“Synthesis and characterization of Zinc based electroluminescent metal complexes for their applications in OLEDs”

A THESIS SUBMITTED

In partial fulfilment of the requirement

For the degree of

MASTER OF TECHNOLOGY

IN

MATERIALS AND METALLURGICAL ENGINEERING

By

Narbadeshwar Prasad Mishra

Roll No. **600802011**

SCHOOL OF PHYSICS AND MATERIAL SCIENCE

THAPAR UNIVERSITY

PATIALA- 147004

JULY 2010

CERTIFICATE

This is to certify that the thesis entitled **"Synthesis and Characterization of Zinc based Electroluminescent Metal Complexes for their applications in OLEDs"** submitted by **Mr. Narbadeshwar Prasad Mishra** is in partial fulfilment for degree of master of technology in Materials and Metallurgical 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.

This work has been carried out from **4 January 2010** to **4 July 2010.**

Supervisors

Ritu Srivastava
Dr. Ritu Srivastava
Scientist 'E1'
Centre for Organic Electronics
National Physical Laboratory
New Delhi – 110012

Dr. D. P. Singh
School of Physics and Material Science
Thapar University
Patiala-147004

Countersigned by:

Prof. O. P. Pandey
Head
School of Physics and Material Science
Thapar University
Patiala- 147004

28.7.10
Prof. R. K. Sharma
Dean, Academic Affair
Thapar University
Patiala-147004

DEDICATION

I would like to express my deepest gratitude to specially my grandfather retired lecturer Sri Ramyash Mishra and my grandmother.

ACKNOWLEDGEMENT

This thesis work is the final examination toward getting my master degree in Materials and Metallurgical Engineering at Thapar University, Patiala. The work has been carried out with the huge blessings of **God**.

I would like to express my deepest gratitude to **Dr. M. N. Kamalasanan** 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 never express my deepest gratitude to **Dr. Ritu Srivastava**, and **Dr. D. P. Singh** for their invaluable guidance and enthusiastic encouragement throughout my thesis work. Their excellent ideas and precious comments have inspired me and taught me a great deal, her strong confidence and farsighted outlook gave me confidence and enhanced my pleasure in the work. Without their genuine concern and unreserved support, I could not have finished my thesis work successfully.

Moreover, I am indebted to **Prof. O. P. Pandey**, Head, School of Physics and Material Science, Thapar University, Patiala for his support. Special acknowledgements are given to **Dr. Ramesh Chandra Budhani (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. Rajeev Chopra Head HRD group, NPL, for their support during the course of thesis work.

I pay thanks to 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. Kulvir Singh, Dr. Sunil Kumar, Dr. Manoj Kumar, Dr. Puneet Sharma, Dr. Loveleen Brar 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 Mr. Amit Kumar, Miss Punita, Miss Gayatri Chauhan, Mr. Arunandan Kumar, Miss Rakhi, Miss Omvati, Mr. Razi Ahmed, Miss Manisha Bajpaiyi, Miss Priyanka Tyagi, and Mr. Anzar Gani, members of Centre for Organic Electronics for their kind support in my work. Miss Priyanka and Mr. Arunandan kumar helped me in all possible ways. Their timely discussions are very much appreciable.

I also would like to thanks my naughty friends Mr. Anil Kumar, Mr. Pankaj Kumar, Mr. Ravinder Kumar, Mr. Mukesh Kumar, Mr. Aniruddha Dey, Mr. Arvind Choudhary, Mr. Ram Kishor, Mr. Karuna Sagar, Mr. Sandeep Singh, Mr. Nitesh k. Singh, and all my classmates, who devoted their valuable time and helped me in all possible ways towards successful completion of this work.

I would like to dedicate this dissertation to my parents, **Mr. Markandey Mishra** and **Smt. Krishna Mishra** and all my family for their love, inspiration, devotion, faith and all kind of support not only during this process but also throughout my life. I would like to express my deepest gratitude to specially my grandfather retired lecturer **Sri Ramyash Mishra** and **my grandmother** for providing me all kind of opportunities throughout my life to do something better. My words can never express my deepest gratitude to my grandfather, for there invaluable guidance and enthusiastic encouragement throughout my life.

Lastly I would like to thanks Uncle Ji, Mr. Raju, and Mr. Hemant Kumar for their help in arranging laboratory materials during experiments.

Narbadeshwar Prasad Mishra

Abstract

Organic semiconductors have attracted lot of attention in technological community due to its potential applications in organic light emitting diodes (OLEDs), organic photovoltaic cells and field effect transistor etc. OLED is being considered as one of the most promising technology for flat-panel displays and in general lighting. An organic light emitting diode (OLED), is a light emitting diode whose emissive electroluminescent layer is composed of a film of organic compounds. The layer usually contains a polymer substance or small molecular weight metal chelates that allow suitable organic compounds to be deposited. The small molecule based metal chelates are the appropriate candidates as they are processed by conventional vacuum deposition techniques. Small molecule based Zn metal complexes can be used in OLED devices as electron and hole transport layer. It can also be used as an emissive layer because of their wide spectral response in the visible region.

