of the chromophore, thus increasing its emission efficiency [15].

Further metal chelates can be prepared very pure and can have high luminescence quantum yields and high stabilities at high operating voltages. The choice of metal ions for EL chelates is limited to those metals which do not exhibit d-d transitions that may interfere with the ligand. Therefore, aluminum (III) (Figure 1.1), boron (III)(Figure 1.2), beryllium (II) (Figure 1.3) and zinc (II) cadmium(II ) (Figure 1.4) are ideal. Since Beryllium (II), boron (III) and aluminium (III) has no 'd' electron and zinc (II) & cadmium (II) have a closed shell of d electrons. These metal ions only have a structural purpose by stabilizing a luminescent ligand [15]. These metal complexes can be used both as an electron transport layer, and as an emissive layer. Zinc metal and Cadmium metal complexes have a wide range of spectrum in the visible region [12]. Extensive research work is going on in various laboratories to synthesize new zinc and cadmium complexes containing new ligands to produce a number of novel luminescent zinc and cadmium complexes as emitters [16-21] and electron transporters [22-24] in OLED research.



*Figure 1.1: Luminescent Aluminium chelates*



*Figure 1.2 : Beryllium metal chelates.*

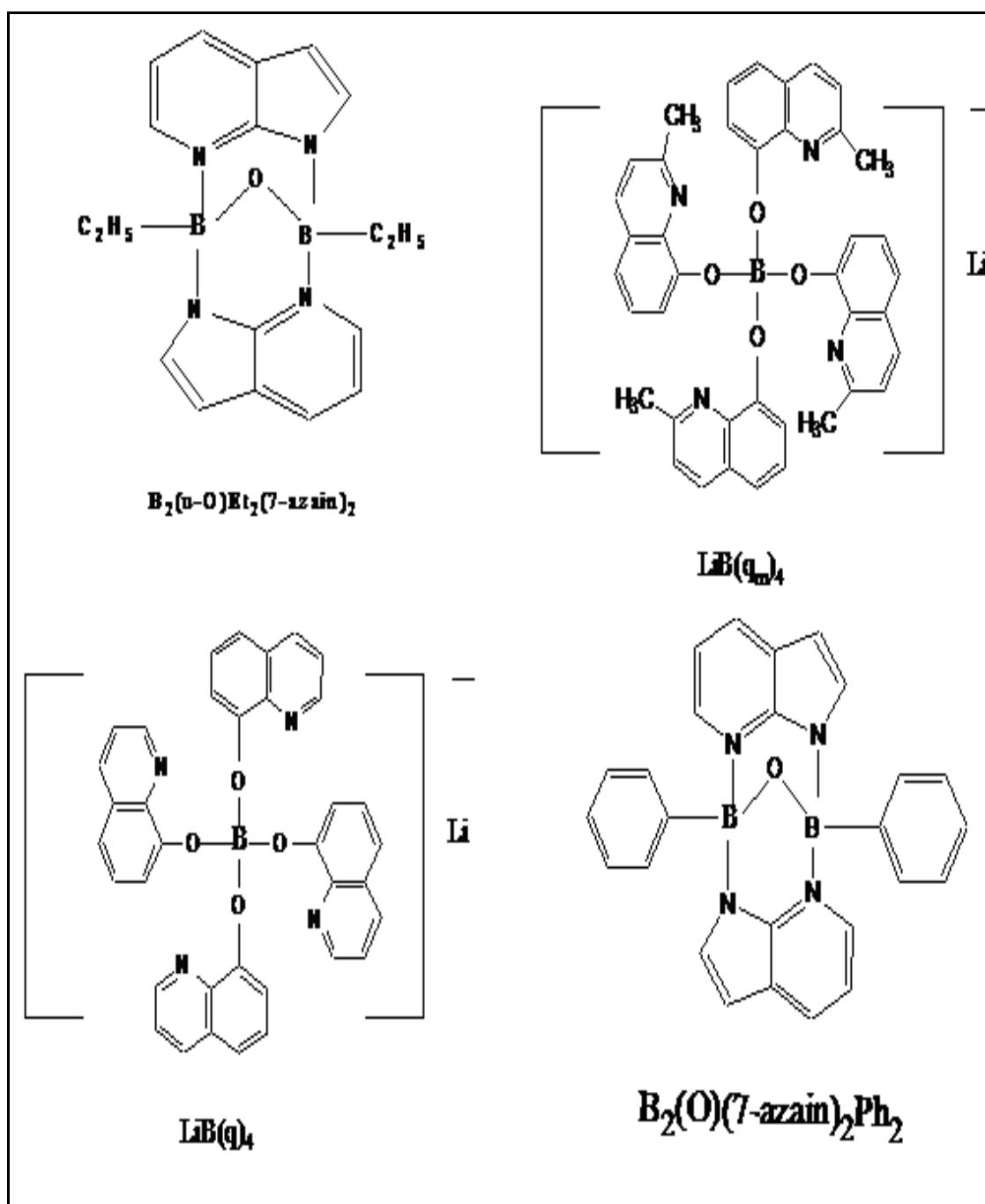
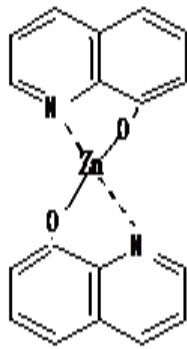
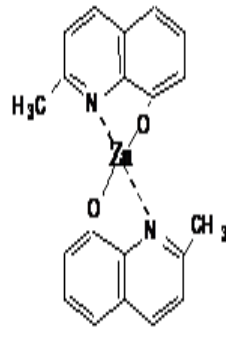


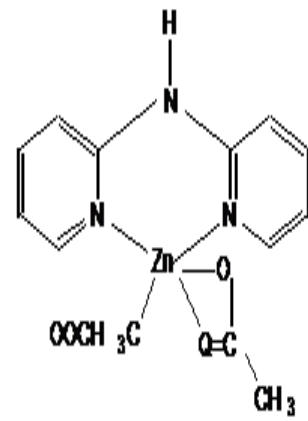
Figure 1.3: Luminescent Boron chelates



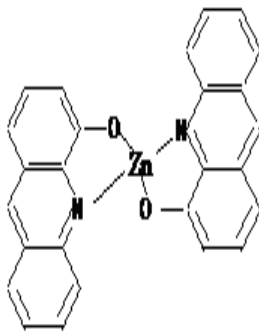
**Znq<sub>2</sub>**



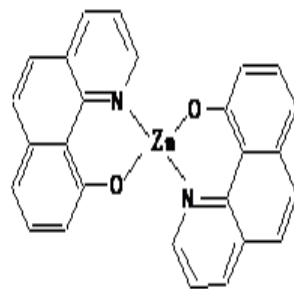
**Znmq<sub>2</sub>**



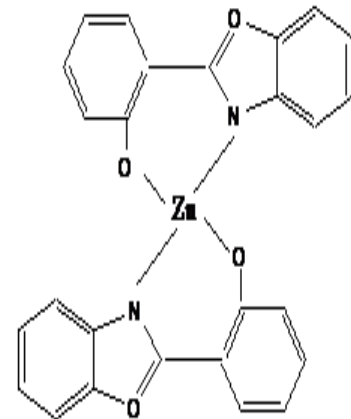
**Zn(dpa)(OAc)<sub>2</sub>**



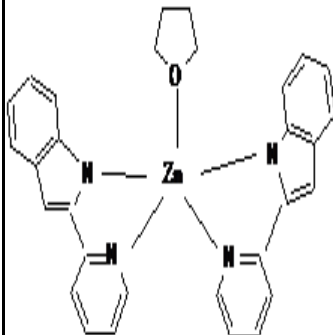
**ZnAc<sub>2</sub>**



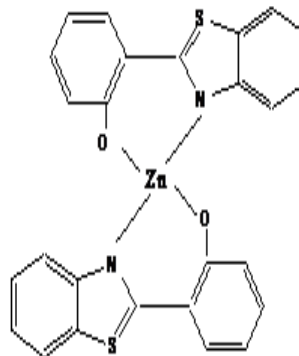
**ZnBq<sub>2</sub>**



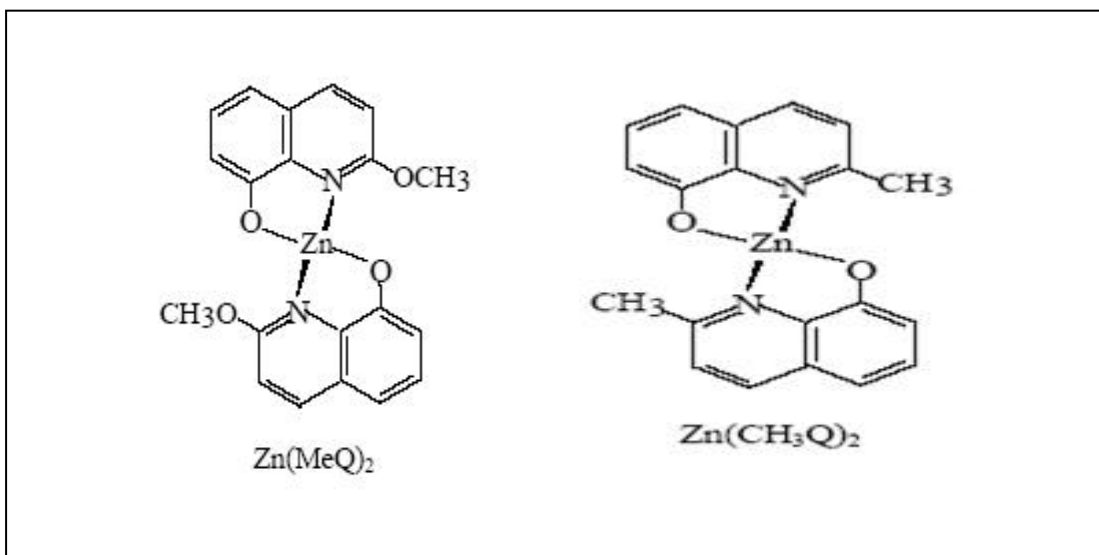
**Zn(BOX)<sub>2</sub>**



**Zn(2-Py-in)<sub>2</sub>(THF)**



**Zn(BTZ)<sub>2</sub>**



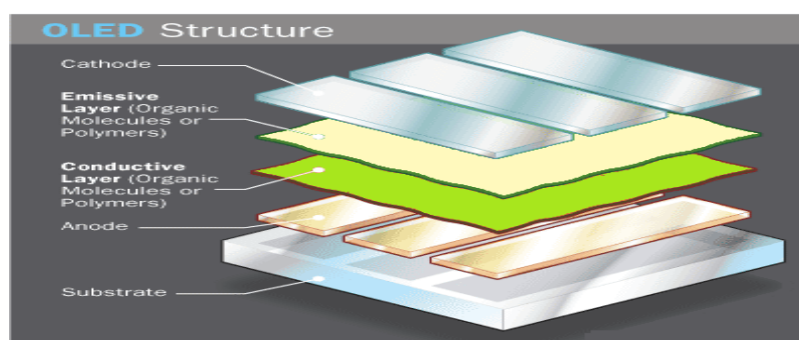
**Figure 1.4: Luminescent Zinc chelates**

### 1.3.1 Construction of an OLED

A typical OLED consists of two organic layers (electron and hole transport layers), embedded between two electrodes. The top electrode is usually a metallic mirror with high reflectivity and the bottom electrode a transparent ITO layer on the top of the glass substrate (Figure 1.5).

### 1.3.2 OLED Components

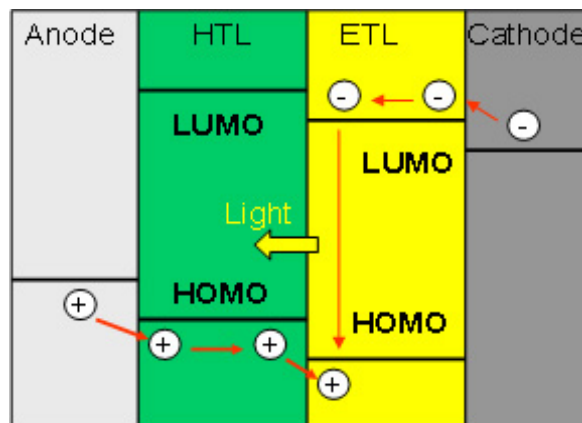
Like an LED, an OLED is a solid-state semiconductor device that is 100 to 500 nanometres thick or about 200 times smaller than a human hair. OLEDs can have either two layers or three layers [25, 20] of organic material; in the latter design, the third layer helps in transportation of electrons from the cathode to the emissive layer.



**Figure 1.5: OLED components.**

### 1.3.3 Working Principle

When electric field is applied to OLED, charge carriers (holes and electrons) are injected from the electrodes into the organic thin films. They migrate through the device under the influence of an electrical field. The charge carriers then recombine, forming excitons. In the past, conventional wisdom suggested that only about 25 % of these excitons could generate light, with the remaining 75 % lost as heat. This was known as fluorescent emission. Through a breakthrough by academic partners at Princeton University and the University of Southern California, however, 100 % of the excitons can be converted into light using a process known as electro phosphorescence, now commonly referred to as phosphorescence. Thus, the efficiency of a phosphorescent OLED is up to four times higher than that of a conventional fluorescent OLED. When a voltage is applied to the electrodes the charges start moving in the device under the influence of the electric field. Electrons leave the cathode and holes move from the anode in opposite direction. The recombination of these charges leads to the creation of a photon with a frequency given by the energy gap ( $E = h\nu$ ) between the LUMO and HOMO levels of the emitting molecules (Figure .6).Therefore, the electrical power applied to the electrodes is transformed into light [26].



**Figure 1.6: Charge transport and light generation in OLED's**

### 1.3.4 Device Efficiency

The efficiency [27] of OLEDs can be characterized by its

- Quantum efficiency,
- Power efficiency (lm/W),
- Luminous efficiency (cd/A), sometimes called luminous yield.

### **a. Quantum efficiency**

The device quantum efficiency  $\eta_q$  has two parts: internal and external:

(1) **Internal quantum efficiency  $\eta_{int}$  or IQE** is the number of photons generated inside the device per number of injected hole – electron pairs. A large fraction of generated photons stay trapped and absorbed inside the device.

(2) **External quantum efficiency  $\eta_{ext}$  or EQE** is the number of photons released from the device per number of injected hole – electron pairs.

### **b. Power efficiency (lm/W)**

Power efficiency  $\eta_p$  is the ratio of the lumen output to the input electrical watts (lm/W).

### **c. Luminous efficiency (Current efficiency) (cd/A)**

Luminous efficacy  $\eta_v$  represents the ratio of the lumen output to the optical watts (radiative power). The luminous efficiency and luminous efficacy of a device account for a spectral sensitivity of a human eye. Therefore, two devices with similar quantum efficiencies can have different luminous performance, depending on the spectrum of the emitted light. In the process of converting electrical power into optical power, losses are incurred due to non-radiative processes (thermal relaxation of excitons, internal reflection and absorption of photons).

## **1.3.5 Advantages & Disadvantages of OLEDs**

**Advantages:** Some advantages self-luminous, low cost, flexibility, power usage etc. are given below:

**Self-luminous-** The efficiency of OLEDs is better than that of other display technologies without the use of backlight, diffusers, and polarizers.

**Low cost and easy fabrication-** Roll-to-roll manufacturing process, such as, inkjet printing and screen printing, are possible for polymer OLEDs.

**Color selectivity-** There is abundant organic materials to produce blue to red light.

Lightweight, compact and thin devices-OLEDs are generally very thin, measuring only~100nm

**Flexibility-** OLEDs can be easily fabricated on plastic substrates paving the way for flexible electronics.

**Robust Design -** OLED's are tough enough to use in portable devices such as cellular phones, digital video cameras, DVD players, car audio equipment and PDA's.

**Viewing Angles –** Can be viewed up to 160 degrees, OLED screens provide a clear and distinct image, even in bright light.

**High Resolution** – High information applications including videos and graphics active-matrix OLED provides the solution. Each pixel can be turned on or off independently to create multiple colors in a fluid and smooth edged display.

**Electronic Paper** – OLED's are paper-thin. Due to the exclusion of certain hardware goods that normal LCD's require, OLED's are as thin as a dime.

**Production Advantages** – Up to 20 % to 50 % cheaper than LCD processes. Plastics will make the OLED tougher and more rugged. The future quite possibly could consist of these OLED's being produced like newspapers, rather than computer "chips".

**Video Capabilities** – They hold the ability to handle

**Hardware Content** - Lighter and faster than LCD's. Can be produced out of plastic and is bendable. Also, OLED's do not need lamps, polarizer, or diffusers.

**Power Usage** – Takes less power to run (2 to 10 volts).

**Fast response**- OLEDs EL decay time is  $< 1\mu\text{s}$ .

### **Disadvantages:**

Highly susceptible to degradation by oxygen and water molecules. Organic materials are very sensitive to oxygen and water molecules which can degrade the device very fast [26]. So the main disadvantage of an OLED is the lifetime. With proper encapsulation, lifetimes exceeding 60,000 hours have been demonstrated. In our laboratory itself, we have been able to increase the shelf life of green Alq3 based OLEDs, from few days to almost a year. Low glass transition temperature  $T_g$  for small molecular devices ( $>70\text{ }^\circ\text{C}$ ). So the operating temperature cannot exceed the glass transition temperature. Low mobility due to amorphous nature of the organic molecules

## **1.3.6 Applications of OLEDs**

### **Monochrome applications**

- Small monochrome displays for hand held electronic devices (cell phones, PDAs, digital cameras, GPS devices etc.) already in the marketplace. Niche applications such as head-mounted displays.

### **Two or multicolor applications**

- Car electronics (radios, GPS displays, maps, warning lights, etc.).

- Instrument electronics, heads-up instrumentation for aircraft and automobiles.
- Rugged PDAs, wrist-mounted, etc. Some are already in the market.

### **Full color application**

- LCD backlights (white light)
- Small full color displays. To be introduced within a year.
- Full color, high-resolution, personal communicators

### **Applications Convertible to OLEDs**

General White applications (to replace incandescent/halogen) and General White applications (to replace fluorescent)

- Lighting panels for illumination of residential and commercial buildings.
- Lighting panels for advertising boards, large signs, etc.
- Ultra-lightweight, wall-size television monitors.
- Office windows, walls and partitions that double as computer screens.
- Color-changing lighting panels and light walls for homes and offices, etc.