Two Zinc based Photoluminescence metal complexes Zinc(2,2'-bipyridine)-5-chloro-8-hydroxyquinoline and Zinc(2,2'-bipyridine)-5-7-dichloro-8-hydroxyquinoline have been synthesized and characterized by different characterization techniques (FT-IR, TGA, UV visible and Photoluminescence Spectroscopy). Both the Photoluminescence and electroluminescence properties are extensively studied. The Photoluminescence properties of Zinc(2,2'-bipyridine)-5-chloro-8-hydroxyquinoline shows maximum absorption at 360 nm, photoluminescence peak at 534 nm and that of Zinc(2,2'-bipyridine)-5-7-dichloro-8-hydroxyquinoline shows maximum absorption at 360 nm, photoluminescence peak at 560 nm.

The x-ray diffraction analysis of the materials Zinc(2,2'-bipyridine)-5-chloro-8-hydroxyquinoline and Zinc(2,2'-bipyridine)-5,7-dichloro-8-hydroxyquinoline have been studied, which shown below in figure 4.5. The result shows the first material is amorphous in nature and second one shows some crystalline nature at an angle $2\theta=23.455$**.** The crystallite size at $2\theta=23.455$, is 168.605nm.

Device have been fabricated with the structure ITO(120nm)/α-NPD(50 nm)/Zinc (2,2'-BPY)-5,7-dichloro-8-hydroxyquinoline(50nm)/LiF(1nm)/Al(150 nm) by using the synthesized zinc complexes, Zinc (2,2'-BPY)-5,7-dichloro-8-hydroxyquinoline as emissive material. Device shows wide electroluminescent spectra which peaks at 560nm and turn-on voltage is 10V.

Contents

Chapter-1

CHAPTER-2

Chapter-3

Chapter-4

Chapter-5

List of Symbols and Abbreviations

OLED	Organic Light Emitting Diode
^{o}C	Degree Celsius
PLED	Polymer Light Emitting Diode
PL	Photoluminescence Spectroscopy
EL	Electroluminescence Spectroscopy
Alq_3	8-hydroxyquinoline aluminium
HTL	Hole Transporting Layer
ETL	Electron Transporting Layer
ELM	Electroluminescent Material
α-NPB	α-Naphthylphenilbiphenyl Diamine
CuPc	Copper Phthalocyanine
BCP	2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline
α	Alpha
LiF	Lithium Fluoride
ITO	Indium Tin Oxide
Ip	Ionization Potential
PPV	Polymer Phenylene Venylene
FT-IR	Fourier Transform Infrared Radiation
XRD	X-ray Diffraction
TGA	Thermal Gravimetric Analysis
DSC	Differential Scanning Calorimetry
TPD	N,N'-diphenyl-N,N'-bis (3-methylphenyl)-[1-1'-biphenyl]-4,4'-diamine

List of Figures and Tables:

Tables

Figures

Chapter 1

Chapter 2

Chapter 4

CHAPTER 1

INTRODUCTION

Organic semiconductors have attracted lot of attention in technological community due to its potential applications in organic light emitting diodes (OLEDs), organic photovoltaic cells and field effect transistor etc. OLED is being considered as one of the most promising technology for flat-panel displays and in general lighting. For the development of new organic electronic applications and improvement of performance of the already existing prototype devices, materials with desired properties play an instrumental role **[1-4].**

OLEDs have many advantages over conventional display technologies such as

1. The fabrication process is easy, and devices are thinner and light weighted than those fabricated by cathode ray tube (CRT) display technology.
2. A significant advantage over traditional liquid crystal displays (LCDs) is that OLEDs do not require a backlight to function, so that they can display deep black levels, draw for less power, and can be much thinner and lighter than an LCD panel.
3. OLEDs can be viewed from different angles.
4. The driving voltage and power consumption are low **[5].**

An organic light emitting diode (OLED), is a light emitting diode whose emissive electroluminescent layer is composed of a film of organic compounds. The layer usually contains a polymer substance or small molecular weight metal chelates that allow suitable organic compounds to be deposited. They are deposited in rows and columns onto a flat carrier by suitable processes. The resulting matrix of pixels can emit light of different colours. The small molecule based metal chelates are the appropriate candidates as they are processed by conventional vacuum deposition techniques. Small molecule based Zn metal complexes can be used in OLED devices as electron and hole transport layer. It can also be used as an emissive layer because of their wide spectral response in the visible region. OLEDs can also be used in light sources for general space illumination, and large-area light emitting elements. OLEDs typically emit less light per area than inorganic solid-state based LEDs which are usually designed for use as point-light sources. OLED displays also naturally achieve much higher contrast ratio than LCD screens using either CCFL or LED Backlights **[6].**

1.1 Historical Background

First produced electroluminescence in organic materials by A. Bernanose and co-workers at the Nancy-University in the early 1950s, by applying high-voltage alternating current (AC) fields in air to acridine orange and quinacridine either deposited on or dissolved in cellulose or cellophane thin films. They proposed a mechanism of either direct excitation of the dye molecules or excitation of electrons **[7, 8].**

Martin Pope **[9, 10]** and his group made the seminal discovery of ohmic, dark injecting electrode contacts to organic crystals **[11]**, in 1960 and described the necessary energetic requirements (work functions) for hole and electron injecting electrode contacts. Dark injecting hole and electron injecting electrode contacts are the basis of all current OLED devices, molecular and polymeric, as will be pointed out in the description of the requirements for the construction of successful OLEDs.