### **1.3.7 Challenges and Critical Issues**

Even though remarkable progress has been made, OLEDs still face great challenges before commercialization as white-light sources can be even considered. OLEDs have [10] already achieved power conversion efficiencies close to those needed for energy efficient operation, but only for the green and red light, and with in sufficient luminescence. Other colors are still far beyond. The peak brightness can be greater than several hundreds of thousands  $\text{cd/m}^2$ , but these devices degrade very quickly. The operating voltages can be as low as the desired 2.6 V- 4 V but the luminance are still too low under those voltages. For white light and the desired luminance, the passing electric currents are still too high, and the power conversion efficiencies are low. The useful lifetime of white-light emitting devices with the desired luminance needs to be increased by more than one order of magnitude. The surface area of the largest devices made to date is only of the order of a couple of square inches, while the illumination panels will have to cover several square feet. The uniformity of these devices is far worse than desired, etc. The technological issues facing [28]. OLEDs can be summarized into the two main categories:

- Operational life and Power conversion efficiency of OLEDs.
- Cost of manufacturing, the lack of infrastructure.

Specifically, to effectively compete with, and eventually displace fluorescent lighting, these challenges are:

- (1) Efficacy improvement to obtain 120 lm/W for white light for a 1000 lm white source and useful life 20,000 hrs.
- (2) Cost of manufacturing so as to be lower than for traditional light sources.
- (3) Development of new infrastructure including powering of high current-low voltage distributed sources, new industries and technologies that are enabled by attributes of OLED.

## **1.4 Electroluminescent Materials used in OLED**

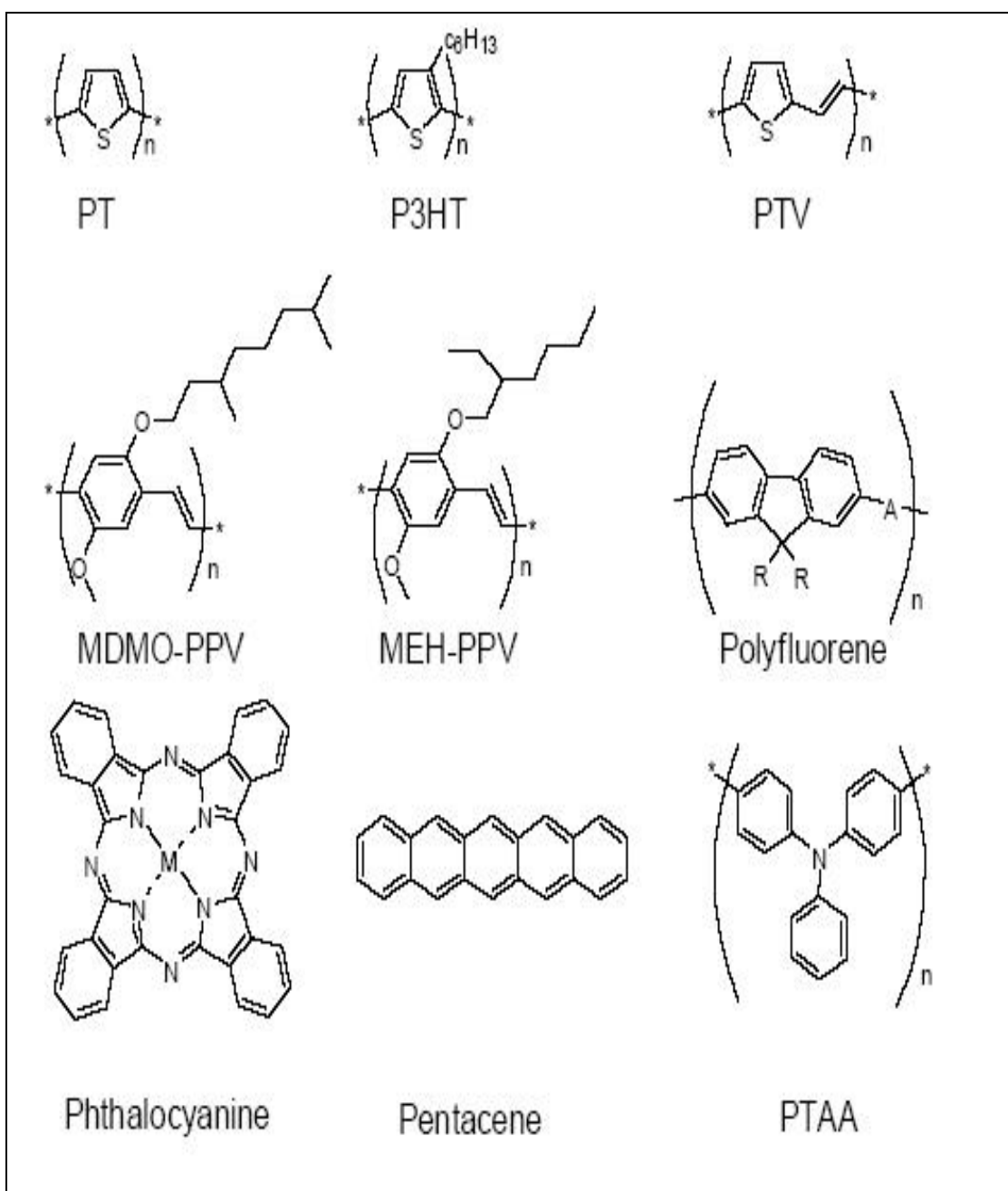
Materials used for the fabrication of organic light emitting diodes are of organic origin and semi conducting in nature, during the fabrication of the OLED it's important to select an appropriate electroluminescent material for proper function and best performance.

The materials for OLED is broadly divided into two categories:

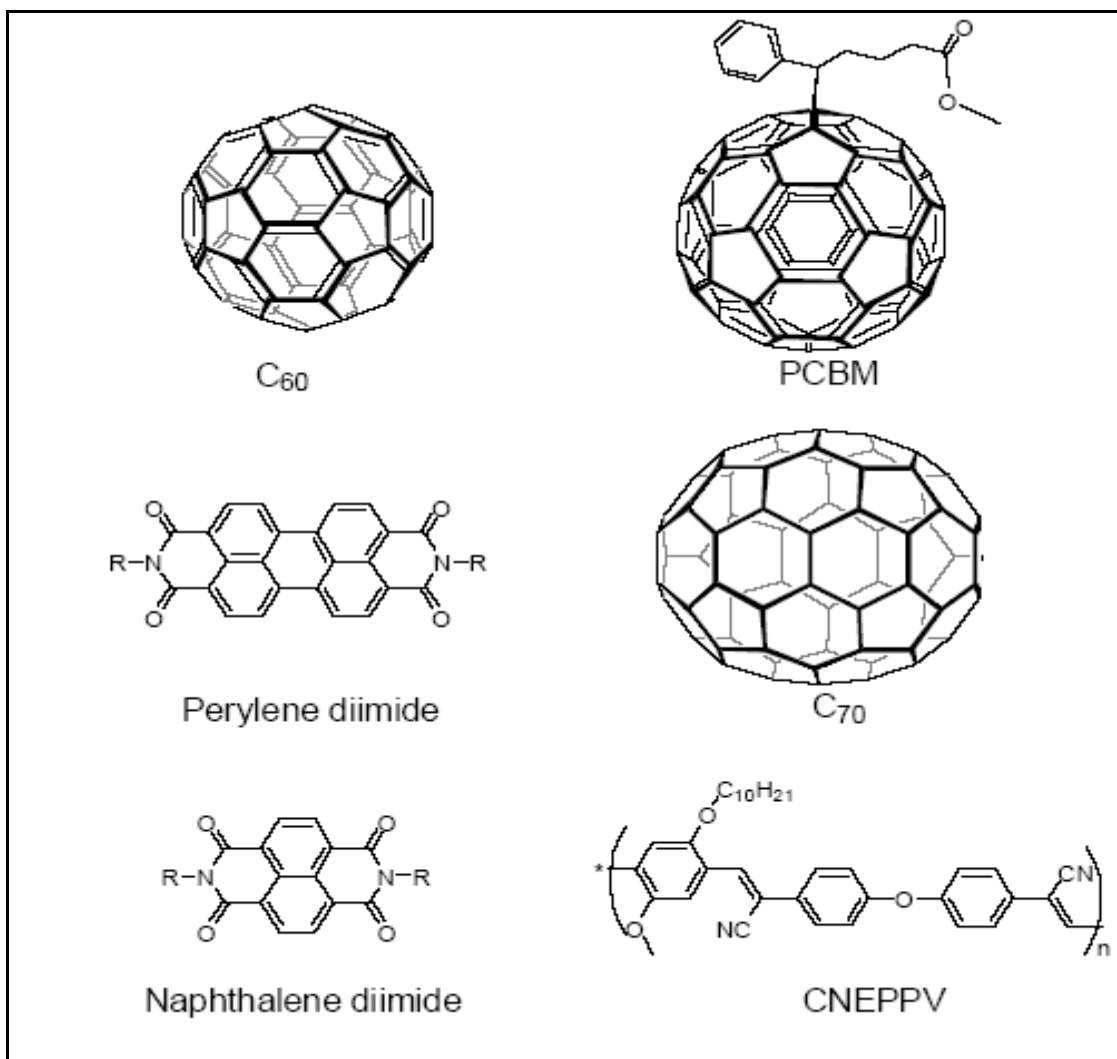
- a. Polymers
- b. Small Molecules

### **1.4.1 Polymers**

Besides their roles as inert binders, polymers have been used [29] in OLEDs as electroluminescent materials since the late 1980s, when emission was observed in poly (1, 4-phenylene vinylene). The major advantage of using polymers [30] 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 printing. 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 $\mu$ m and a 100 nm thick layer, ink-jet printing can use polymer solutions with concentration as low as 1 %. Polymers in OLEDs are used as emissive as well as hole transport layer and electron transport layer. Polymers are of two types 'n' type and 'p' type.



**Figure 1.7: P type polymer**



**Figure 1.8: N-type polymer**

### 1.4.2 Small Molecules

Small molecule materials [12, 31] 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[11,13] as an efficient electron transport and

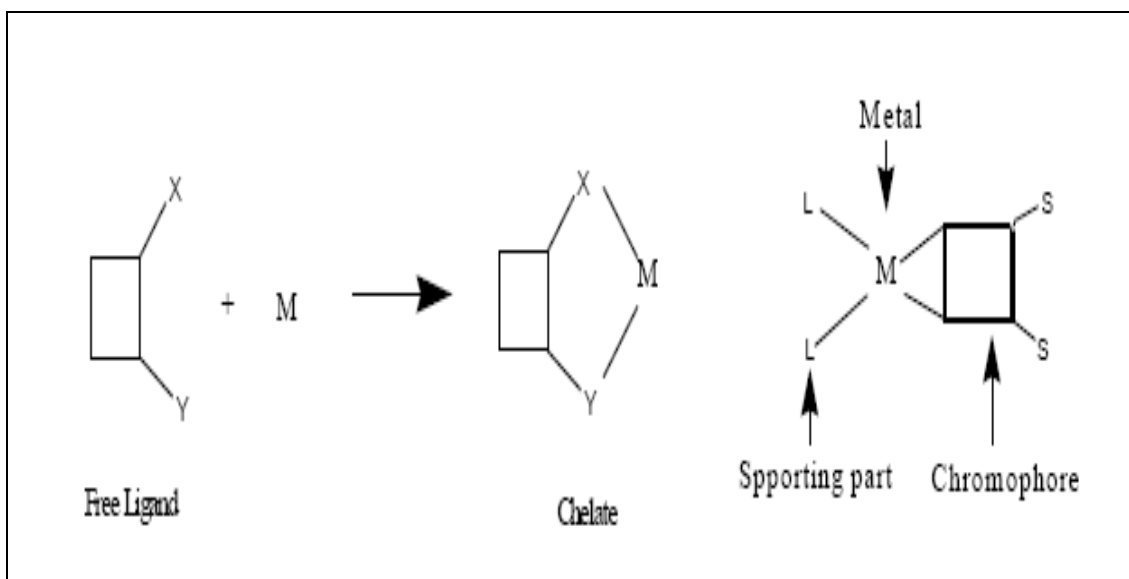
electroluminescent material leads to further research and development in this field, and now there are a wide variety of small molecule emitters with varied emission wavelengths to choose from. Because light emission from the Alq<sub>3</sub> complexes originates from the electronic transitions located 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 substituent to the phenolate ring results in a red-shifted emission, while the attachment of electron-donating substituent's 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.

### **Progress of Small Organic Molecular Luminescent Materials**

Small organic molecules and some coordination complexes are considered promising luminescent materials because they have obvious advantages over polymers. First they can be purified easily so that they may have high fluorescence efficiency. Second they can be fabricated into thin films by sublimation. The most important advantage is that small molecular materials have a wider selection of emission color than polymers, especially in the blue region, since the structure of a small molecule can be modified readily to achieve the desired energy band gap.

### **Principles of Luminescent Metal chelate**

The requirement for a material to be a good electro luminescent material is that it must be a good photo luminescent material. A good photo luminescent compound should also have high thermal and air stability, high volatility and high emission efficiency. A promising strategy for the reduction of useful luminescent materials involves the synthesis of metal chelates. The metal typically acts as a Lewis acid, associating with one or more ligands with luminescent properties. Luminescent metal chelates contain one or more organic chromophores and supporting metal substituent ligands attached to the metal centre (or a main group element such as Boron) via a donor acceptor bond or a covalent bond. Because metal chelate (Figure 1.9 (a)) compounds are supporting part chromophore (Figure 1.9(b)) small molecules, they can be sublimed readily; Luminescent chelate when appropriate ligands are present.



**Figure 1.9(a)**

**Figure 1.9(b)**

**Figure 1.9 (a): Principle of Luminescent metal chelate Figure 1.9(b): Luminescent chelate**

## 1.5 Metal complexes and their Selection Criteria

We have concentrated on the studies of small molecules, because they are easy to handle in conventional vacuum deposition equipment. There are a large variety of small fluorescent molecules but not so many molecules that can make uniform thin films in vacuum vapour deposition. If a small molecule can be sublimed in vacuum successfully, it often forms a polycrystalline film with many pinholes, which leads to device failure. Even when a uniform thin film is obtained, carrier transport ability and fluorescent yield of the film are then extra problems. Knowing the energy bands of the HOMO and LUMO levels for a compound is also important in fabricating an organic EL cell.

To summarize, the following properties are strongly required or indispensable for the EL materials: (1) form a uniform thin film; (2) carrier (hole/electron) transport, ability; (3) high fluorescent yield; (4) stable to heat (have a high glass-transition temperature); (5) suitable HOMO/LUMO levels for the carrier injections[32]. There are many factors affecting the emission efficiency of photoluminescence.

- The most common and important factor is the thermal vibration of the chromophore, which provides a path for the loss of energy via a radiation less pathway. One can

reduce the loss of energy via thermal vibration by increasing the rigidity of the chromophore. For coordination compounds, this reduction can be achieved by chelating the appropriate chromophore to a suitable metal ion, which reduces the degree of freedom of the thermal vibrations of the chromophore, thus increasing its emission efficiency.

- Compared with polymers, another advantage of metal chelates is that they can be prepared in very pure form. Therefore, they may have high luminescence quantum yield and high stabilities at high operating voltages.
- The choice of metal ions for EL chelates is limited to those metals which do not exhibit d-d transitions that may interfere with the luminescence of the ligand. Therefore, aluminium (III), boron (III), beryllium (II) and zinc (II) Cadmium (II)) are ideal. Since beryllium (II), boron (III) and aluminium (III) has no d electrons and zinc (II)and Cadmium (II) have a closed shell of d electrons. The metal ions only serve a structural purpose by stabilizing a luminescent ligand.
- Zinc and Cadmium metal complexes can be used both as an electron transport layer, hole transport layer or as an emissive layer.
- Zinc and Cadmium metal complexes have a wide range of spectrum in the visible region [13, 16].

Photoluminescence emission (nm) of Zinc metal complexes can be summarized in the following table (2).

Compounds	PL Emission (nm)	
	Solution (in MeOH)	Solid
Znq <sub>2</sub>	-	535,567
ZnBq <sub>2</sub>	-	572
Zn(Ac) <sub>2</sub>	-	647
Zn(BTZ) <sub>2</sub>	-	486,524
Zn(BOX) <sub>2</sub>	-	478
Zn(dpa)(OAC) <sub>2</sub>	-	378
Zn(dpa)Cl <sub>2</sub>	-	378
Zn(dpa)(CN) <sub>2</sub>	359	363,418
Zn(dpa)(4-MeC <sub>6</sub> H <sub>4</sub> S) <sub>2</sub>	354	481
Zn(dpa) <sub>2</sub> [(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> ]	360	373
Zn(tdpa)(OAC) <sub>2</sub>	394	411
Zn(tdpa)Cl <sub>2</sub>	392	403

**Table (2): PL emission (nm) of different Zinc metal complexes**

## 1.6 Deposition Techniques for OLED Fabrication

Deposition techniques for the Organic materials can be classified in the following two broad categories.

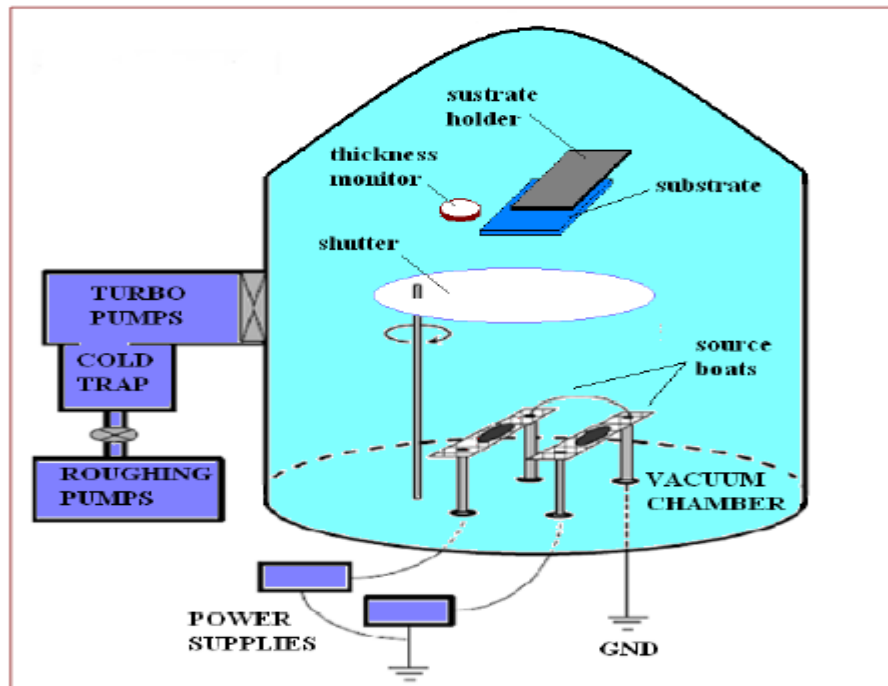
### (A) Evaporation (Suitable for small molecules)

Evaporation techniques which are suitable for small molecules can be of following three types:

- Sputtering
- E-beam evaporation
- Vapour deposition

Electron -beam evaporation and sputtering are for high temperature material, (both available in clean room). Sputtering is especially useful for large substrates (Used for ITO). These methods can damage the organic layers since organic materials have low glass transition temperatures. Vacuum evaporation (Figure 1.10) by direct heating is the most appropriate for organic materials. The pressure needed to deposit organic devices is about  $10^{-5}$ - $10^{-6}$  torr. Deposition rate for organics is about 1-10 Å/s.