The first observation of direct current (DC) electroluminescence made by Martin Pope and his group in 1963 under vacuum, on a pure, single crystal of anthracene, and also on anthracene crystal doped with tetracene **[12].** The injecting electrode was a small area silver electrode, at 400 V DC, and the proposed mechanism was field accelerated electron excitation of molecular fluorescence.

Martin Pope and his group refined their experiment in 1965 **[13]** and showed that in the absence of an external electric field, the electroluminescence in anthracene single crystal was caused by the recombination of a thermalized electron and hole. This paper proved conclusively that the conducting level of anthracene is higher in energy than the exciton energy level.

W. Helfrich and W.G. Schneider produced double injection recombination electroluminescence for the first time in 1965, **[14]** in an anthracene single crystal using hole and electron injecting electrodes whose work functions satisfied the requirements specified by Pope's group. Electroluminescent materials can be insulators or doped insulators. **[15]** The Helfrich and Schneider paper is the forerunner of all double injection induced OLED devices.

Researchers at Dow Chemical in 1965, developed high voltage (500-1500 V) AC-driven (100-3000 Hz), electrically insulated thin (1 mil) layers of a melted phosphor consisting of ground anthracene powder, tetracene, and graphite powder. **[16]** Their proposed mechanism was electronic excitation at the contacts between the graphite particles and the anthracene molecules. Conductivity of such materials limited light output until more conductive organic materials became available, especially the polyacetylene, polypyrrole, and polyaniline "Blacks".

In a 1963 series of papers, Weiss et al. first reported high conductivity in iodine-doped oxidized polypyrrole. They achieved a conductivity of 1 S/cm. Unfortunately; this discovery was "lost", as was a 1974 report of a melanin-based bistable switch with a high conductivity "ON" state. This material emitted a flash of light when it switched.

In a subsequent 1977 paper, Hideki Shirakawa reported high conductivity in similarly oxidized and iodine-doped polyacetylene.

Alan J. Heeger, Alan MacDiarmid & Hideki Shirakawa received the 2000 Nobel Prize in Chemistry for "The discovery and development of conductive organic polymers". The Nobel citation made no reference to the earlier discoveries.

The first attempt to create a polymer LED was by Roger Partridge at the UK's National Physical Laboratory. The project succeeded, being patented in 1975 though publication was delayed until 1983 **[17].**

The first diode device was invented at Eastman Kodak by Dr. Ching W Tang and Steven Van Slyke in the 1980s**.** This diode, giving rise to the term "OLED" used a novel two-layer structure with separate hole transporting and electron transporting layers such that recombination and light emission occurred in the middle of the organic layer. This resulted in a reduction in operating voltage and improvements in efficiency, and started the current era of OLED research and device production.

Later, this concept was adapted for use with polymers culminated in the Burroughes *et al* **[18]**. 1990 paper in the journal Nature reporting a very-high-efficiency green-light-emitting polymer.

1.2 Basics of Light Emission

Light is one type of energy. So in order to emit light, the molecules must absorb energy from other sources. Once a molecule has absorbed enough energy, it can go to the excited electronic state. When the molecule relaxes to the ground singlet state, it can use different processes, one of which is to emit light **[19]**.

1.2.1 Fluorescence

Once a molecule has absorbed enough energy, it can go to the excited electronic state. Fluorescence occurs when it returns from an excited singlet state to the ground singlet states. Because the two states have same multiplicity, it is spin-allowed and is very fast (10^{-5} to 10^{-8} seconds).

1.2.2 Phosphorescence

Phosphorescence occurs when it returns from an excited triplet state. This is spin-forbidden and is often slow (10^{-4} seconds to minutes).

Figure (1.1) shows the basic principle of an OLED. By applying a bias voltage, holes are injected into highest occupied molecular orbital (HOMO) from the anode, to form radical cations, while electrons, injected into lowest occupied molecular orbital (LUMO) from the cathode, form radical anions. The anions and cations will move under the influence of the electrical field. When some of radical anions and cations meet somewhere in the electroluminescent layer, this will form singlet and triplet excited states, but light can only be emitted when singlet excitons form in the emissive layers. This is because the materials currently employed are typically fluorophores, and have a low probability to emit light from a triplet state.

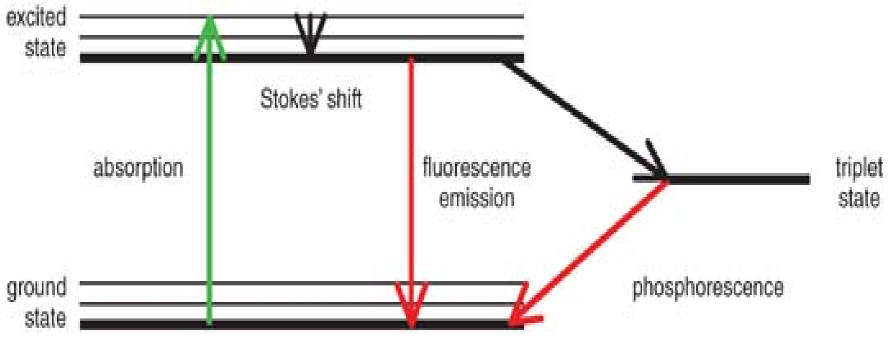


Figure 1.1: The process of light emission from OLEDs [20]