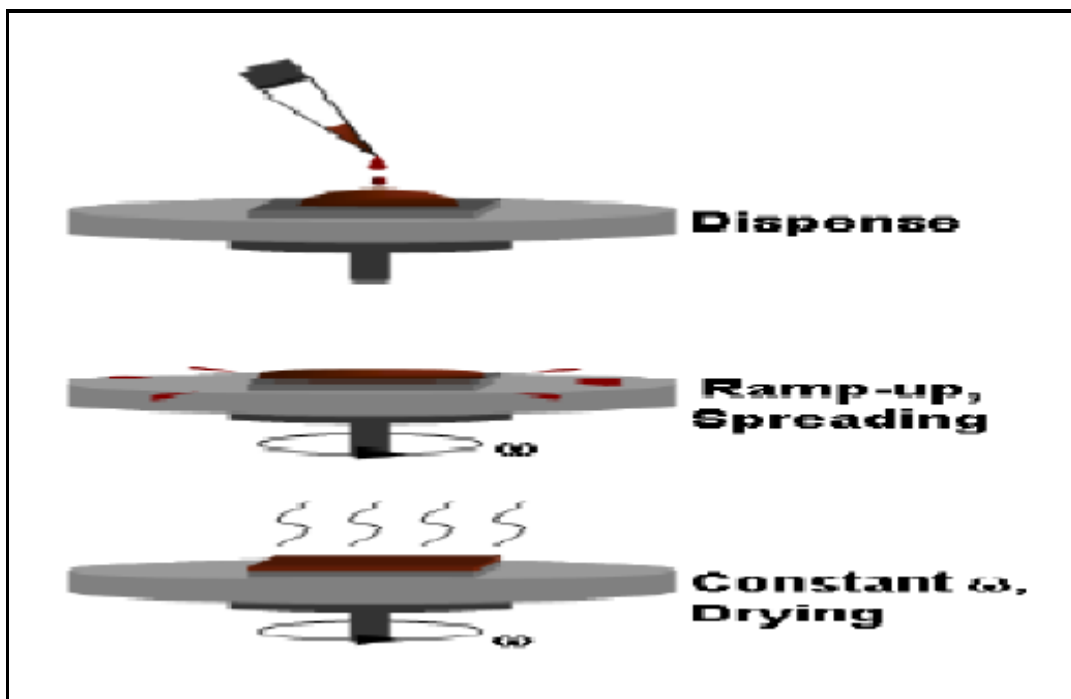
Deposition Temperature depends on vacuum quality and material. Substrates should be kept at low temperature during deposition. Deposition rate is controlled by crystal monitor.



**Figure 1.10: Thermal Vapour evaporation Technique**

**(B) Wet processing (Suitable for polymers)**

Wet processing which is suitable for polymers can be of two types: Spin coating and Inkjet printing. In the Spin Coating (Figure 1.11) process for polymer film deposition polymer solution is dropped on the rotating substrate. By centrifugal force, solution spreads on the substrate. Thin film properties depend on rotation speed curve, solution, temperature, vapor pressure of material. With inkjet technology, OLEDs are sprayed onto substrates just like inks are sprayed onto paper during printing. Inkjet technology greatly reduces the cost of OLED manufacturing and allows OLEDs to be printed onto very large films for large displays like 80-inch TV screens or electronic billboards.



*Figure 1.11: Spin Coating*

## **CHAPTER 2**

### **MOTIVATIONS AND SCOPE OF THE WORK**

## 2.1 Motivations

For the first time in the year 1987 C.W Tang and S.A Van Slyke [11] constructed electroluminescent device using organic materials as the emitting elements. It has been found that the Electron-hole recombination and green electroluminescent emissions are confined near the organic interface region. High external quantum efficiency (1 % photon/electron), luminous efficiency (1.5 lm/W), and brightness (>1000 cd/m<sup>2</sup>) have been achieved at a driving voltage below 10 V.

There is another work reported by Yuji Hamada [12] in 1997 in which several chelate metal complexes have been developed. RGB (red, green, and blue) emission has been achieved using only chelate metal complexes, after successfully obtaining high-luminance blue-emitting materials, such as azomethine-zinc complex. This shows that the chelate metal complexes can be applied to full-color flat displays as an emitting material. Bis (10-hydroxybenzo quinolinato) beryllium (BeBq<sub>2</sub>) has been reported as an electron transport layer in OLED devices, with a lifetime (initial luminance: 500 cd/m<sup>2</sup>) of more than 3500 h, which is a practical level.

Yoshiharu Sato, Shoko Ichinosawa et al [40] in the year 1998 reported that the degradation of the organic electroluminescent (EL) device is closely related to the physical and chemical stability of the organic thin films. They described three important aspects as:

- (1) An effect of glass transition temperature of hole transport materials on thermal stability of the device;
- (2) A role of interface layers at both the anode and cathode; and
- (3) An improvement of operation stability by doping technology.

Considering the above points, an organic EL device has been fabricated with a good operation performance: lifetime of longer than 3000 h at an initial luminance of 500cd/m<sup>2</sup>.

A better performance has been observed by S. E. Shaheen, G. E. Jabbour, et al [41] using a triphenyldiamine side-group polymers as hole transport layers in multilayer organic light-emitting diodes using 8-hydroxyquinoline aluminum (Alq<sub>3</sub>) as an emission layer. The comparative study of electroluminescent properties of Tris (8-hydroxyquinoline) gallium Gaq<sub>3</sub> and 8-hydroxyquinoline zinc (Znq<sub>2</sub>) has been investigated by Yong Qiu,

Wenhua Hu et al. [42] in the year 2000. It has been reported that the solid film of Gaq<sub>3</sub> could yield a very strong photoluminescence (PL) and an EL device with Znq<sub>2</sub> could harvest a higher brightness even than Alq<sub>3</sub>.

In the same year 2000 Yoshitaka Nishio, Yuji Hamada et al. [43] reported the studies of small molecules which can form thin films on thermal vapour deposition. Following properties have been reported for the EL materials:

- (1) Form a uniform thin film
- (2) Carrier (hole/electron) transport ability
- (3) High fluorescent yield
- (4) Stable to heat (have a high glass-transition temperature)
- (5) Suitable HOMO/LUMO levels for the carrier injections

Degradation mechanisms in small molecule-based organic light-emitting devices (OLEDs) have been reviewed in the year 2002 by Zoran D. Popovic and Hany Aziz [44].

In the year 2004 the electrical and optical properties of the NiO films deposited under various conditions have been first characterized by I-Min Chan and Franklin C. Hong et al [45]. It has been suggested that the NiO/ITO anode is an excellent choice to enhance the hole injection in OLED devices.

Again in the same year it has been reported by N. N. Dinh, D. V. Thanh et al [46] that the enhancement in both the onset electric field (onset voltage) and the reverse current are due to lowering the work function of Al/Alq<sub>3</sub> by the application of the super-thin LiF layer. These enable electrons better inject into the emissive Alq<sub>3</sub> material, consequently one can have higher possibility of emissive recombination of excitons in the devices.

In the year 2005 Naiying Du, Qunbo Mei et al [24] reported that the electron donating substituent increased the solubility of the corresponding metal quinolate complexes in nonpolar solvents and caused a red-shift in the emission wavelength. The end groups of two compounds facilitated polymerization to form the metalloquinolate-containing polymers.

An azomethin-zinc complex, bis[salicylidene(4-dimethylamino)aniline]zinc(II) (Zn(sada)<sub>2</sub>) has been synthesized and structurally characterized by Junfeng Xie, Juan Qiao et al [47]. It has been found that compared with the typical bilayer device of N,N'-diphenyl-N,N'-bis(1-naphthyl)-benzidine(NPB)/tris-(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>), the device with Zn(sada)<sub>2</sub> as the electron transporting layer

exhibited a much lower turn-on voltage of 2.5 V (it is usually 3.5 V for an NPB/Alq<sub>3</sub> device).

In the recent years more work has been done on electroluminescent small molecules based on zinc metal complexes.

In 2006 new electroluminescence materials, including [2-(2-hydroxyphenyl)benzoxazole] (Zn(HPB)<sub>2</sub>) and [(1,10-phenanthroline)(8-hydroxyquinoline)] Zn(phen)q has been synthesized by Yoon-Ki Jang, Dong-Eun Kim[22]. The photoluminescence (PL) spectra of Zn(HPB)<sub>2</sub> and Zn(phen)q has been observed to be blue and yellowish green, respectively.

In the same year zinc complexes (Zn(HPB)<sub>2</sub> and Zn(HPB)q) has been synthesized by Kim, Won Sam; You, Jung Min; et al [48]. It has been reported that the ITO/NPB (40 nm)/Alq<sub>3</sub> (60 nm)/Zn(HPB)<sub>2</sub> (5 nm)/LiF/Al device showed increased luminance of  $L = 17000 \text{ cd/m}^2$  compared to  $L = 12000 \text{ cd/m}^2$  for similar device fabricated without the hole-blocking layer.

Again in the same year Christopher Williams et al [49] reported High performance organic light-emitting diodes (OLEDs) implemented on transparent and conductive single-wall carbon nanotube sheets.

Enhanced photoluminescence intensity has been observed in the same year for the samples annealed in oxygen near 100 °C by Vivek Kumar Shukla, Satyendra Kumar et al [50]. Sudden change in roughness which may be as a consequence of change in surface morphology due to phase change and fraction of new phase is estimated by phase images taken by Atomic Force Microscopy (AFM) has been reported. The enhanced photoluminescence has been understood in terms of formation of a new phase.

The electroluminescence devices with the ZnL(where L is the ligand) complex as the emitting layer has been constructed, by Tianzhi Yu et al [51], in the year 2007 which exhibited blue emission with a peak at 455 nm and the maximum brightness of  $650 \text{ cd m}^{-2}$

In 2007 a new metal complex was successfully synthesized by the reaction of 8-hydroxy quinoline and 2,2' bipyridine with Zinc acetate by Virendra Kumar Rai, Ritu Srivastava. The thermal stability and electroluminescence properties of Zn(Bpy)q suggests a promising yellow emitting material.

**Table (3): Summary**

Author	Work	Result
C.W Tang and S.A VanSlyke  (1987)	Constructed electroluminescent device ( $Alq_3$ based) using organic materials as the emitting elements.	High external quantum efficiency (1% photon/electron), luminous efficiency (1.5 lm/W), and brightness ( $>1000\text{ cd/m}^2$ ) has been achieved at a driving voltage below 10 V.
Yuji Hamada  (1997)	Developed several chelate metal zinc complexes. RGB (red, green, and blue) emission has been achieved.	The chelate metal complexes can be applied to full-color flat displays as an emitting material.
Yoshiharu Sato, Shoko Ichinosawa et al  (1998)	They reported that the degradation of the organic electroluminescent (EL) device is closely related to the physical and chemical stability of the organic thin films.	An organic EL device has been fabricated with a good operation performance: lifetime of longer than 3000 h at an initial luminance of $500\text{ cd/m}^2$
S. E. Shaheen, G. E. Jabbour, et al  (2000)	Used triphenyldiamine side-group polymers as hole transport layers in multilayer organic light-emitting diodes using 8-hydroxyquinoline aluminum ( $Alq_3$ ) as an emission layer.	A better performance has been observed.
Yong Qiu, Wenhua Hu et al  (2000)	Comparative study of electroluminescent properties of Tris (8-hydroxyquinoline) gallium $Gaq_3$ and 8-hydroxyquinoline zinc ( $Znq_2$ )	It has been reported that the solid film of $Gaq_3$ could yield a very strong photoluminescence (PL) and an EL device with $Znq_2$ could harvest a higher brightness even than $Alq_3$ .
Zoran D. Popovic and Hany Aziz  (2002)	Degradation mechanisms in small molecule-based organic light-emitting devices (OLEDs) have been reviewed	

Junfeng Xie, Juan Qiao, et al  (2005)	An azomethin- zinc complex, bis[salicylidene(4-dimethylamino)aniline]zinc(II) ( $Zn(sada)_2$ ) has been synthesized and structurally characterized	It has been found that compared with the typical bilayer device of (NPB)/tris-(8-hydroxyquinoline)aluminum ( $Alq_3$ ), the device with $Zn(sada)_2$ as the electron transporting layer exhibited a much lower turn-on voltage of 2.5 V (it is usually 3.5 V for an NPB/ $Alq_3$ device)
Yoon-Ki Jang, Dong-Eun Kim  (2006)	Synthesized new electroluminescence materials, ( $Zn(HPB)_2$ ) and $Zn(phen)q$	The photoluminescence (PL) spectra of $Zn(HPB)_2$ and $Zn(phen)q$ has been observed to be blue and yellowish green, respectively.
Christopher Williams et al  (2006)	Implemented transparent and conductive single-wall carbon nanotube sheets on the substrate.	High performance of organic light-emitting diodes (OLEDs) has been reported.
Vivek Kumar Shukla, Satyendra Kumaret et al  (2006)	Annealed ITO coated substrate in oxygen near 100 °C	Sudden change in roughness which may be as a consequence of change in surface morphology due to phase change and fraction of new phase is estimated by phase images taken by AFM has been reported.
Tianzhi Yu et al  (2007)	The electroluminescence devices with the $ZnL$ (L=ligand) complex as the emitting layer have been constructed.	Blue emission with a peak at 455 nm and the maximum brightness of $650 \text{ cd m}^{-2}$

## 2.2 Scope of the work

There are a number of problems which are hindering these Zinc chelates for being utilized in OLED devices. They are life time, efficiency, operating voltage, stability.

Our aim of the thesis is to improve the device performance by the following means

- Anode modification.
- Multi layer structure to increase the efficiency of OLED.
- Synthesis of novel organic emissive, hole transport, electron transport and electron injector for the enhancement of life time, efficiency and reduction in operating voltage in OLED.

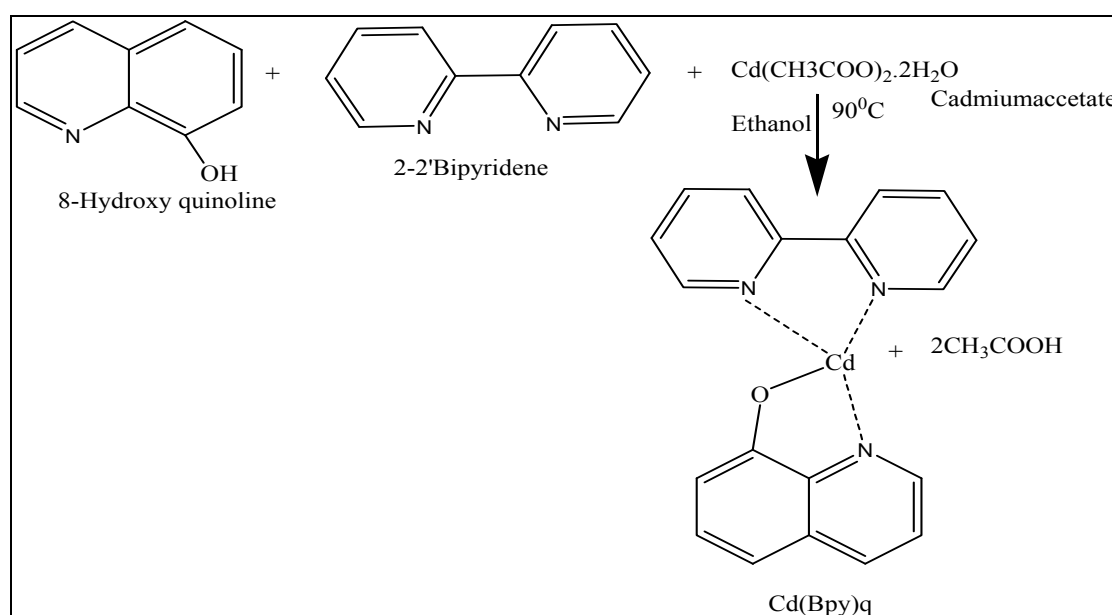
- Charge confinement and interfacial engineering of OLED devices (Confinement of charge carrier and exciton is the essential factor for enhancing the efficiency and stability of the electro luminescence devices) by transport studies.

**CHAPTER 3**  
**EXPERIMENTAL DETAILS**

### 3.1 Synthesis

#### 3.1.1 Synthesis of cadmium (2, 2' bipyridine) 8-Hydroxyquinoline (Cd(Bpy)q)

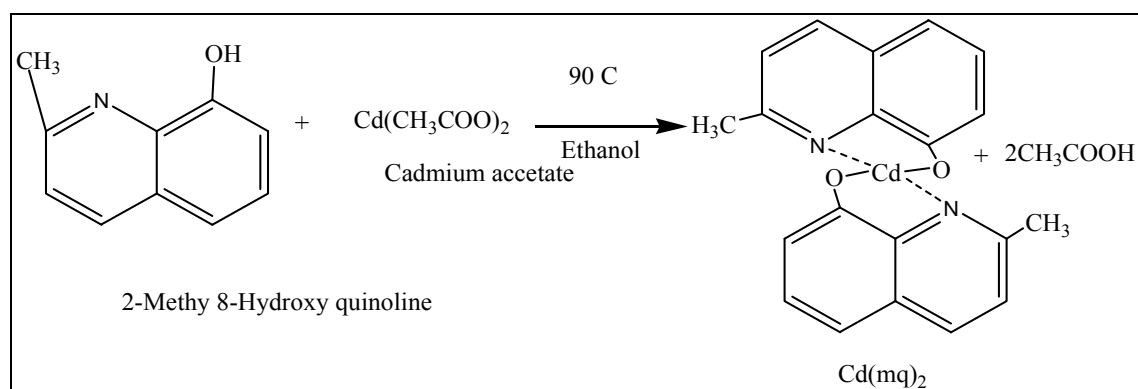
The synthesis of Cd(Bpy)q compound was accomplished by the processes, as shown in the Figure 3.1 The material was obtained by the reaction of the two ligands, bipyridine (BPy) and 8-hydroxyquinoline(q) with zinc acetate (metal ligand) at 1:1:1 molar ratio in ethyl alcohol. A solution of bipyridine 0.18 g (0.001 mol) (Qualigens Fine Chemicals, India) was prepared in 20 ml absolute ethanol (s.d. Fine Chem Limited India) in a 100 ml three neck flask and stirred in nitrogen atmosphere for 30 min and then a solution of 8-hydroxy quinoline 0.145 g (0.001 mol) (Merck, India) in 20 ml of absolute ethanol was added to the reaction mixture, and stirred at 90 °C for 2 h. This was allowed to cool to 70°C and a solution of cadmium acetate 0.267g (0.001 mol) in 3 ml of deionized water was added drop wise to the reaction mixture. After 2 h of stirring a yellowish precipitates of the complex were separated from the reaction mixture which was filtered and dried at 90°C in vacuum oven for 24 h. The synthesized material was further purified by vacuum sublimation and stored in desiccator.