1.3 Electroluminescent Materials

Electroluminescent (EL) devices are constructed using multilayer organic thin films. The basic structure consists of a hole-transport layer and a luminescent layer. The hole-transport layer is an amorphous diamine film in which the only mobile carrier is the hole. The luminescent layer consists of a host material, 8-hydroxyquinoline aluminium (Al_{q3}), which predominantly transports electrons. High radiance has been achieved at an operating voltage of less than 10V. By doping the Alq_3 layer with highly fluorescent molecules, the EL efficiency has been improved by about a factor of 2 in comparison with the undoped cell. Representative dopants are coumarins and DCMs. The EL quantum efficiency of the doped system is about 2.5%, photon/electron. The EL colors can be readily tuned from the blue-green to orange-red by a suitable choice of dopants as well as by changing the concentration of the dopant. In the doped system the electron-hole recombination and emission zones can be confined to about 50 Å near the hole-transport interface. In the undoped Al_{q3} the EL emission zone is considerably larger due to exciton diffusion. The multilayer doped EL structure offers a simple means for the direct determination of exciton diffusion length. Electroluminescence refers to the phenomenon in which a solid (phosphor or semiconductor) emits light when an electric field is applied to it. Generally, EL can be classified into two types according to the active materials used in the device.

1. Inorganic EL
2. Organic EL

Organic EL is the emission of light upon electric excitation that leads to the radiative recombination of electron and hole pairs injected into an organic semiconductor. Inorganic EL involves inorganic direct band gap semiconductors such as GaAs and ZnS. These materials for EL devices can be classified into three categories according to their molecular structure.

a. The first one is the small molecular organic compounds (no metal element), that can be sublimed under a vacuum for thin film deposition.
b. The second one is the conjugated polymer that can be coated on different kinds of substrates from a solution **[21]**.
c. The other one is the chelate metal complexes **[22]**.

The chelate metal complexes are especially important because of the simplicity in synthesis procedures, ease of fabrication, high thermal stability and the wide spectral response **[22, 23].** There are many factors affecting the photoluminescence efficiency **[24]** of these metal complexes. Metal chelates can be prepared very pure and can have high luminescence quantum yields and high stabilities at high operating voltages. The one of the important layer of OLED devices is the electroluminescence layer, for which small molecular weight metal chelates can be used. The small molecule based metal chelates are the appropriate candidates as they are processed by conventional vacuum deposition techniques. 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. So that, aluminium (III), boron (III), beryllium (II) and zinc (II) are ideal. Since beryllium (II), boron (III) and aluminium (III) has no'd' electron and zinc (II) has a closed shell of 'd' electrons. The metal ions only serve a structural purpose by stabilizing a luminescent ligand **[24]**. Small molecule based Zn metal complexes can be used in OLED devices as electron and hole transport layer. It can also be used as an emissive layer because of their wide spectral response in the visible region **[21]**. Small organo-metallic complexes of Zinc have high stability, high efficiency, and longer life and are ideal for as emitter materials in OLEDs. Extensive research work is going on in various laboratories to synthesize new zinc complexes containing new ligands to produce a number of novel luminescent zinc complexes as emitters **[25-30]** and electron transporters **[29-31]** in OLED research.

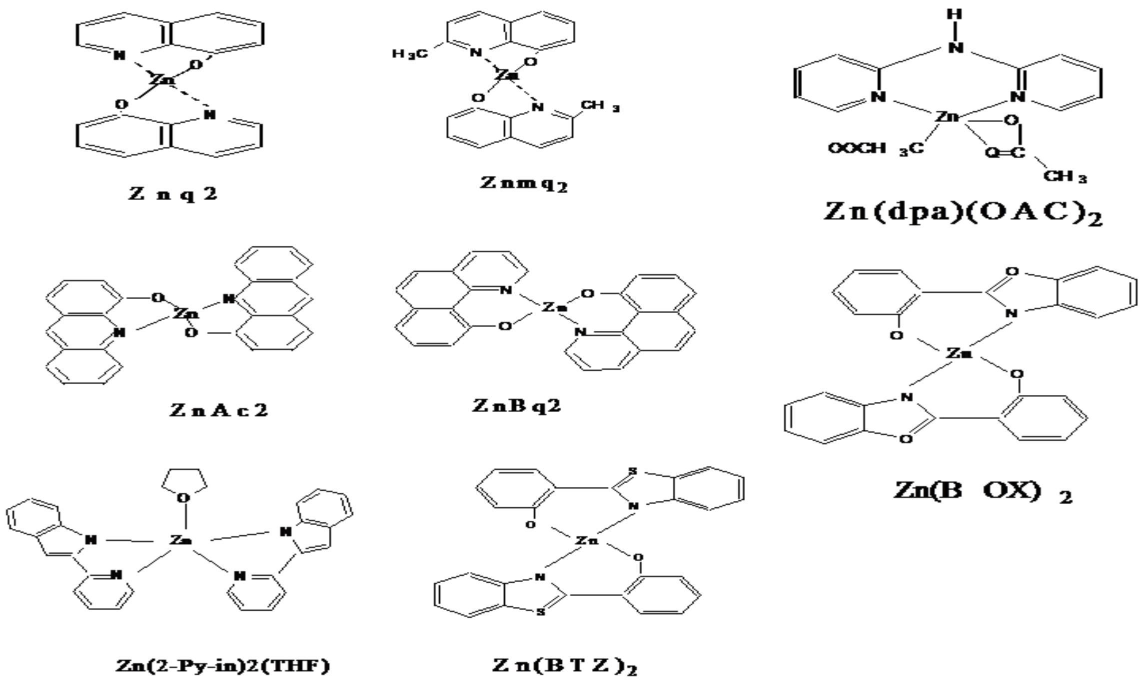


Figure 1.2: Luminescent Zinc chelates

1.4 Selection Criteria for Metal Complexes

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 the next 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 **[31].**

Table: PL Emission (nm) of Different Zinc Metal Complexes

Compounds	PL Emission (nm)	
	Solution (in MeOH)	Solid
Znq_2	-	535,567
$ZnBq_2$	-	572
$Zn(Ac)_2$	-	647
$Zn(BTZ)_2$	-	486,524
$Zn(BOX)_2$	-	478
$Zn(dpa)(OAC)_2$	359	378
$Zn(dpa)Cl_2$	360	378
$Zn(dpa)(CN)_2$	359	363,418
$Zn(dpa)(4\text{-}MeC6H4S)_2$	354	481
$[Zn(dpa)_2][CF_3SO_3]_2$	360	373
$Zn(tdpa)(OAC)_2$	394	411
$Zn(tdpa)Cl_2$	392	403
$[Zn(tdpa)][CF_3SO_3]_2$	390	398

1.5 OLED Structure

The basic OLED structure is shown in **Figure (1.3).** The hole transporting layer (HTL) can transport holes from the anode to the emitting layer (EML). The electron transporting layer (ETL) is used to transport electrons from the metal cathode to the EML. **[32]** The mobility of electrons and holes is different in organic compounds. The key point to operate OLEDs is to control the excitons (electron and hole pairs), so that holes and electrons meet in the emissive layer in equal quantities **[33, 20].**

Figure 1.3: The structure of OLEDs

In device structure the HOMO level of the molecules in the HTL is below the Fermi energy of the anode. The HOMO of HTL is also slightly above that of the ETL, so that holes can readily enter into the ETL. The ETL has a LUMO level, so that the energy barrier of electron injection from cathode is minimized. The LUMO of the ETL is significantly below that of the HTL, so that the electrons are confined in the ETL, increasing the possibility of exciton formation.

Using proper materials can also optimize device performance. Organic materials offer two key advantages over inorganic materials: they are made into films more easily, and have high fluorescence efficiency. The common hole transport material is TPD, **Figure (1.4).** The most important electron-transport material is Alq_3, which is also used as an emissive material. For polymer based-OLEDs, PPV is widely used as the active material. Because PPV itself is insoluble and difficult to process, the synthesis of PPV is typically performed via a solution-processable precursor, which is spin-coated on the proper substrate and converted to PPV by thermal treatment **[35]**. 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 (1.3).**

1.6 Construction of OLED Components

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 of organic materials, in the latter design; the third layer helps in transportation of electrons from the cathode to the emissive layer **[36].**

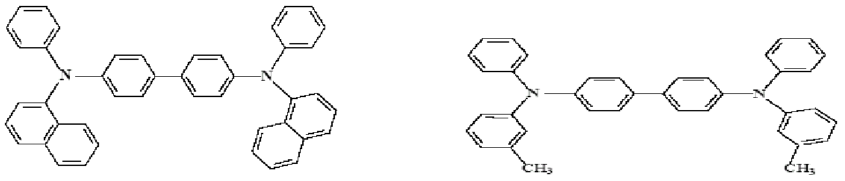
1.6.1 Anode

Indium tin oxide (ITO) is often used as the anode material for hole injection. It has a high work function, to match the HOMO of the organic material. ITO is also transparent, so that the light can leave the device. The work function of ITO can be controlled by surface treatment. The most common method is UV ozone treatment, to increase the ITO work function, which increases hole-injection efficiency into HTL from the ITO anode. The surface energy of ITO can affect the electrical properties of OLEDs. The dependences from the surface energy are been obtained changing the ITO surface chemical-physical properties through well known treatments.

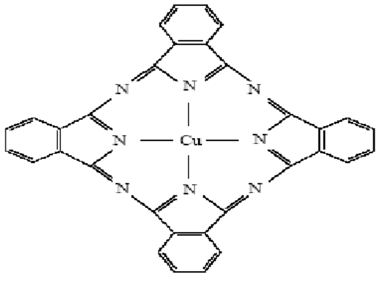
1.6.2 Hole Transporting Materials

The hole-transporting layer (HTL) can greatly improve the performance, i.e. the operational stability and EL efficiency, of OLED. It assists hole injection as a result of a better matching with the work function of the anode. It also facilitates hole (positive charge carriers) transports from the anode to the recombination zone, thus reducing the accumulation of charges at the anode and HTL interface. The material used in this layer is called hole transporting material (HTM). The choice of HTMs for organic electroluminescence (EL) applications is mainly focused on materials with a high thermal stability, high glass transition temperature (T_g), small energy barrier at the interface of anode/HTL (i.e low ionization potential, I_p) and good film forming properties. Aromatic amines are commonly used as HTL materials. Within this amine class, one of the most widely used HTM material in small molecule OLED is α-naphthylphenylbiphenyl diamine (NPB). NPB was first demonstrated by VanSlyke and Tang and is a benzidine derivative with naphthyl substituents. The bulky naphthyl moiety in the molecule provides a more rigid structure and thus substantially high T_g of 98 °C. It is considerably higher than that of another well known HTM of N,N′-diphenyl-N,N′-bis (3-methyl phenyl) (1,1′-