**Figure 3.1: Scheme- Synthesis of Cd(Bpy)q**

### 3.1.2 Synthesis of bis(2-methyl- 8-Hydroxyquinolate)(cadmium) Cd(mq)<sub>2</sub>:

A solution of 2-methyl 8-hydroxy quinoline 0.32 g (2 m mol) (Merck, India) was prepared in 40 ml absolute ethanol (s.d. Fine Chem Limited India) in 100 ml three neck flask and stirred with a magnetic stirrer for one hour at a constant temperature of 70 °C in an oil bath. A solution of cadmium acetate 0.267 g (1 m mol) in 2 ml of deionised water was added drop wise to the reaction mixture. After 2 h stirring a yellowish green precipitates of the complex were separated from the reaction mixture which was filtered and dried at 70 °C in vacuum oven for 24 h. The synthesized material was further purified by vacuum sublimation and stored in desiccators. The schematic diagram of synthesis is shown in following Figure 3.2.

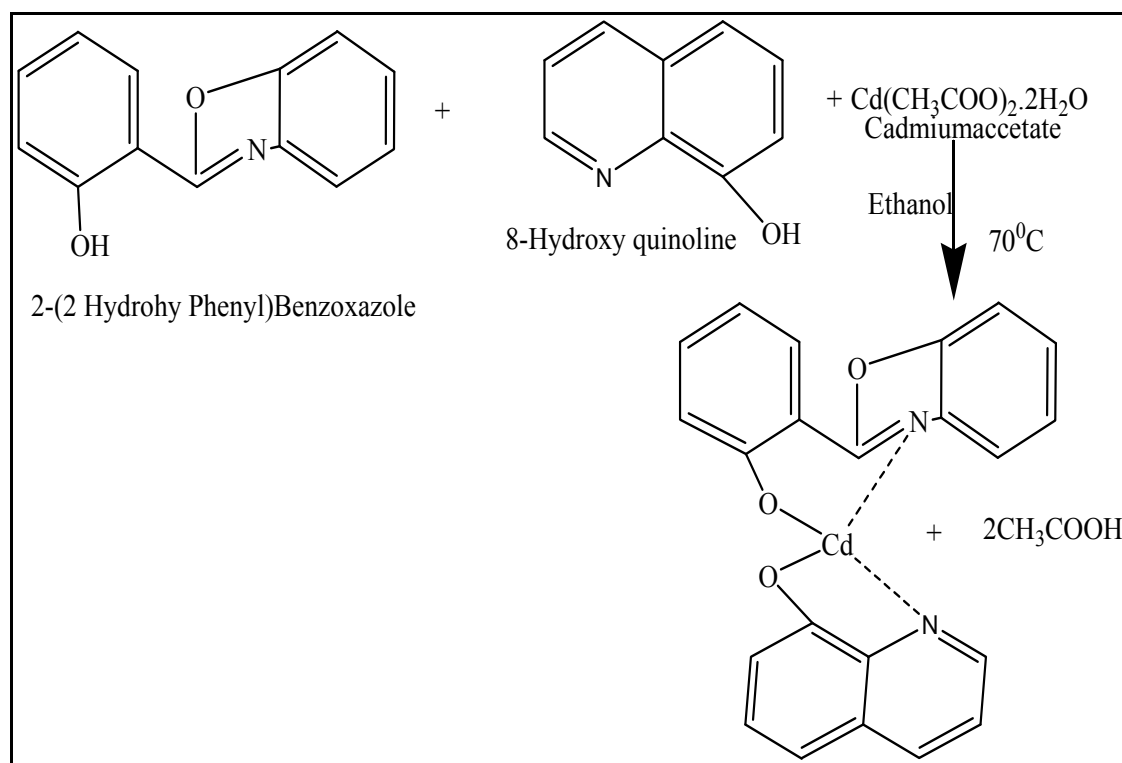


**Figure 3.2: Scheme- Synthesis of Cd(mq)<sub>2</sub>.**

### 3.1.3 Synthesis of Cadmium 2-(2-hydroxyphenyl) benzoxazole (8-Hydroxyquinoline) Cd(HPB)q

A solution of 2-(2-hydroxyphenyl) benzoxazole (HPB) 0.211 g (1 m mol) (Merck, India) was dissolved in 20 ml of absolute ethanol (s.d. Fine Chem Limited India) in a 100 ml three neck flask and stirred with a magnetic stirrer for one hour at a constant temperature of 70 °C in nitrogen atmosphere. The solution was stirred for 1 h, after which Cadmium acetate dihydrate 0.267 g (1 m mol) in water (3 ml) and 8-hydroxyquinoline (q) (0.145 g) in absolute ethanol (10 ml) were added drop wise while the stirring continued. After the addition was completed, the reaction was further carried out for 3 h. The yellow precipitates were collected by filtration,

purified by re-crystallization from acetone and ethanol and dried overnight. The schematic diagram of synthesis is shown in following Figure 3.3.



**Figure 3.3: Scheme- Synthesis of Cd(HPB)q**

### 3.3 Material Characterization, device fabrication techniques:

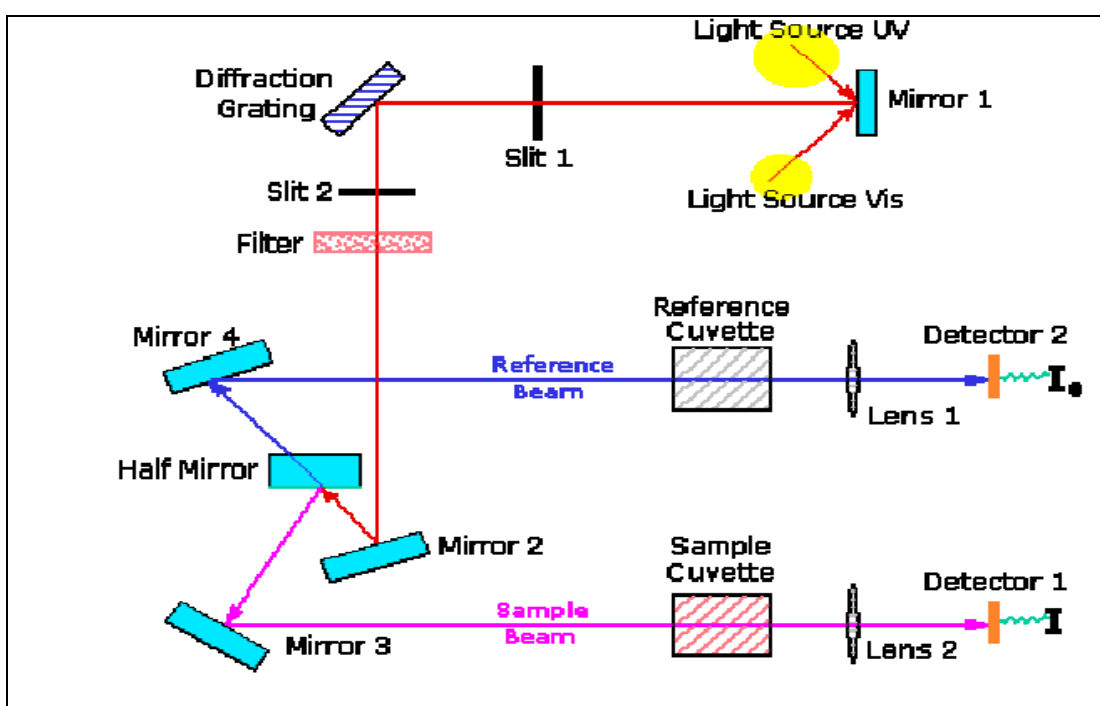
#### 3.3.1 Materials characterization

In material characterization basically we have tried 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 materials are described below.

##### 3.3.1.1 UV-Visible Absorption Spectroscopy

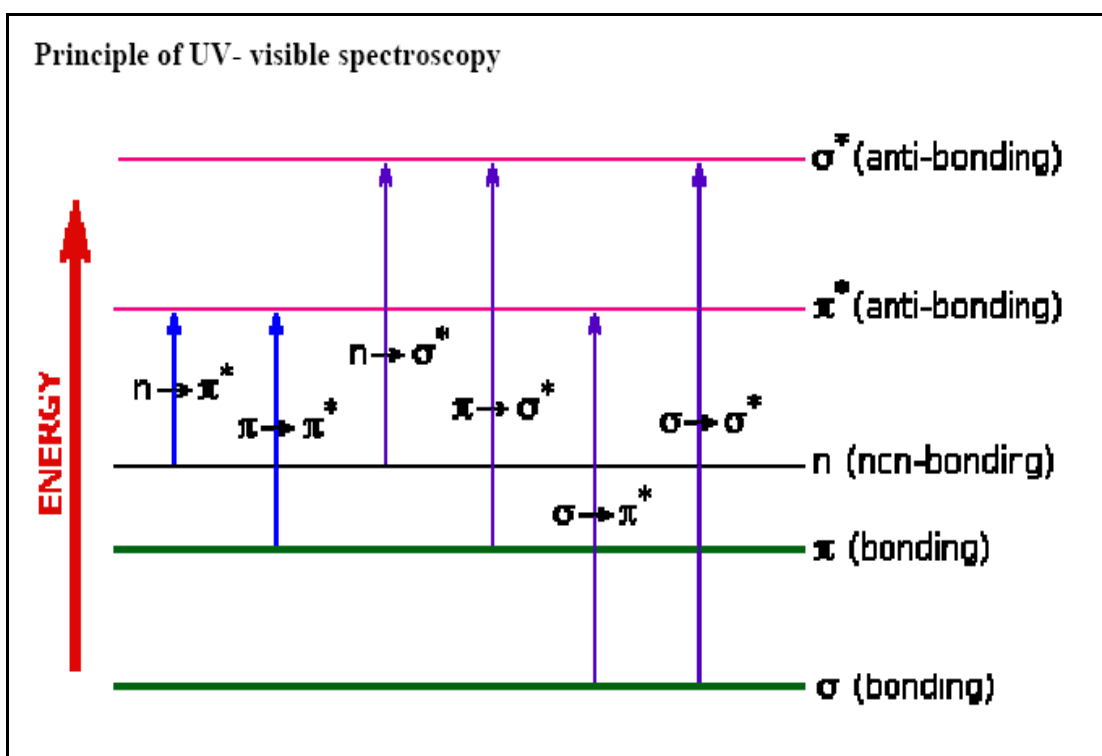
A diagram of the components of a typical spectrometer is shown in the following diagram (Figure 3.4). The functioning of this instrument is relatively straightforward. A beam of light from a visible and/or UV light source (colored red) is separated into its component wavelengths by a prism or diffraction 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 from normally 200nm to 400nm and the visible portion from 200nm to 800nm [52].



**Figure.3.4 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 graph versus wavelength. Absorption may be presented as transmittance ( $T=I/ I_0$ ) or absorbance ( $A=\log I/ I_0$ ). If no absorption has occurred,  $T=1.0$  and  $A=0$ . Most spectrometers display absorbance on the vertical axis, and the commonly observed range from 0 to 100% transmittance) to 2 (1% transmittance). The wavelength of maximum absorbance is characteristic value, designated as  $\lambda_{max}$  [53].



**Figure: 3.5 Energy level diagram**

The energies noted above are sufficient to promote or excite a molecular electron to a higher energy orbital. Consequently, absorption spectroscopy carried out in this region is sometimes called "electronic spectroscopy". A diagram showing the various kinds of electronic excitations that may occur in organic molecules are shown on the left. Of the six transitions outlined, only the two lowest energy ones (left-most, colored blue) are achieved by the energies available in the 200 to 800 nm spectrum. As a rule, energetically favored electron promotion will be from the **highest occupied molecular orbital (HOMO)** to the **lowest unoccupied molecular orbital (LUMO)**, and the resulting species is called an **excited state** [54].

When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance (A) versus wavelength, as in the isoprene spectrum shown below. Since isoprene is colorless, it does not absorb in the visible part of the spectrum and this region is not displayed on the graph. **Absorbance** usually ranges from 0 (no absorption) to 2 (99% absorption), and is precisely defined in context with spectrometer operation.

Because the absorbance of a sample will be proportional to the number of absorbing molecules in the spectrometer light beam (e.g. their molar concentration in the sample tube), it is necessary to correct the absorbance value for this and other operational factors if the spectra of different compounds are to be compared in a meaningful way. The corrected absorption value is called "molar absorptivity", and is particularly useful when comparing the spectra of different compounds and determining the relative strength of light absorbing functions (chromophores). **Molar absorptivity** ( $\epsilon$ ) is defined as

$$\text{Molar Absorptivity, } \epsilon = A / c l$$

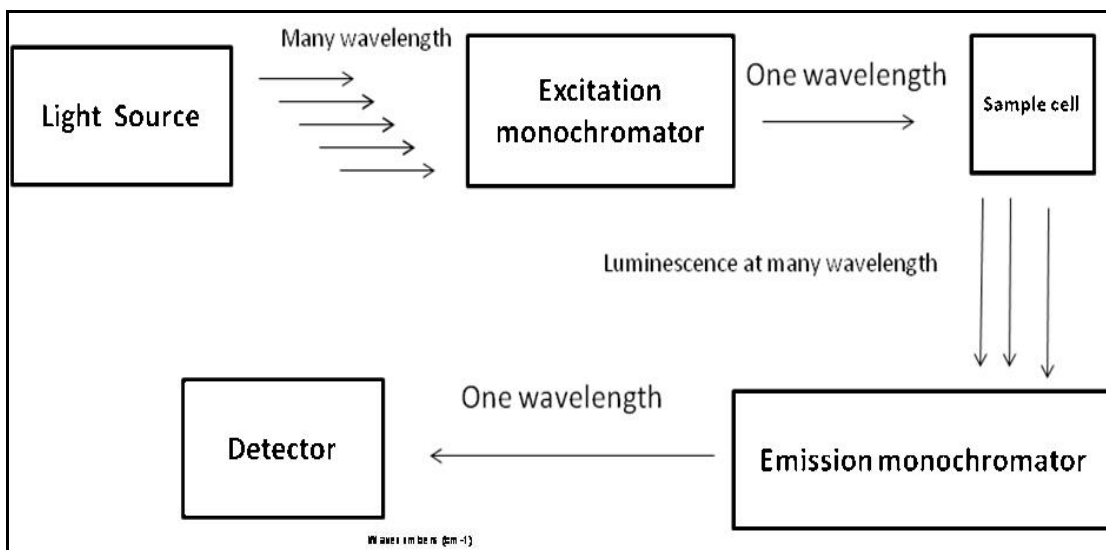
Where  $A$  = absorbance,

$c$  = sample concentration in moles/liter &

$l$  = length of light path through the sample in cm

### 3.3.1.2 Photoluminescence Spectroscopy

Photoluminescence spectroscopy (Schematic diagram in Figure 3.6) is a contactless, non destructive method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation. One way this excess energy can be dissipated by the sample is through the emission of light, or luminescence. In the case of photo-excitation, this luminescence is called photoluminescence. The intensity and spectral content of this photoluminescence is a direct measure of various important material properties. Photo-excitation causes electrons within the material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and may include the emission of light (a radioactive process) or may not (a non-radioactive process). The energy of the emitted light (photoluminescence) relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radioactive process [55].

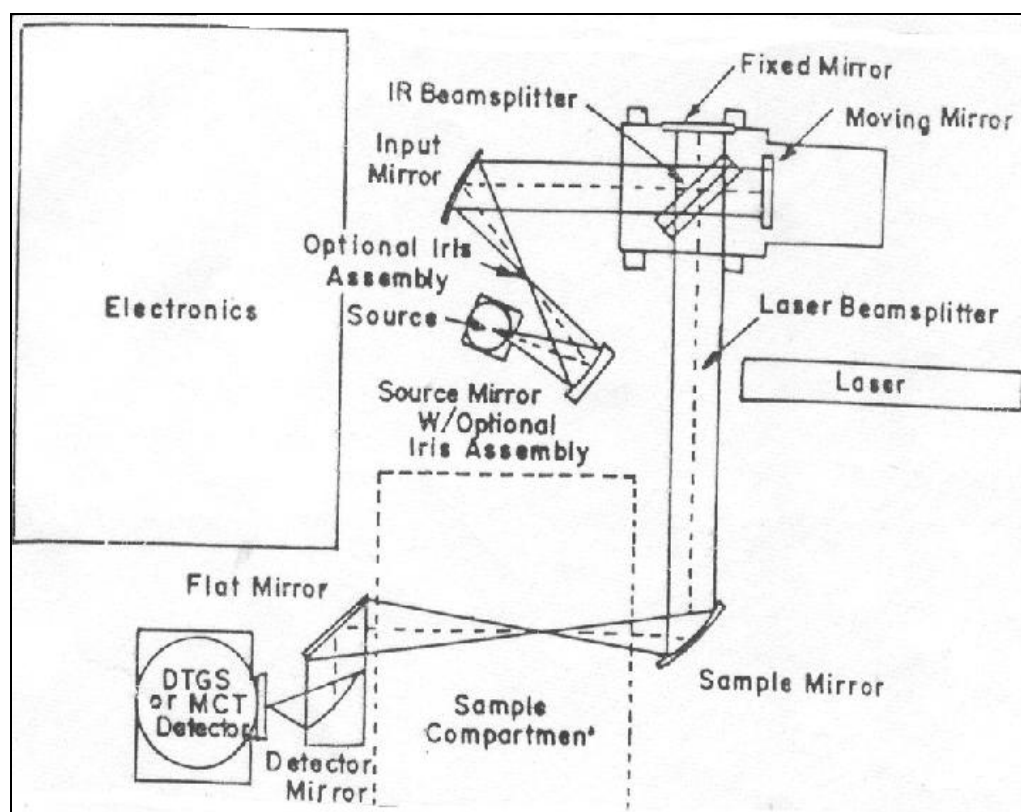


**Figure: 3.6 Schematic diagram of luminescence experiment**

### 3.3.1.3 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. 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.

FT-IR spectroscopy employs an interferometer in place of monochromatic (fig.3.6). 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, increased signals-to-noise (S/N) ratio and higher wave number accuracy than is possible with a conventional light dispersive spectrometer [54].