biphenyl)-4,4′-diamine (TPD) (T_g=60°C). Another commonly used HTM is copper phthalocyanine (CuPc) which is combined with NPB to construct double HTLs. Actually, CuPc inhibits hole injection and is detrimental to the device characteristics. The most appealing advantages of CuPc is its ability to planarize the irregularities present at the ITO surface, and its superior film uniformity. NPB organic molecules grow in island-like modes on a pristine ITO surface using atomic force microscopy. However, they grow layer by layer with the presence of CuPc. This excellent uniformity apparently improves film adhesion, and is crucial to the operational stability of the devices. The chemical structures of NPB, TPD and CuPc are shown in **Figure (1.4)**.



NPB TPD



CuPc

Figure 1.4: Chemical structure of typical hole transporting materials

1.6.3 Electron Transporting Material

An electron-transport layer is introduced to reduce the electron injection barrier of the cathode and transport electrons from the cathode to recombine with holes. An effective ETM has a low lowest unoccupied molecular orbital (LUMO) and a high ionization potential (I_p). Metal chelates and in particular Alq_3 are of most prevalent ETMs. Alq_3 is the most commonly used ETM due to its relatively good overall performance. It gives green emission at around 530 nm in the photoluminescence (PL) spectrum. In addition, it has a large electron affinity (EA of 3.1ev), which minimizes the electron injection barrier from the cathode. It has also an unusually good thermal and morphological stability because of its high molecular symmetry.

1.6.4 Emissive Material

Holes and electrons are recombined in the EML so as to prevent quenching of the excitons near the metallic cathode surface. Light will be emitted upon hole-electron recombination, and the emissive wavelength depends on the band gap of the EML material. Alq_3 can be utilized as the EML because it is a good material for transporting electrons. Also, it is capable of emitting with very good operational stability. It has been reported that the emissive material has an electron transporting nature since the recombination of the charge carriers takes place in the narrow Alq_3 layer which is far away from the metal cathode.

1.6.5 Cathode

The cathode is a low-work function metal, which is useful for electron injecting: $Mg_{0.9}Ag_{0.1}$, Ca and Al are commonly used as cathodes. For the $Mg_{0.9}Ag_{0.1}$, Ag is deposited with the Mg, for the purpose of providing nucleation sites, to enable the deposition of the Mg, because Mg has a low sticking coefficient on the surfaces of organic molecules, and Ag protects the Mg from oxygen and water **[37].**

1.7 Basic Principles of OLEDs

An electroluminescent device is composed of a body of small molecule organic material(s) sandwiched between a first and a second electrode, wherein a layer of first insulative material is placed between the body of small molecule organic material(s) and the first electrode, and an optional layer of second insulative material is placed between the body of small molecule organic material(s) and the second electrode. The layer of first insulative material has a thickness which allows first carriers from the first electrode to tunnel there through and the second insulative material has a thickness which allows second carriers from the second electrode to tunnel there through. Further, the layer of first insulative material provides a barrier to the second carriers and the layer of second insulative material provides a barrier to the first carriers. A typical OLED is composed of an emissive layer, a conductive layer, a substrate, and anode and cathode terminals. The layers are made of organic molecules that conduct electricity. The layers have conductivity levels ranging from insulators to conductors, so OLEDs are considered organic semiconductors. The first, most basic OLEDs consisted of a single organic layer, for example the first light-emitting polymer device synthesised by Burroughs et al. **[18]** involved a single layer of poly(p-phenylene vinylene). Multilayer OLEDs can have more than two layers to improve device efficiency. As well as conductive properties, layers may be chosen to aid charge injection at electrodes by providing a more gradual electronic profile, or block a charge from reaching the opposite electrode and being wasted. When a voltage is applied across the OLED such that the anode is positive with respect to the cathode, this causes a current of electrons to flow through the device from cathode to anode. Thus, the cathode gives electrons to the emissive layer and the anode withdraw electrons from the conductive layer; in other words, the anode gives electron holes to the conductive layer. Soon, the emissive layer becomes negatively charged, while the conductive layer becomes rich in positively charged holes. Electrostatic forces bring the electrons and the holes towards each other and they recombine. This happens closer to the emissive layer, because in organic semiconductors holes are more mobile than electrons. The recombination causes a drop in the energy levels of electrons, accompanied by an emission of radiation whose frequency is in the visible region. That is why this layer is called emissive.