**Fig. 3.7 Set-up of FT-IR (model 510p)**

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  $\text{cm}^{-1}$ . The relation between velocity  $c$ , wavelength  $\lambda$  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 spectra transmittances (T) versus wave number ( $\text{cm}^{-1}$ ) have been plotted.

### 3.3.1.4 Thermo Gravimetric Analysis

Thermo Gravimetric Analysis (TGA) [105] is a thermal analysis technique used to measure changes in the weight (mass) of a sample as a function of temperature and/or

time. TGA is commonly used to determine polymer degradation temperatures, residual solvent levels, absorbed moisture content, and the amount of inorganic (noncombustible) filler in polymer or composite material compositions.

A simplified explanation of a TGA sample evaluation may be described as follows. A sample is placed into a tared TGA sample pan which is attached to a sensitive microbalance assembly. The sample holder portion of the TGA balance assembly is subsequently placed into a high temperature furnace. The balance assembly measures the initial sample weight at room temperature and then continuously monitors changes in sample weight (losses or gains) as heat is applied to the sample. TGA tests may be run in a heating mode at some controlled heating rate, or isothermally. Typical weight loss profiles are analyzed for the amount or percent of weight loss at any given temperature, the amount or percent of non-combusted residue at some final temperature, and the temperatures of various sample degradation processes [56].

### **3.3.2 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 sputter-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. Before preparing a device its patterning is very important. To obtain desired patterns from OLEDs the layer of ITO on glass surface is shaped in a certain manner. It is achieved by Photolithography.

### **Vacuum evaporation techniques:**

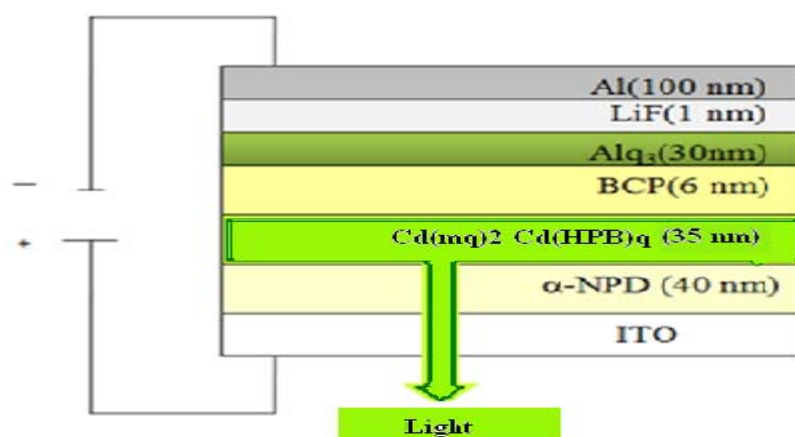
Vacuum deposition, some time called vacuum evaporation technique, is a major physical deposition technique that is extensively used for the deposition of thin films on the surface of a substrate. The vacuum thermal evaporation deposition technique consists in heating until evaporation of the material to be deposited. The material vapor finally condenses in the 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 of 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 (i.e.  $kT$ , order of 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.

### 3.4 Device Fabrication

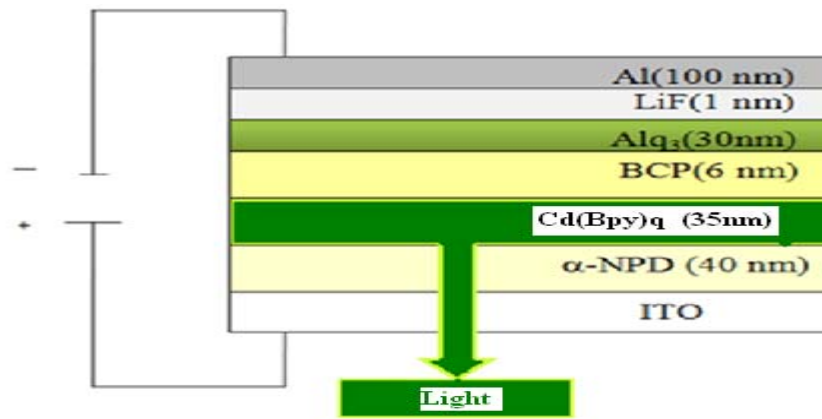
#### 3.4.1 Cd(Bpy)q and Cd(mq)<sub>2</sub> Cd(HPB)q based Organic Light

##### Emitting Device:

The OLED device was fabricated in a configuration ITO/ $\alpha$ -NPD (40 nm)/ Cd(Bpy)q or Cd(mq)<sub>2</sub> or Cd(HPB)q (35 nm)/BCP(6 nm)/Alq<sub>3</sub>(30 nm)/LiF(1 nm)/Al(100 nm)(as shown in schematic diagram of OLED Device Figure 3.8). Indium-tin oxide (ITO) coated glass substrates with sheet resistance of 20  $\Omega/\square$  were patterned using photolithography and cleaned using trichloroethylene, acetone, isopropyl alcohol and deionised water sequentially for 20 minutes using an ultrasonic bath and dried in flowing nitrogen. Prior to film deposition, the ITO substrates were treated with oxygen plasma for 5 minute. On the substrate, the hole transport layer and the emitting layers were deposited sequentially under a high vacuum ( $1 \times 10^{-5}$  torr) at a deposition rate of 0.2 - 0.5  $\text{\AA}/\text{sec}$  and LiF at 0.1-0.2  $\text{\AA}/\text{sec}$ . Thickness of the deposited layers were controlled by a quartz crystal monitor. The cathode was deposited on the top of the structure through a shadow mask. A 40 nm N,N diphenyl-N'N'-bis (1-naphthyl)-1,1'-biphenyl-4,4'-diamine( $\alpha$ -NPD) (Sigma Aldrich) was used as hole transport layer. Cd(Bpy)q or Cd(mq)<sub>2</sub> or Cd(HPB)q was used as the emitting layer and aluminium tris-8-hydroxyquinoline(Alq<sub>3</sub>) (Sigma Aldrich) was used as electron transport layer. The electron injection was facilitated using a 1nm thin LiF (Merck, Germany) layer followed by a thick layer of aluminium. The size of each pixel was  $5 \times 3 \text{ mm}^2$ .



**Figure 3.8(a): Device structure of OLED ( Cd(mq)<sub>2</sub>/ Cd(HPB)q as an emitter)**



**Figure 3.8(b): Device structure of OLED (Cd(Bpy)q as an emitter)**

The luminance–current–voltage (I-V-L) characteristics were measured using a luminance meter (LMT 1009) and a Keithley 2400 programmable voltage-current digital source meter.

## **CHAPTER 4**

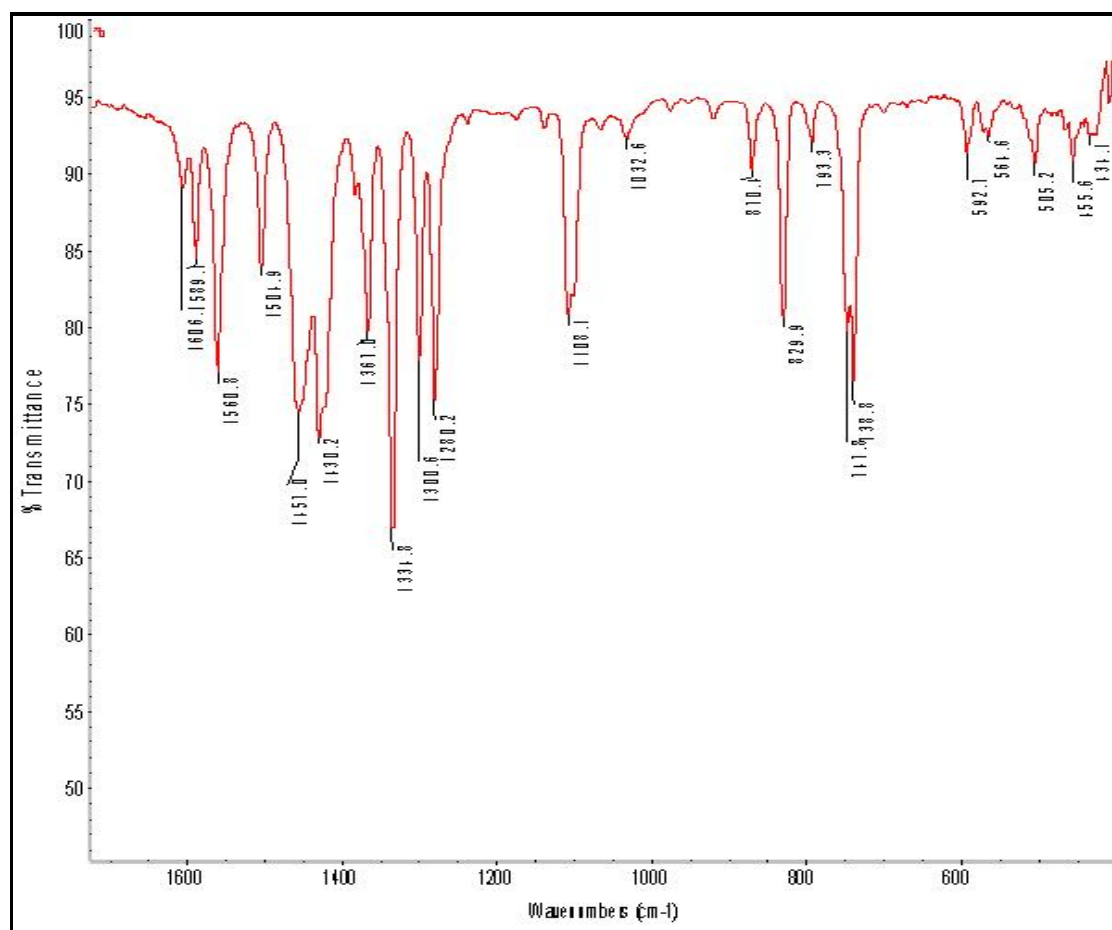
### **RESULT AND DISCUSSION**

## 4.1 Structural and thermal characterization

The infrared absorption spectrum of the material in KBr pellets has been studied using a Nicolet 5700 spectrometer. The Thermo gravimetric Analysis (TGA) has been done by using SDTA851Metter-Toledo-star system in the temperature range 0-800 °C.

### 4.1.1 Structural and Thermal Characterization of Cd(Bpy)q

Following Figure 4.1 shows the FTIR spectrum of the material carried out of sample, prepared by pellets containing Cd(Bpy)q powder (0.1weight %) dispersed in KBr powder. The FTIR spectra were recorded on Nicolet 5700 in the region  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ . The main peak of cadmium 2,2-bipyridine quinoline the FTIR spectrum is shown in Fig.4.1.

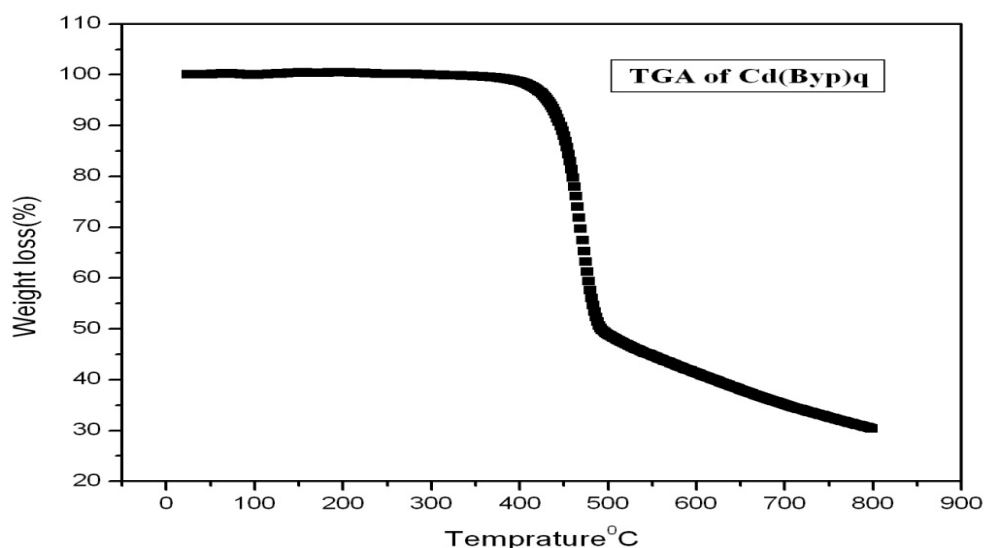


**Figure 4.1 Shows the FTIR of Cd(Bpy)q**

Each peak in the graph corresponds to a functional group present in the molecule. The peak at  $1580\text{ cm}^{-1}$  is an indicative peak of C=C aromatic stretching and  $2925\text{ cm}^{-1}$  is a characteristic peak for aromatic C-H stretching. Aromatic amine resonance peak of C-N-C at  $1280\text{ cm}^{-1}$  and  $1385\text{ cm}^{-1}$ , C=N stretching at  $1425\text{ cm}^{-1}$  and aromatic C-O

stretching at  $1109\text{ cm}^{-1}$  were observed in the spectrum. The spectrum shows the characteristics peaks of aromatic ring stretching at  $738\text{ cm}^{-1}$  &  $743\text{ cm}^{-1}$ ,  $793\text{ cm}^{-1}$ ,  $829\text{ cm}^{-1}$ . This showed the existence of quinolinic rings. The cadmium ion is a soft acid which tends to form a stable complex with quinoline by metal–nitrogen bond. The Cd-O bond stretching was observed at  $505\text{ cm}^{-1}$  while Cd-N bond stretching was observed at  $490\text{ cm}^{-1}$ .

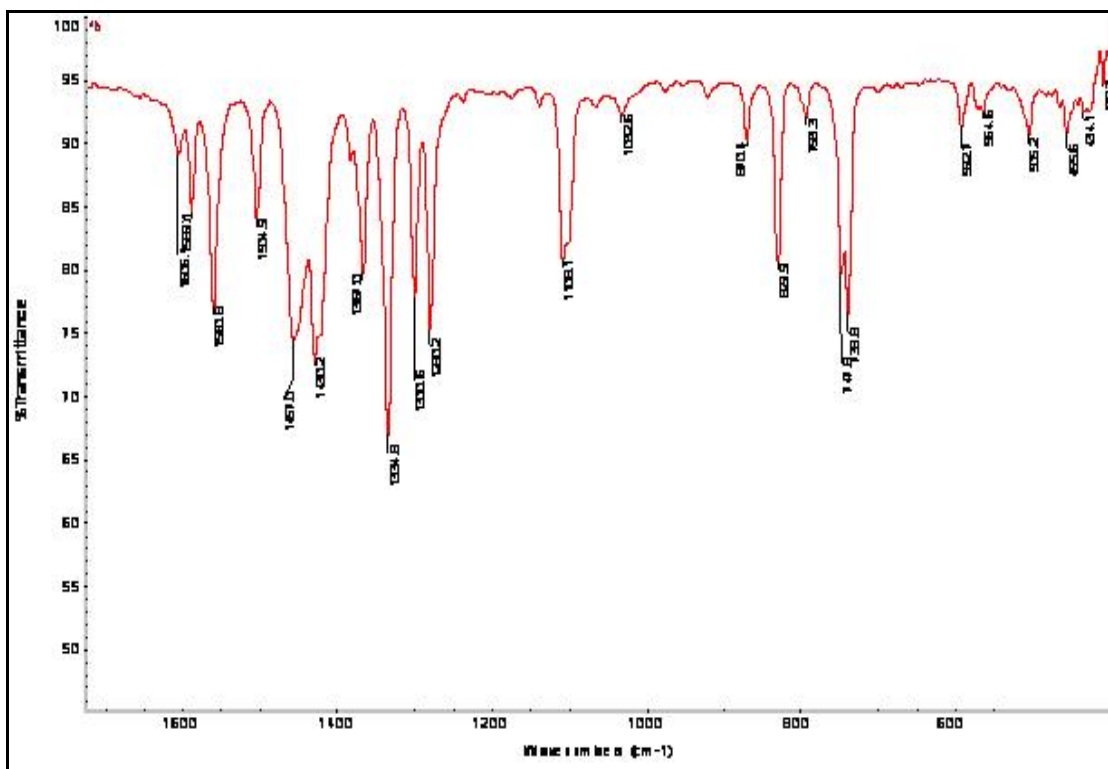
TGA of synthesized Cd(Bpy)q was carried out in temperature range  $0\text{--}800^\circ\text{C}$  as shown in figure 4.2. At temperature around  $384^\circ\text{C}$  the material starts weight loss and  $440^\circ\text{C}$  completely. Hence the material is stable upto  $384^\circ\text{C}$ .



**Figure 4.2. Thermo Gravimetric analysis of Cd(Bpy)q**

#### **4.1.2 Structural and thermal characterization of Cdmq<sub>2</sub>**

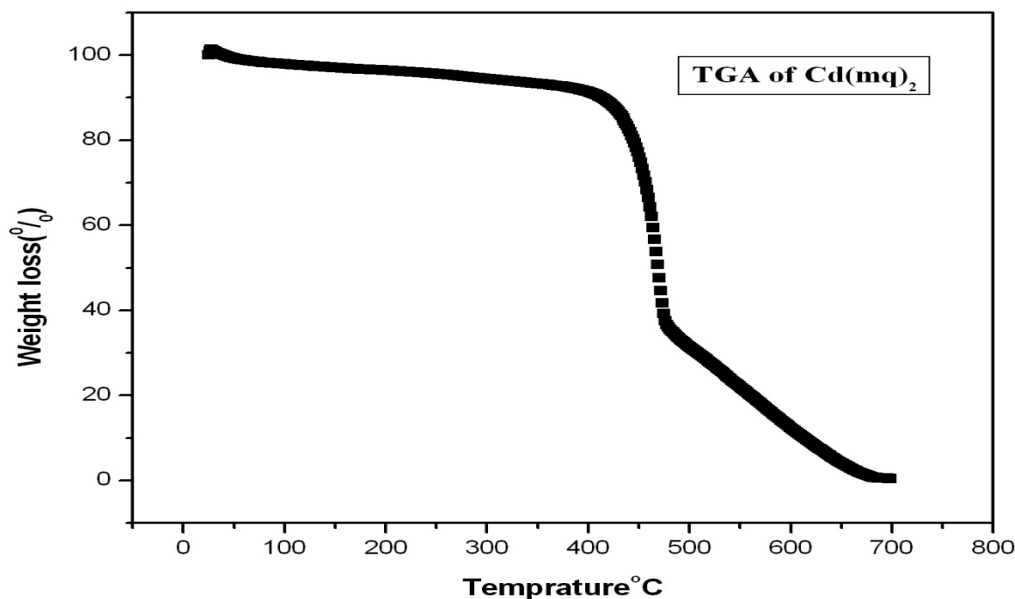
Figure 4.3 shows the FTIR spectrum of the material carried out of sample, prepared by pellets containing Cdmq<sub>2</sub> powder (0.1 weight%) dispersed in KBr powder. The FTIR spectra were recorded on Nicolet 5700 in the region  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ . The main peak of bis 2-methyl 8hydroxy quinoline Cadmium, shown in the in the FTIR spectrum as shown in Figure 4.3 Each peak in the graph corresponds to a functional group present in the molecule.



**Figure: 4.3 FTIR of Cdmq<sub>2</sub>**

In case of bis 2-methyl 8hydroxy quinoline cadmium the presence of characteristic absorption band are observed at  $3043\text{ cm}^{-1}$  for aromatic C-H stretching and for methyl C-H str the band are present at  $2961\text{ cm}^{-1}$ ,  $2923\text{ cm}^{-1}$ , and  $2875\text{ cm}^{-1}$  along with C=C (str) at  $1605\text{ cm}^{-1}$ ,  $1495\text{ cm}^{-1}$ ,  $1466\text{ cm}^{-1}$  while out of plane =C-H str band is observed at  $743\text{ cm}^{-1}$  these band clearly indicate the presence of methyl group along with all the peaks of hydroxyl quinoline ring clearly indicate the presence of bis 2-methyl 8hydroxy quinoline ring . The Cd-O bond stretching was observed at  $564\text{ cm}^{-1}$   $508$  while Cd-N bond stretching was observed at  $490\text{ cm}^{-1}$

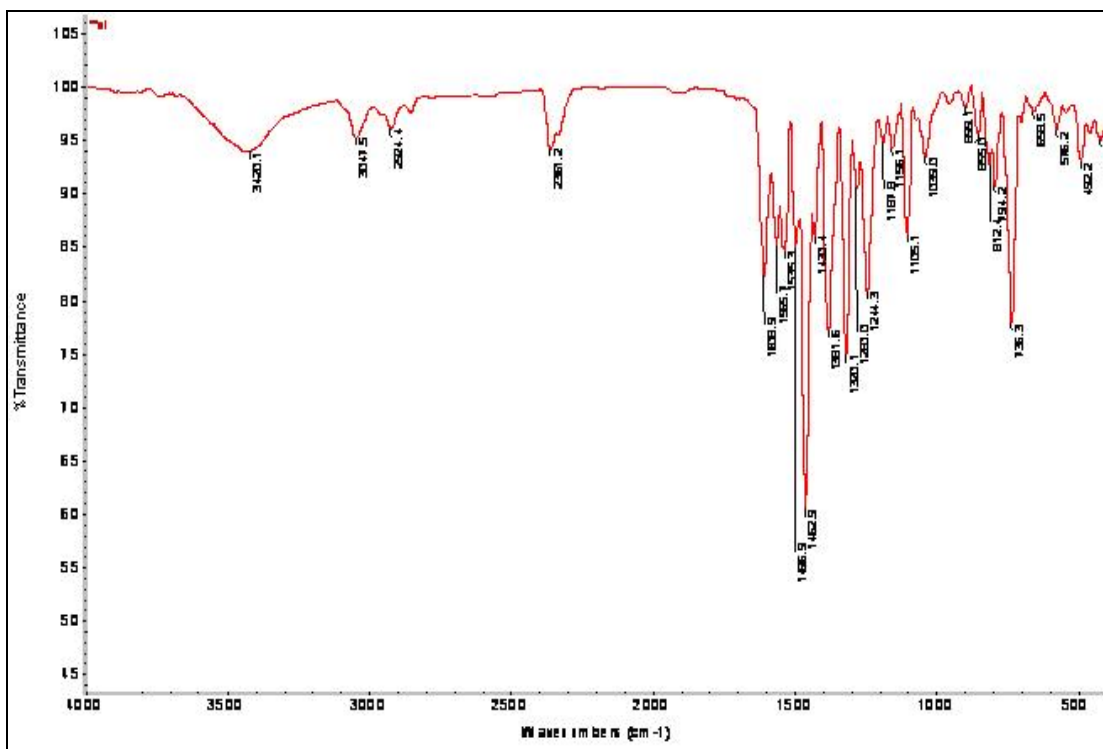
TGA of synthesized Cdmq<sub>2</sub> was carried out in temperature range 0-800°C as shown in Figure 4.4 .At temperature around  $430^{\circ}\text{C}$  the material starts weight loss and  $438^{\circ}\text{C}$  completely. Hence the material is stable upto  $438^{\circ}\text{C}$ .



**Figure: 4.4 Thermo gravimetric analysis of Cdmq<sub>2</sub>:**

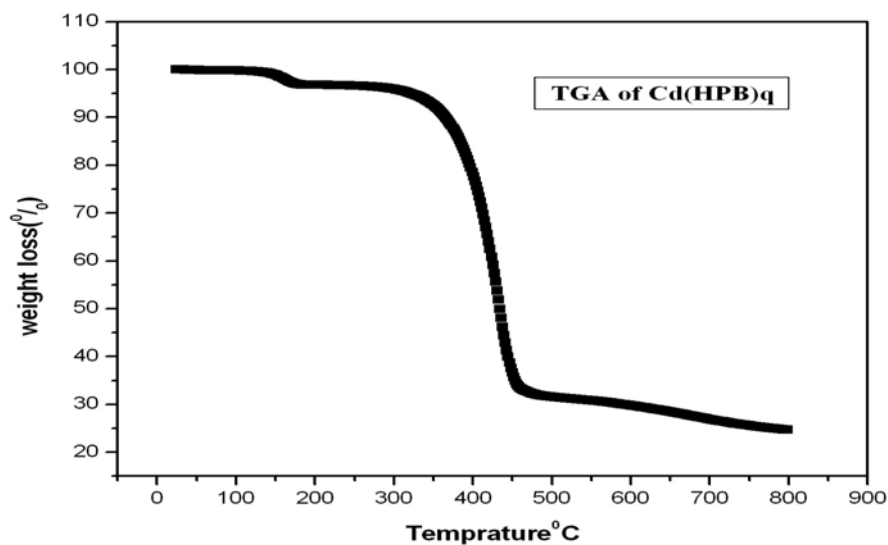
### 4.1.3 Structural and thermal characterization of Cd(HPB)q

Following Fig. 4.5 shows the FTIR spectrum of the material carried out of sample, prepared by pellets containing Cd(HPB)q powder(0.1weight<sup>0</sup>%) dispersed in KBr powder. The FTIR spectra were recorded on Nicolet 5700 in the region 4000 cm<sup>-1</sup> to 400cm<sup>-1</sup>. The main peak of Cadmium 2-(2-hydroxyphenyl) benzoxazole (8-hydroxyquinoline) Cd(HPB)q shown in the in the FTIR spectrum are shown in Fig 4.5 Each peak in the graph corresponds to a functional group present in the molecule. In case of Cd(HPB)q the main characteristic band are observed at 1614 cm<sup>-1</sup>,1600 cm<sup>-1</sup>,1570 cm<sup>-1</sup>, 1495 cm<sup>-1</sup> for the aromatic phenyl ring ,1321 cm<sup>-1</sup> 1279 cm<sup>-1</sup> for C-N-C ,and at 1106 cm<sup>-1</sup> for C-O bond stretching while the band between 760-735 represent the C-H out of plane bending vibration for the four adjacent hydrogen atom along with the band at 576 cm<sup>-1</sup> ,493 cm<sup>-1</sup> and 462 cm<sup>-1</sup> represent Cd-O and Cd-N bond stretching respectively.



**Figure 4.5 FTIR of Cd(HPB)q**

TGA of synthesized Cd(HPB)q was carried out in temperature range 0-800°C as shown in figure 4.6 . The TGA plot shows some weight loss around temperature 150 °C which is due to some volatile impurities or moisture present in material but no weight loss in Cd(HPB)q. At temperature around 370 °C the material degrade completely. Hence the material is stable upto 370°C.



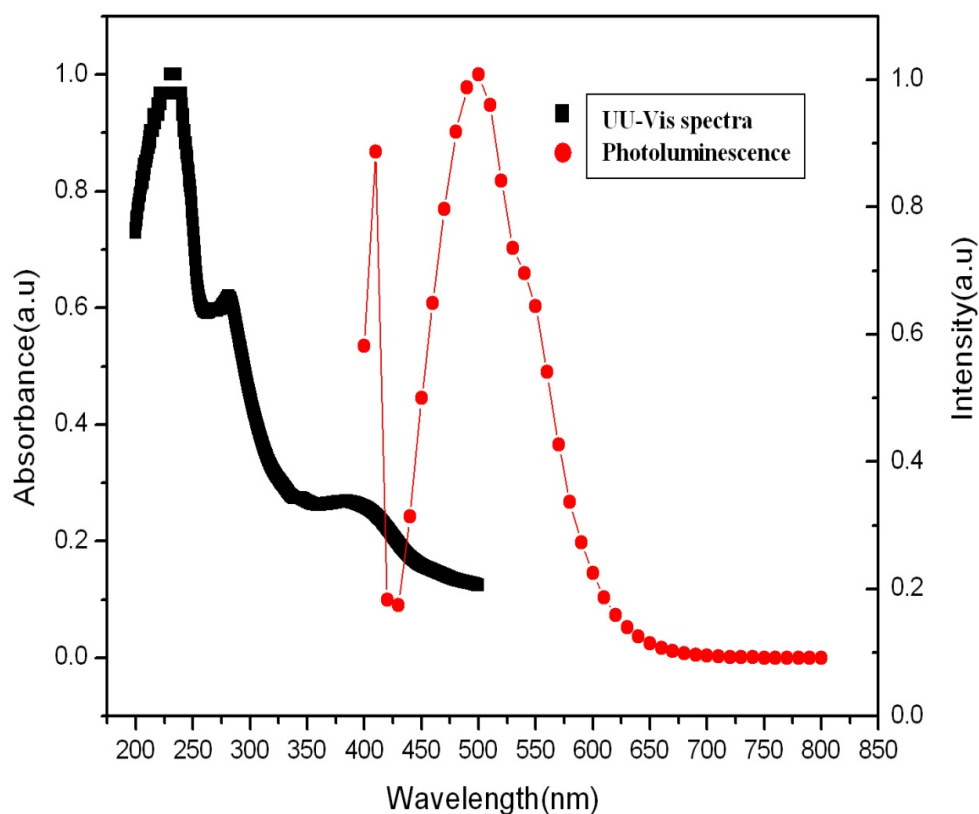
**Figure: 4.6 Thermo gravimetric analysis of Cd(HPB)q.**

## 4.2 Optical Characterization:

UV-visible absorption spectra were recorded on a Shimadzu UV-2401 spectrophotometer. The excitation and emission spectra of a material were recorded with a Fluorolog Spectrofluorometer (Horiba Jobin YVON Fluolog Model FL 3-11) at room temperature.

### 4.2.1 Optical Characterization of Cd(Byp)q:

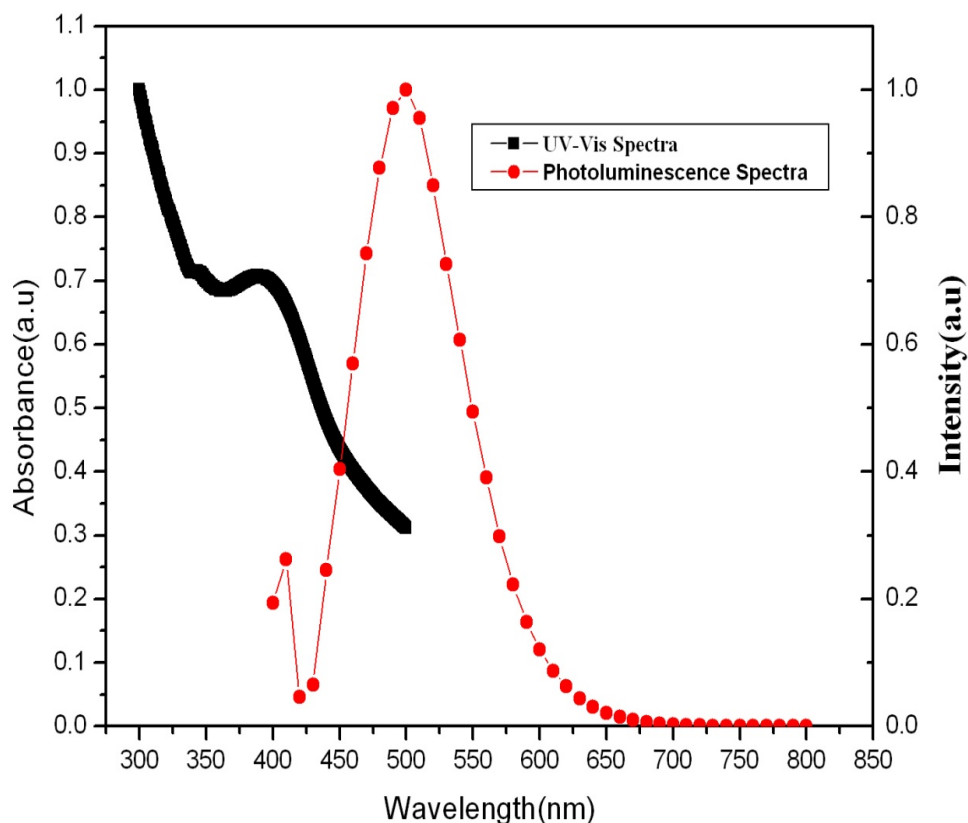
The UV-Vis absorption and photoluminescence spectra were obtained in a solution of toluene and are shown in Figure 4.7 respectively. The maximum of the UV-Vis absorption peaks of Cd(Byp)q was observed at 389 nm and 347nm, which is due to the  $\pi$ - $\pi^*$  transition of aromatic ring. The peak of the PL spectrum of Cd(Byp)q was observed at 500 nm.



**Figure: 4.7 UV-Vis and Photoluminescence spectra of Cd(Bpy)q.**

### 4.2.2 Optical Characterization of $\text{Cdmq}_2$ .

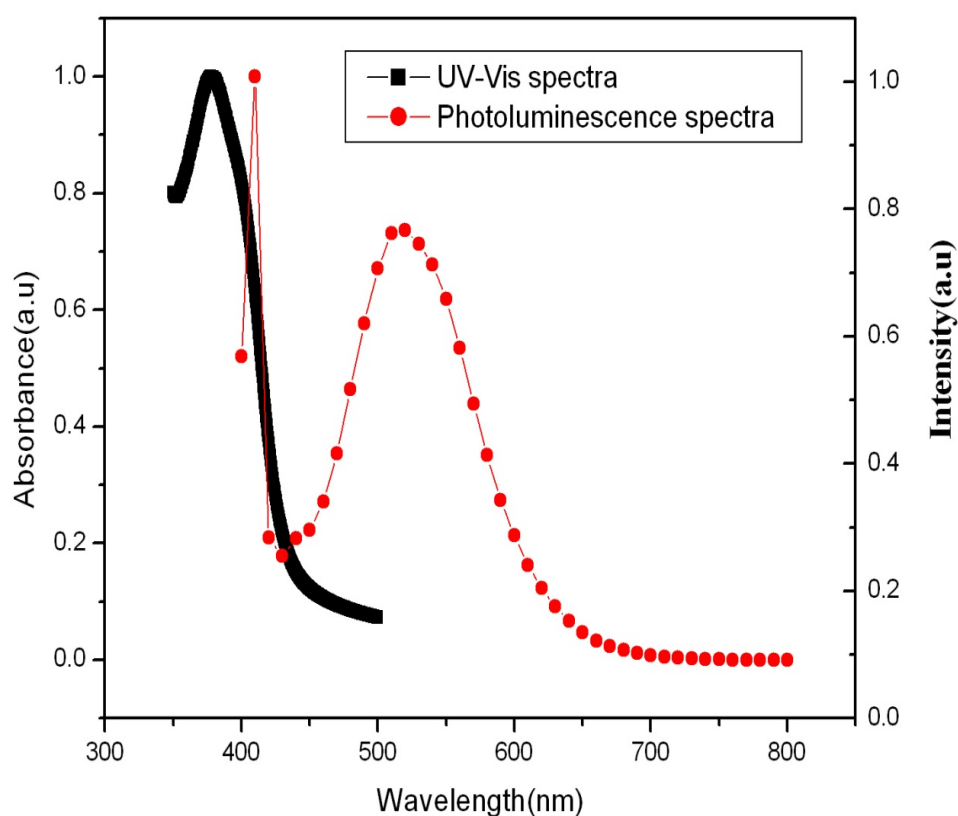
The UV-Vis absorption and photoluminescence spectrum were obtained in a solution of toluene and are shown in Figure 4.8. The maximum of the UV-Vis absorption peaks of  $\text{Cdmq}_2$  was observed at 390 nm, which is due to the  $\pi$ - $\pi^*$  transition of aromatic ring. The peak of the PL spectrum of  $\text{Cdmq}_2$  was observed at 500 nm.



**Figure: 4.8 UV-Vis and Photoluminescence spectra of  $\text{Cdmq}_2$ .**

### 4.2.3 Optical Characterization of $\text{Cd(HPB)q}$ :

The UV-Vis absorption and photoluminescence spectrum were obtained in a solution of toluene and are shown in Figure 4.9. The maximum of the UV-Vis absorption peak of  $\text{Cd(HPB)q}$  was observed at 378 nm, which is due to the  $\pi$ - $\pi^*$  transition of aromatic ring. The peak of the PL spectrum of  $\text{Cd(HPB)q}$  was observed at 520 nm.