The device does not work when the anode is put at a negative potential with respect to the cathode. In this condition, holes move to the anode and electrons to the cathode, so they are moving away from each other and do not recombine. Indium tin oxide is commonly used as the anode material. It is transparent to visible light and has a high work function which promotes injection of holes into the polymer layer. Metals such as aluminium and calcium are often used for the cathode as they have low work functions which promote injection of electrons into the polymer layer **[6].**

1.8 Device Efficiency

The efficiency **[31]** of OLEDs can be characterized by its

a. Quantum efficiency

b. Power efficiency (lm/W)

c. Luminous efficiency (cd/A), sometimes called luminous yield

a. Quantum Efficiency

The device quantum efficiency η_q has two parts: internal and external.

(1) Internal Quantum Efficiency- η_{int} or I_{QE} is the number of photons generated inside the device per number of injected hole–electron pairs. A large fraction of generated photons stays trapped and absorbed inside the device.

(2)External Quantum Efficiency- η_{ext} or E_{QE} is the number of photons released from the device per number of injected hole–electron pairs. It is a critical figure of merit for evaluating device performance.

b. Power Efficiency (lm/W):

Luminous (Power) efficiency η_p is the ratio of the emitted flux in lumens to the input electrical watts (lm/W).

c. Luminous Efficiency (Current Efficiency) (cd/A): [34]

Luminous efficacy η_v represents the ratio of the emitted flux in candelas to the optical watts (radiative power). The luminous efficiency and luminous efficacy of a device account for a spectral sensitivity of a human eye. The, 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).

1.9 Deposition Techniques for OLED Fabrication

Deposition techniques for the Organic materials can be classified as the following categories-

1.10 Evaporation (Suitable for Small Molecules)

Evaporation techniques are of 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 material have low glass transition temperatures. Vacuum evaporation, 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.

CHAPTER 2

EXPERIMENTAL DETAILS

In this Chapter, the main organic materials used in this study will be introduced, which includes their molecular structures and relevant physical properties. Optical and photoluminescence (PL) properties of these synthesized materials have been studied in detail.

2.1 Materials and Their Properties

Two materials Zinc-5-chloro-8-hydroxyquinoline **[26]** and Zinc-5,7-dichloro-8-hydroxyquinoline **[39]** have been synthesized first and its optical and photoluminescence (PL) properties have been studied in detail. Organic light emitting device was fabricated using these materials as emissive layer to study its electroluminescence (EL) properties.

In this study, two new materials Zinc(2,2′ bipyridine)-5-chloro-8-hydroxyquinoline and Zinc(2,2′ bipyridine)-5,7-dichloro-8-hydroxyquinoline have been synthesized and their optical and photoluminescence (PL) properties have been studied in detail. The method of synthesis and processing of these materials have been discussed in subsequent sections.

2.1.1 Zinc(2,2′ bipyridine)-5-chloro-8-hydroxyquinoline

The synthesis of the title compound was accomplished by the processes, as shown in the **Figure (2.1)**.

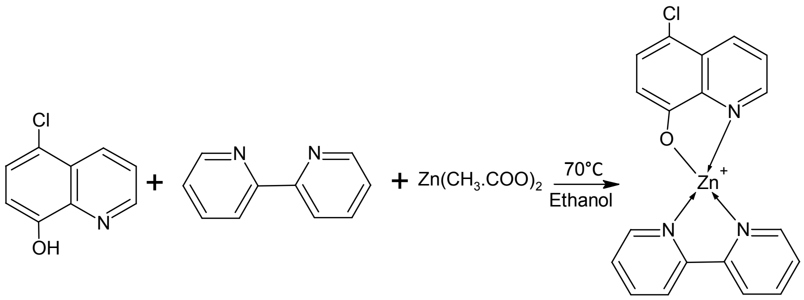


Figure 2.1: Reaction for synthesis of the material Zn(2,2’BPY)-Cl-8-HQ

The materials was obtained by the reaction of the two ligands, 2,2'-bipyridine (BPy) and 5-chloro-8-hydroxyquinoline with zinc acetate (metal ligand) at 1:1:1 molar ratio in ethyl alcohol. A solution of 2,2'-bipyridine 0.94 g was prepared in 30 ml of absolute ethanol in a 100ml three neck flask and stirred in nitrogen atmosphere for 30 min and then a solution of 5-chloro-8-hydroxyquinoline 1g in 30 ml of absolute ethanol was added to the reaction mixture, and stirred at 70 °C for 2 hours. This reaction was allowed to cool to 50 °C and a solution of zinc acetate 1.10 g in 10-15 ml of deionised water added drop wise to the reaction mixture and then the reaction mixture was stirred for 2 hours. After 2 hours a yellowish precipitate of the complex was separated from the reaction mixture which was filtered and dried at 70 °C in vacuum oven for 24 hours. The synthesized material was further purified by vacuum sublimation and stored in desiccators.

2.1.2 Zinc(2,2' bipyridine)-5-7-dichloro-8-hydroxyquinoline

The synthesis of the title compounds was accomplished by the processes, as shown in the **Figure (2.2)**.