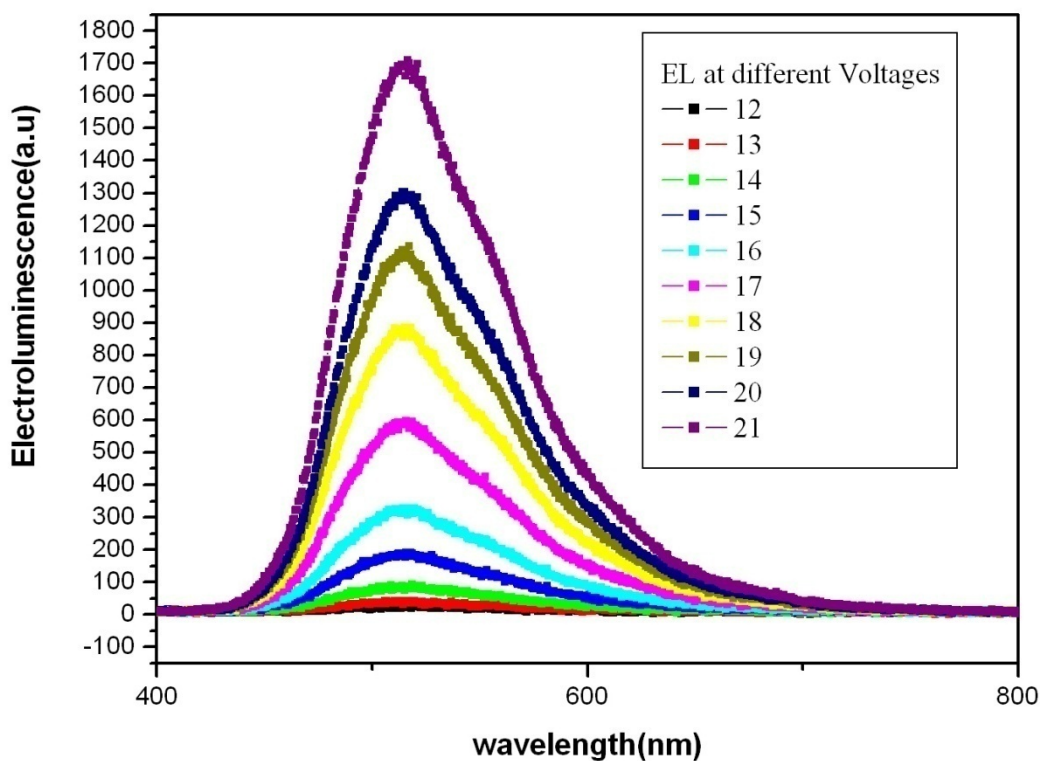
**Figure: 4.9 UV-Vis and Photoluminescence spectra of Cd(HPB)q.**

### **4.3 Device characterization**

The electroluminescent (EL) spectrum was recorded on a high-resolution spectrometer (Ocean Optics, HR-2000CG UV-NIR). The luminance–current–voltage (I-V-L) characteristics were measured using a luminance meter (LMT 1009) and a Keithley 2400 programmable voltage-current digital source meter.

#### **4.3.1 Device characterization of Cd(Bpy)q:**

The EL spectra were recorded at various applied voltages as shown in Figure 4.10. The EL intensity of the device increases with increase in voltage from 12V to 21 V, and the peak position remains unchanged at 515 nm.



**Figure: 4.10 EL Vs Wavelength at different voltages of Cd(Bpy)q.**

The current density- voltage (J-V) characteristic of the fabricated device was recorded by applying voltage across the device with ITO as an anode and aluminium as cathode (forward bias) as shown in Figure 4.11. From the J-V characteristic it has been seen that the onset of light emission starts at about 11.5 V (threshold voltage). Above this voltage, the current rises non-linearly due to the space charge effects. Above the threshold voltage the device emits a greenish light. Below this voltage the J-V characteristics shows Ohmic current indicating the presence of thermally generated carrier. The Current density- Voltage- Luminescence curve is shown in Figure 4.11.

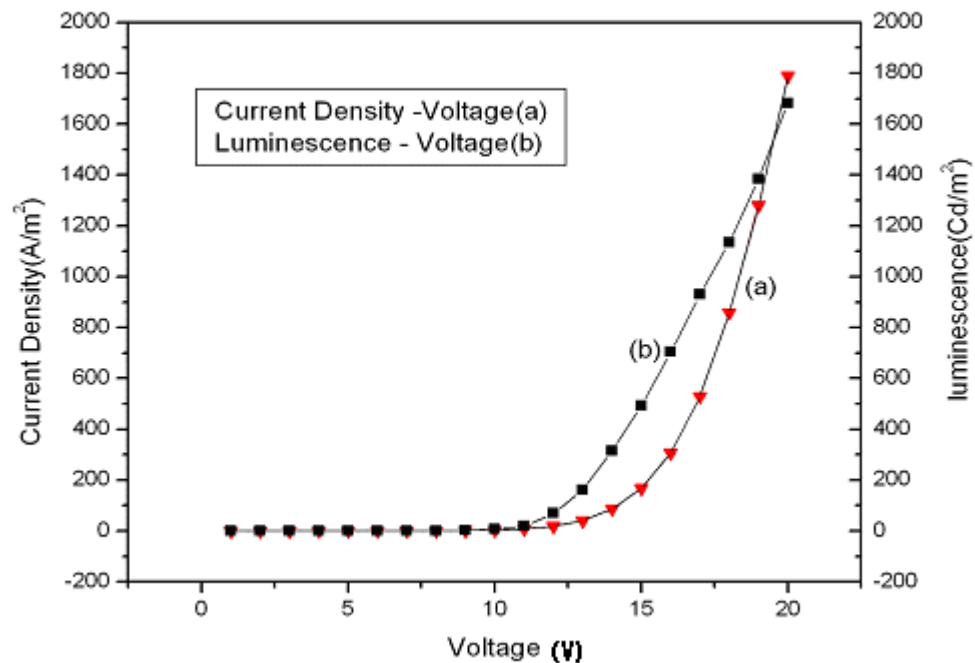


Figure: 4.11 Current density-Voltage-Luminescence curve of Cd(Bpy)q.

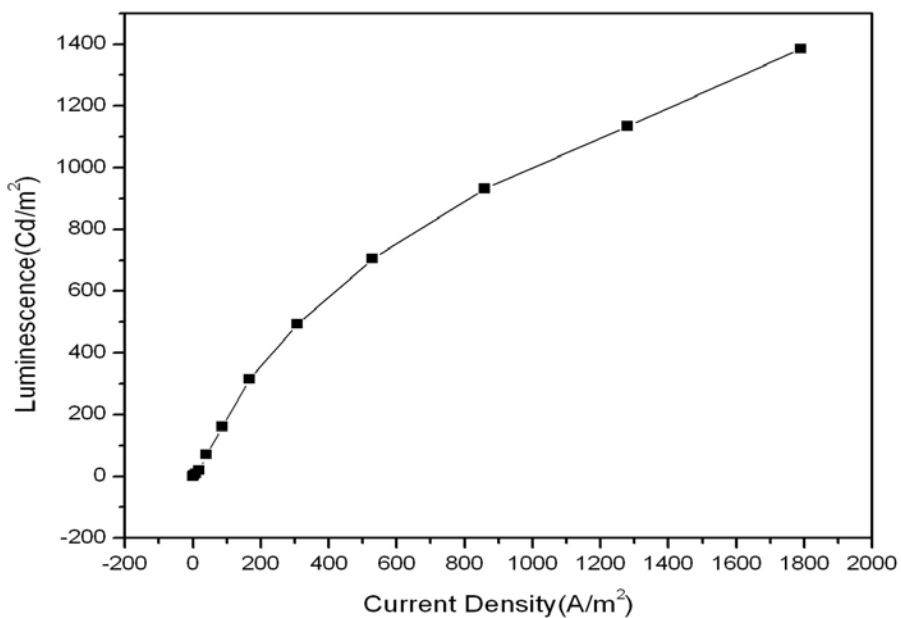
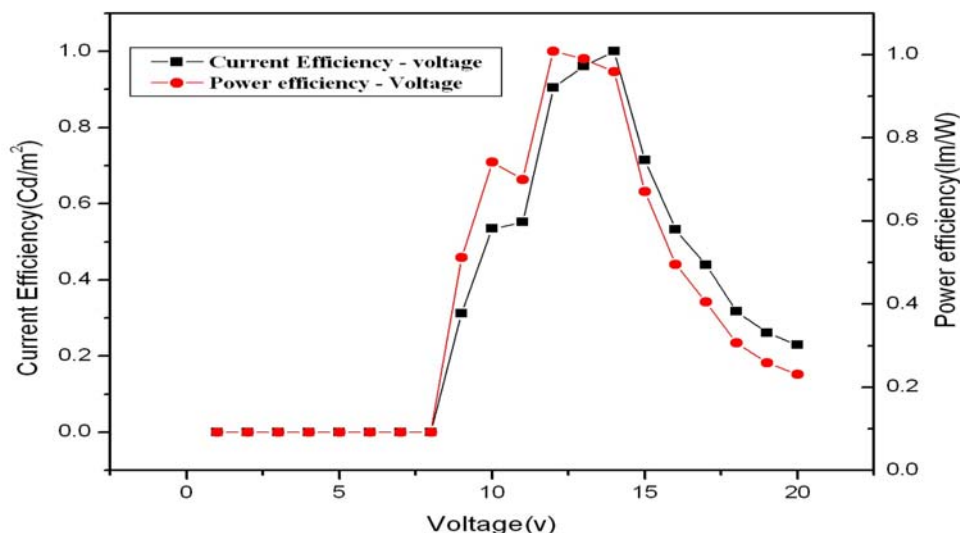


Figure 4.12 Luminescence –current density curve of Cd(Bpy)q.



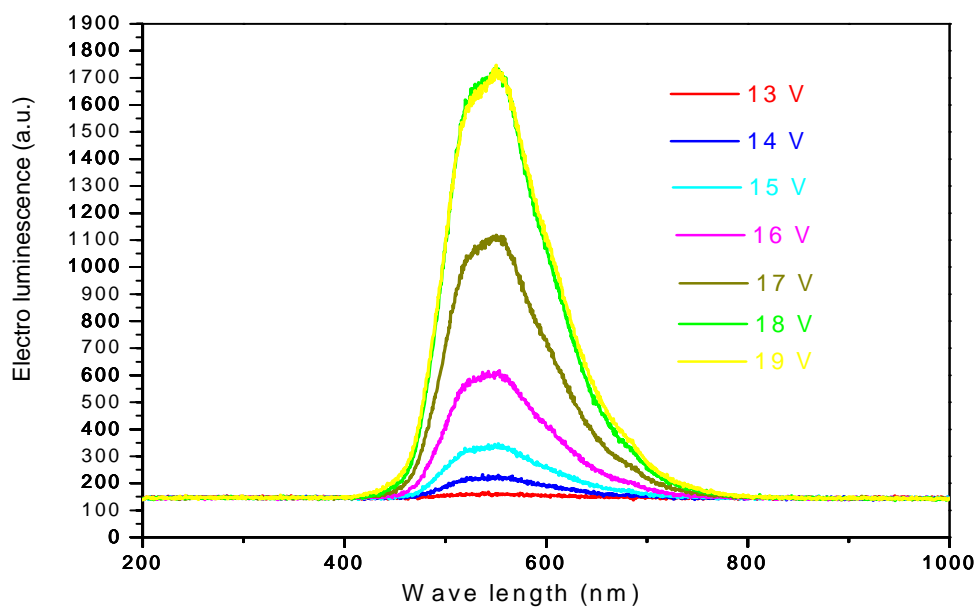
**Figure: 4.13 Current Efficiency – Voltage- Power Efficiency curve of Cd(Bpy)q.**

The maximum luminescence in the EL cell was 1681 cd/m<sup>2</sup> at 20 V with current density of 1789 A/m<sup>2</sup> (Figure 4.11). The device shows maximum current efficiency 4.1 cd/A and maximum power efficiency .952 lm/W at 14 V.

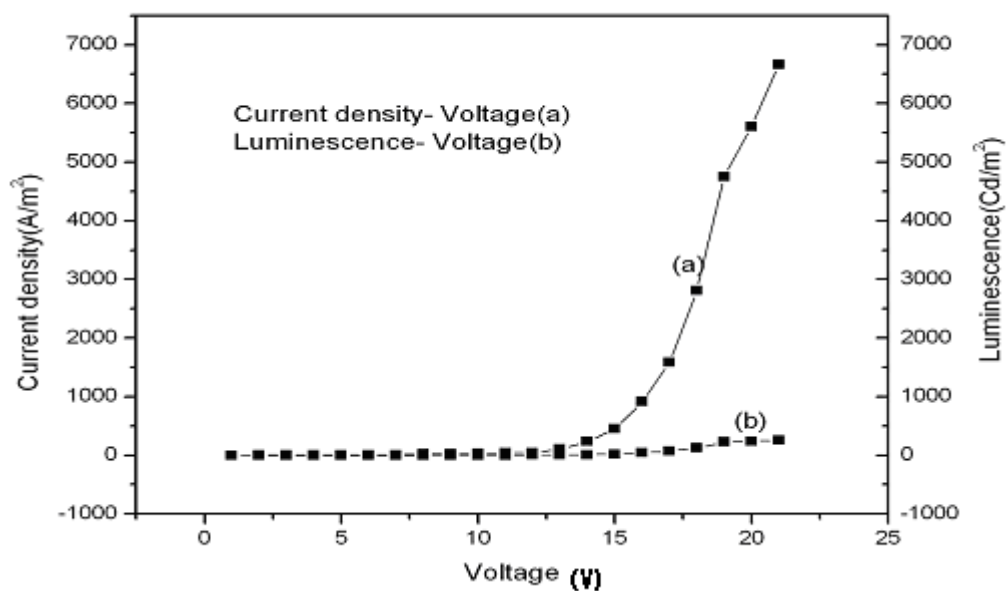
### 4.3.2 Device Characterization of Cd(HPB)q:

The EL spectra were recorded at various applied voltages as shown Figure 4.14. The EL intensity of the device increases with increase in voltage from 12V to 21 V, and the peak position remain unchanged at 550 nm.

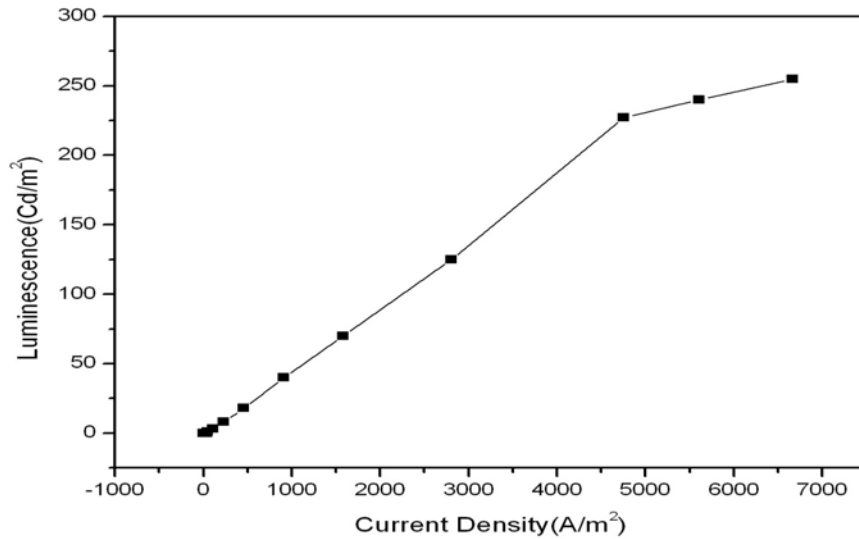
The current density- voltage (J-V) characteristic of the fabricated device was recorded by applying voltage across the device with ITO as an anode and aluminium as cathode (forward bias) as shown in Figure 4.15. From the J-V characteristic it has been seen that the onset of light emission starts at about 11 V (threshold voltage). Above this voltage, the current rises non-linearly due to the space charge effects. Above the threshold voltage the device emits a green light. Below this voltage the J-V characteristics shows Ohmic current indicating the presence of thermally generated carrier. The current density-voltage-luminescence curve is shown in Figure 4.15.



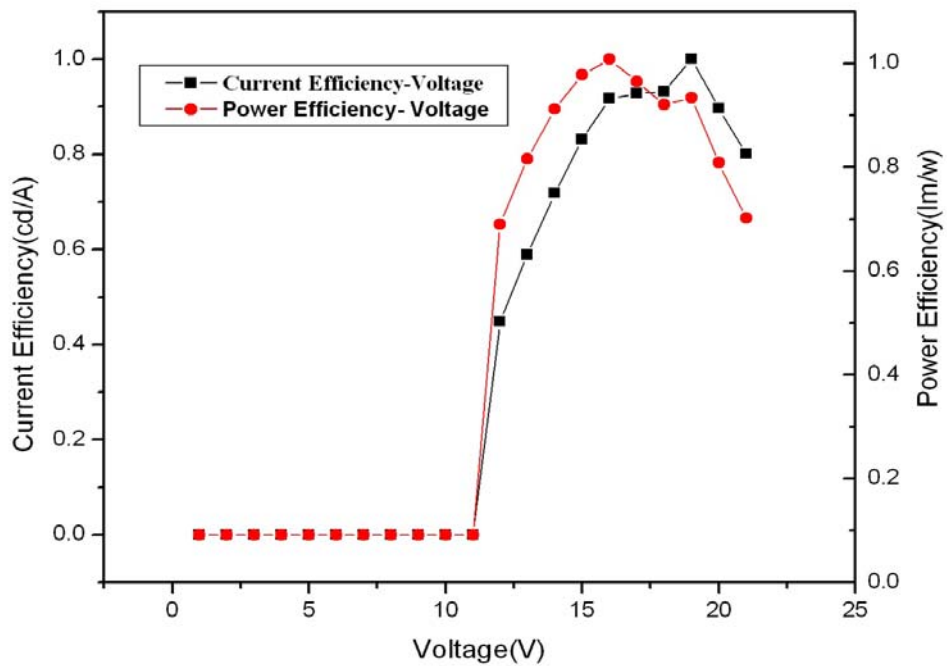
**Figure 4.14 Electroluminescence Spectra at different Voltages for Cd(HPB)q**



**Figure: 4.15 Current density-voltage- luminescence curve for Cd(HPB)q**



**Figure: 4.16 Luminescence-Current density curve for Cd(HPB)q.**



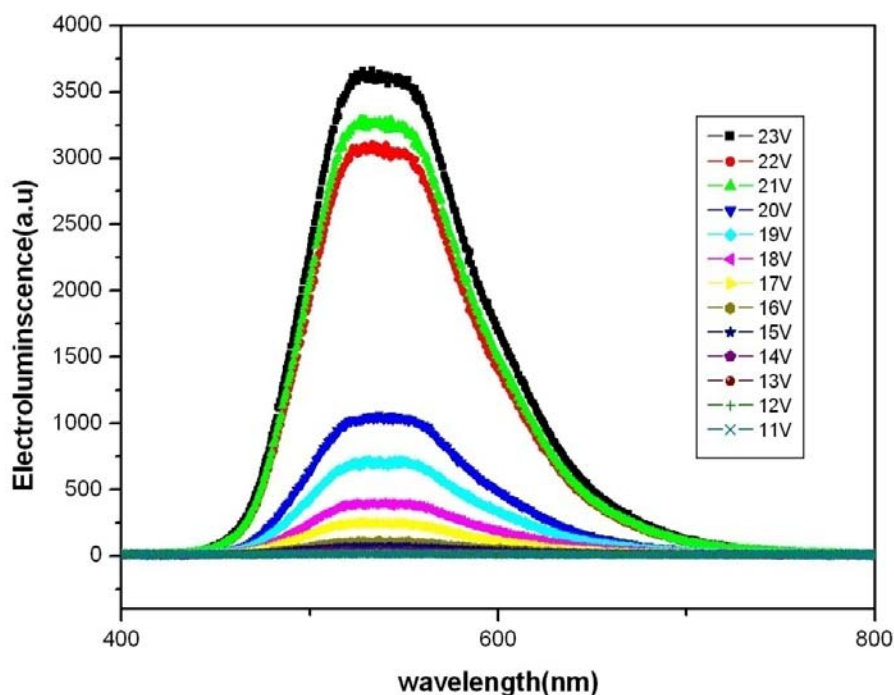
**Figure: 4.17 Current efficiency-voltage- Power efficiency curve for Cd(HPB)q.**

The maximum luminescence in the EL cell was 295 cd/m<sup>2</sup> at 20 V with current density of 6687 A/m<sup>2</sup> (Figure 4.15). The device shows maximum current efficiency

1.01 cd/A and maximum power efficiency 1.01 lm/W at 17 V as shown in Figure 4.17.

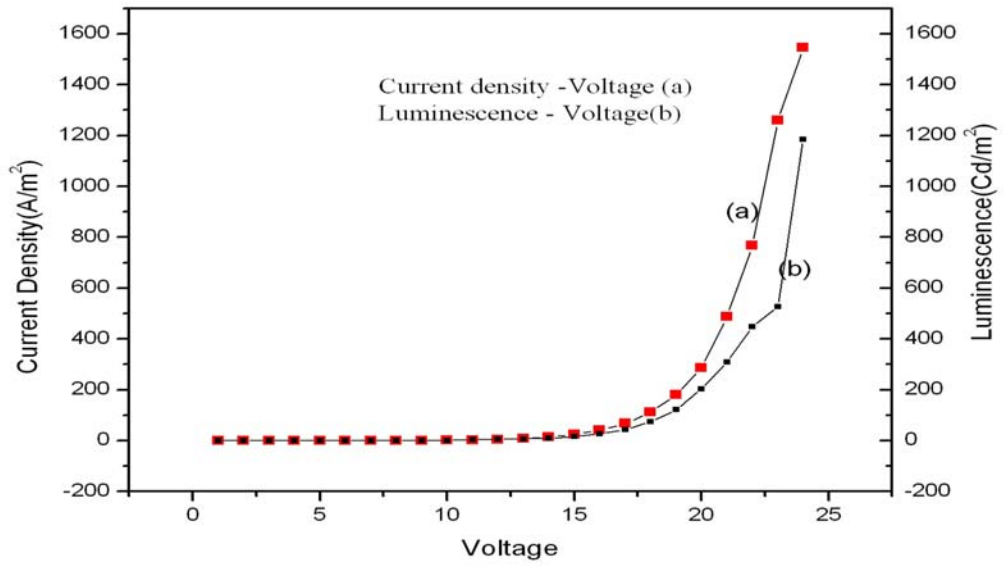
### 4.3.3 Device Characterization of $\text{Cdmq}_2$ :

The EL spectra were recorded at various applied voltages as shown Figure 4.18. The EL intensity of the device increases with increase in voltage from 11V to 23 V, and the peak broaden from 524nm to 550nm.

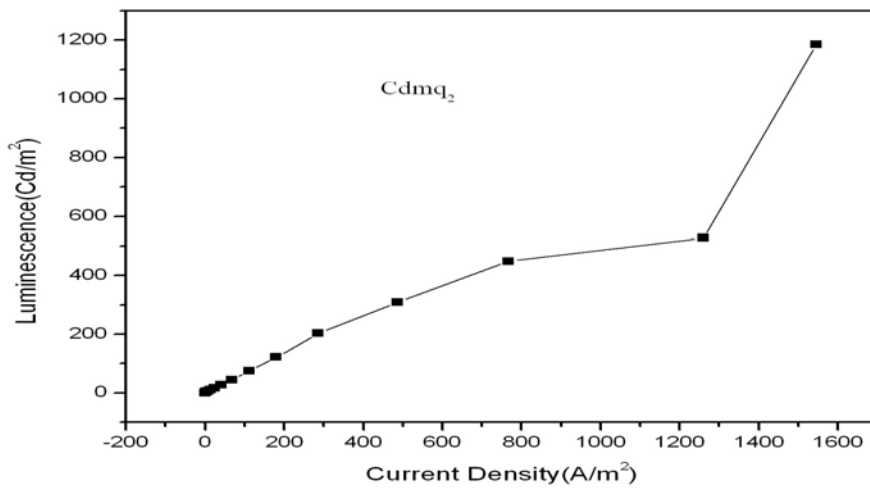


**Figure: 4.18 Electroluminescence spectra for  $\text{Cdmq}_2$  at different voltages.**

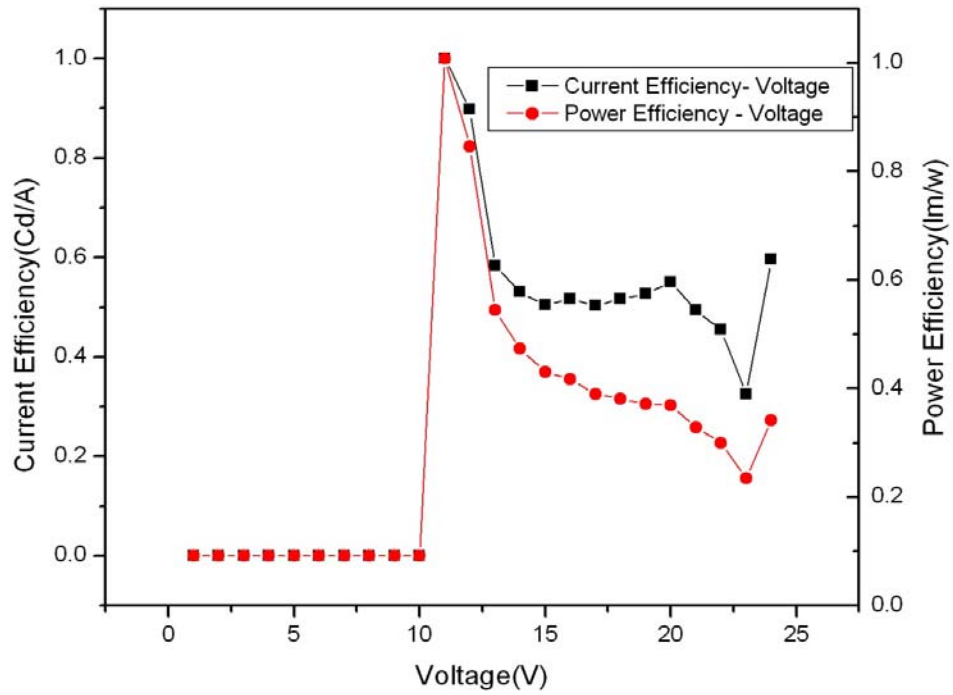
The current density- voltage (J-V) characteristic of the fabricated device was recorded by applying voltage across the device with ITO as an anode and aluminium as cathode (forward bias) as shown in Figure 4.19. From the J-V characteristic it has been seen that the onset of light emission starts at about 10.5 V (threshold voltage). Above this voltage, the current rises non-linearly due to the space charge effects. Above the threshold voltage the device emits a green yellowish light. Below this voltage the J-V characteristics shows Ohmic current indicating the presence of thermally generated carrier. The current density-voltage-luminescence curves are shown in Figure 4.19.



**Figure 4.19 Current Density- Voltage- Luminescence curve for CdMg<sub>2</sub>**



**Figure 4.20 Luminescence- current density curve for CdMg<sub>2</sub>**



**Figure 4.21 Current Efficiency-Voltage-Power efficiency curve for Cdmg<sub>2</sub>**

The maximum luminescence in the EL cell was 1185 cd/m<sup>2</sup> at 20 V with current density of 1550 A/m<sup>2</sup> at 23V (Figure 4.19). The device shows maximum current efficiency 1.28 cd/A and maximum power efficiency 0.36 lm/W at 17 V as shown in Figure 4.21.

**CHAPTER-5**

**CONCLUSION AND FUTURE SCOPE**

## 5.1 CONCLUSION

Three Cadmium complexes, cadmium (2, 2' bipyridine) 8-hydroxyquinoline Cd(Bpy)<sub>q</sub> bis(2-methyl 8-hydroxy quinolate) Cadmium Cd(mq)<sub>2</sub> and Cadmium 2-(2'-hydroxyphenyl) benzoxazole Cd(HPB)<sub>q</sub> have been synthesized and characterized by different characterization techniques (FTIR, TGA, UV visible and Photoluminescence Spectroscopy). Both the photoluminescence and electroluminescence properties are extensively studied. The Photoluminescence properties of Cd(Bpy)<sub>q</sub> shows maximum absorption at 389 nm, 347nm and photoluminescence peak at 500nm. The decomposition temperature was observed at 384 °C of Cd(Bpy)<sub>q</sub>. The Photoluminescence properties of Cd(mq)<sub>2</sub> shows maximum absorption at 390 nm and photoluminescence peak at 500 nm. The decomposition temperature was observed at 438 °C of Cd(mq)<sub>2</sub>. The photoluminescence properties of Cd(HPB)<sub>q</sub> (shows maximum absorption at 378 nm and photoluminescence peak at 520 nm. The decomposition temperature was observed at 370 °C of Cd(HPB)<sub>q</sub>. Organic light emitting diode have been fabricated with the structure ITO/ $\alpha$ NPD(40nm)/Cd(Bpy)<sub>q</sub>, Cd(mq)<sub>2</sub>, Cd(HPB)<sub>q</sub>, (35nm)/BCP(60nm)/Alq<sub>3</sub>(30nm)/LiF(1nm)/Al(100 nm), which shows an electroluminescence peak at 515 nm when Cd(Bpy)<sub>q</sub> was used as an emissive material and shows a broad electroluminescence peak at 540nm when Cd(mq)<sub>2</sub> was used as an emissive material and shows a electroluminescence peak at 550 nm when Cd(HPB)<sub>q</sub> was used as a emissive material. The maximum brightness of OLED device for Cd(Bpy)<sub>q</sub> has been found to increase as compared to the OLED device for Cd(mq)<sub>2</sub> and Cd(HPB)<sub>q</sub> also the turn on voltage Cd(mq)<sub>2</sub> device is less compared to Cd(Bpy)<sub>q</sub> and Cd(HPB)<sub>q</sub>. All three materials Cd(Bpy)<sub>q</sub>, Cd(mq)<sub>2</sub>, Cd(HPB)<sub>q</sub> are used as emissive materials and also used as hole and electron transport materials.

## 5.2 Future Scope

The studies presented in thesis further suggest that there are areas of academic and technological interest. These areas require further investigation. Some of the areas are mentioned as follows. A comparative study of Cd(Bpy)<sub>q</sub>, Cd(mq)<sub>2</sub> and Cd(HPB)<sub>q</sub> has been done. The effect of attachment of methyl group to some other metal complexes (Al, Be, B etc. and other rare earth elements) could be tried for optimizing quantum efficiency, brightness and operating voltage. Temperature dependent photoluminescence could also be carried out in order to get information about the variation of traps, excitonic vibrations etc.



## References

- [1] C. W. Tang and S. A. VanSlyke, *Apl. Phys. Lett.* **51**, 913 (1987)
- [2] C. W. Tang, S. A. VanSlyke and C. H. Chen, *J. Appl. Phys.* **65**, 3610 (1989)
- [3] M. Pope, H. P. Kallmann, and P. magnante, *J. Chem. Phys.* **38**, 2042 (1963);  
M. Sano,  
M. Pope, and H. Kallman, *J. Chem. Phys.* **43**, 2920 (1965)
- [4] P. S. Vincentt, W. A. Barlow, R. A. Hann, and G. G. Roberts, *Thin Solid Films*  
**94**, 171 (1982)
- [5] C. Adachi, S. Tokito, T. Tsutsui, and S. Saito, *J. Appl. Phys.* **27**, L269 (1988)
- [6] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H.  
Friend, P. L. Burns, and A. B. Holmes, *Nature* **347**, 539 (1990)
- [7] S. Hotta and K. Waragai, *Adv. Mater.* **5**, 896 (1993)
- [8] F. Garnier, R. Hajloui, A. Yassar, and P. Srivastava, *Science* **265**, 1684 (1994); T.  
R. Hebner, C. C. Wu, D. Marcy, M. H. Lu, and J. C. Sturm, *Appl. Phys. Lett.* **72**,  
519 (1998)
- [9] M. A. Baldo, D. F. O'Brein, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson,  
and S. R. Forest, *Nature* **395**, 151 (1998)
- [10] G. G. Malliaras and R.H. Friend, *Physics Today* **53**, 58(2005).
- [11] C. W. Tang, S.A. Van Slyke, *Appl. Phys. Lett.* **51**, 913(1987).
- [12] Yuji Hamada, *IEEE transactions on electron devices* **44** (1997) 1208.
- [13] C.W. Tang, S.A. Van Slyke, C.H. Chen, *J. Appl. Phys.* **65** (1989) 3611.
- [14] Y. Hamada., T. Sano, M. Fujita, T. Fujii, Y. Nishio, K. Shibata, *Jpn. J. Appl.*  
*Phys.* **324A** (1993) 514.
- [15] Luminescent Zinc and Lanthanide Complexes Based on 2,2'-Dipyridylamine  
Derivatives, Wen Yu Yang, Department of Chemistry Queen's University  
Kingston, Ontario, Canada (August 2000) 22-30.
- [16] V. K. Rai, R. Srivastava, G. Chauhan , K. Saxena, S. Chand, and M.N.  
Kamalasanan, *Jap.J Appl. Phys.* **47** (2008) ( Article in press).
- [17] V. K. Rai, R. Srivastava, G. Chauhan , K. Saxena, R.K. Bharadwaj, S. Chand,  
and M. N. Kamalasanan, *Mater. Lett.* 2008 (Article in press).
- [18] Y. Hamada , T. Sano, H. Fujii, Y. Nishio, H Takahashi, K. Shibata, *Jpn J. Appl.*  
*Phys.* **35** Part2 (1996) 1339.

- [19] J. Kido, K. Hongawa, K. Okuyama, K. Nagai, *Appl. Phys. Lett.* **64** (1994) 815.
- [20] S. F. Liu, Q. Wu, H. L. Schmider, H. Aziz, N.X Hu, Z. Popovic, S. Wang, *J Am. Chem. Soc.* **122** (2000) 3671.
- [21] Q. Wu, J. A. Lavigne, S. Wang, *Inorg. Chem.* **39** (2000) 5248.
- [22] Y. K. Jang, D. E. Kim, O. K. Kwon, Y.S Kwon, *Journal of the Korean Physical Society* **49** (2006) 1057.
- [23] N. Donze, P. Pechy, M. Gratzel, M. Schaer, L. Zuppiroli, *Chem Phys. Lett.* **315** (1999) 405.
- [24] A.N. Du, Q. Me, M. Lu, *Synth. Metals* **149** (2005) 193.
- [25] <http://science.howstuffworks.com/oled.htm>.
- [26] <http://en.wikipedia.org/wiki/oled>.
- [27] Organic Light Emitting Diodes (OLEDs) for General Illumination Update 2002  
Published by: Optoelectronics Industry Development Association  
(<http://www.oida.org>).
- [28] Universal Display Corporation (website).
- [29] L. M. Leung, C. F. Kwong, C. C. Kwok and S.K. So, *IEEE*, (1999) **18**.
- [30] Electroluminescence of conjugated aromatic polymers in organic light emitting diodes Robert h. Lambeth (iii) February 14, 2004.
- [31] Y. Shao, Y. Qiu, W.Hu, Xiaoyin Hong *Adv. Mater. Opt. Electron.* **10** (2000) 285.
- [32] T. Sano, Y. Nishio, Y. Hamada, H. Takahashi, T. Usuki and K. Shibata, *J. Mater. Chem.* **10** (2000) 157.
- [33] D. Braun, *Journal of Polymer Science: Part B: Polymer Physics* **41** (2003) 2622.
- [34] A. Yeh, S. Cherng, *Journal of American Science* **3** (2007) 4.
- [35] M. A. Lampert, P. Mark, *Current Injection in Solids*, Academic: New York, 1970.
- [36] P. Mark, W. Helfrich, *J Appl Phys* **33** (1962) 205.
- [37] T. Mori et al. *Applied Surface Science* **212–213** (2003) 458–463.
- [38] R. D.Young, *Physical Review* **113** (1959) 1.
- [39] S. Barth, U. Wolf, and H. Bassler, *Physical Review B* **60** (1999) 12.
- [40] Y. Sato, S. Ichinosawa, and H. Kanai, *IEEE journal of selected topics in quantum electronics* **4** (1998) 1.
- [41] S. E. Shaheen, G. E. Jabbour, B. Kippelen, and N. Peyghambarian *Applied Physics Letters* **74** (1999) 21.
- [42] Y. Shao, Y. Qiu, W. Hu, X. Hong, *Adv. Mater. Opt. Electron.* **10** (2000) 288.

- [43] T. Sano, Y. Nishio, Y. Hamada, H. Takahashi, T. Usuki and K. Sibata, *J. Mater. Chem.* **10** (2000) 157.
- [44] Z. D. Popovic and H. Aziz *IEEE Journal on Selected Topics in Quantum Electronics* **8** (2002) 2.
- [45] I. M. Chan and F. C. Hong, *Thin Solid Films* **450** (2004) 304.
- [46] N. N. Dinh, D. V. Thanh, P. D. Long, T. Q. Trung *International Workshop on Photonics and Applications, Hanoi Vietnam, April 5-8, 2004.*
- [47] J. Xie, J. Qiao,, L. Wang, J. Xie and Y. Qiu, *Inorganica Chimica Acta*, **358** (2005) 4451.
- [48] K. W. Sam, Y. J. Min, L. B. Jong, J. Y. Ki, K. D. Eun, K. Y. Soo, *Journal of Nanoscience and Nanotechnology*, **6** (2006) 3637.
- [49] C. Williams et.al *Applied Physics Letters* **88** (2006) 183104.
- [50] V.K. Shukla , S. Kumar and D. Deva, *Journal of Luminescence*, **121** (2006) 132.
- [51] T. Yu, W. Su, W. Li, Z. Hong, R. Hua and B. L. Thin, *Solid Films* **515** (2007) 4080.
- [52] The Royal Society of Chemistry Fine Chemicals and Medicinals Group.
- [53] [http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/UV- Vis/uvspec.htm](http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/UV-Vis/uvspec.htm).
- [54] *Organic Spectroscopy by Willium Kemp.*
- [55] <http://science.howstuffworks.com/oled.htm>.
- [56] <http://www.impactanalytical.com/tga.html>.