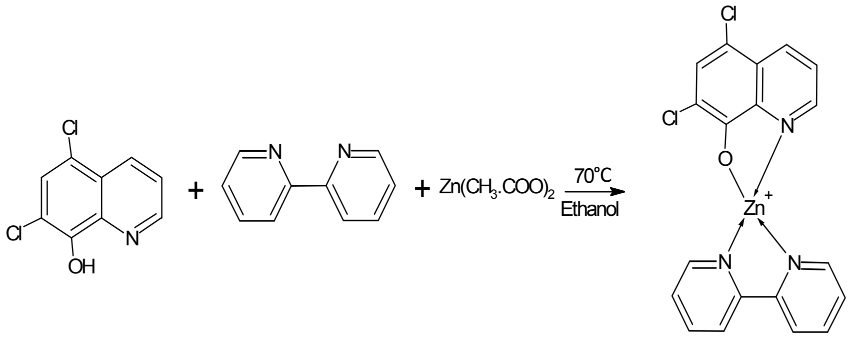


Figure 2.2: Reaction for synthesis of the material Zn(2,2'BPY)-Cl_2-8-HQ

The materials was obtained by the reaction of the two ligands, 2,2'-bipyridine (BPy) and 5-7-dichloro-8-hydroxyquinoline with zinc acetate (metal ligand) at 1:1:1 molar ratio in ethyl alcohol. A solution of 2,2'-bipyridine 0.182 g was prepared in 15 ml of absolute ethanol in a 100 ml three neck flask and stirred in nitrogen atmosphere for 30 min and then a solution of 5,7-dichloro-8-hydroxyquinoline 0.25 g in 10 ml of absolute ethanol was added to the reaction mixture, and stirred at 70 °C for 2 hours. This reaction was allowed to cool to 50 °C and a solution of zinc acetate 0.214 g in 5 ml of deionised water added drop wise to the reaction mixture and then the reaction mixture was stirred for 2 hours. After 2 hours a yellowish precipitate of the complex was separated from the reaction mixture which was filtered and dried at 70 °C in vacuum oven for 24 hours. The synthesized material was further purified by vacuum sublimation and stored in desiccators.

2.1.3 Hole Conduction Materials for hole transport and electron blocking

A typical hole conduction material usually has a hole mobility several orders of magnitude higher than its electron mobility so that its electron transport ability can be neglected. Hole conduction materials were used in this study as matrix of the hole transport layer, as electron blocker. In this work alfa-NPD has been used as hole transport layer and electron blocker for OLED. Other hole transporter material are 2,2',7,7'-tetrakis-(N,N-diphenylamino)-9,9′-spirobifluorene (Spiro-TAD), N,N,N',N'-tetrakis(4-methoxyphenyl)-benzidine (MeO-TPD), N, N'-di(naphthalen-2-yl)-N, N'-diphenyl-benzidine (alfa-NPD), CuPc, TPD etc.

2.1.4 Electron Conduction Materials for electron transport and hole blocking

In contrast to hole conduction materials, an electron transport material has much smaller hole mobility compared to its electron mobility. They were used in this study as matrix of the electron transport layer and as the hole blocking layer. In this study Lithium Fluoride (LiF) is used as electron transporter and hole blocking material. Other electron transport materials are 4,7-diphenyl-1,10-phenanthroline (Bphen)Bis (2-methyl-8-quinolinolato)-(paraphenylphenolato) -aluminium(III) (BAl_q).

2.4 Optical Characterization Techniques

The optical characterization technique used in present study includes UV-absorption and Photoluminescence spectroscopy. The details of these techniques are given in subsequent section.

2.4.1 UV-Visible Absorption Spectroscopy

The process of absorption is caused by the onset of optical transitions across the fundamental band gap of the material. When electrons are excited between the bands of a solid by making optical transitions that are dictated by selection rules it is called interband absorption **[40].**

An absorption spectrophotometer is an instrument that measures the amount of optical absorption in a material, as a function of wavelength. There are four main components of a spectrophotometer:

(1) A light source which is usually a tungsten filament or gas-discharge lamp. Different light sources are used in different regions of the spectrum.

(2) A monochromator, the input to the monochromator is the broadband light from the light source; the output is tuneable and highly monochromatic light.

(3) A sample chamber which holds the sample under investigation.

(4) A detector which measures the amount of light that passes through the sample. Typically, detectors are either solid state photodiodes (silicon, germanium, etc.) or photomultiplier tubes. The basic setup for measuring the absorption or transmission of light through a sample is shown in **Figure (2.3) [42]**.

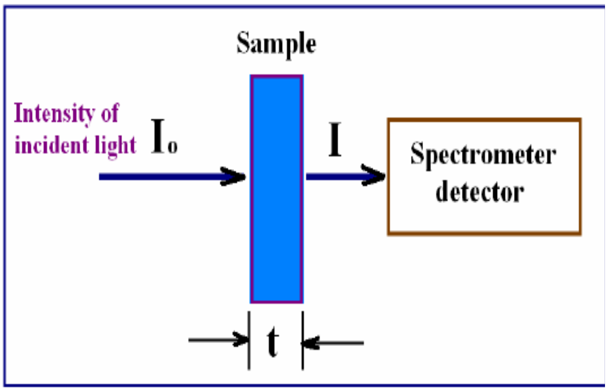


Figure 2.3: Light of intensity I_0 incident upon a sample of thickness t undergoes a loss in intensity upon passing through the sample

When light of some wavelength with intensity I_o passes through the sample the intensity of the light is reduced to a value I, due to absorption within the sample and reflection at the surfaces of the sample. Measuring I_o and I can be used to determine the transmission of the sample at wavelength. In addition to transmission, another useful way to report the optical absorption is in optical absorbance or optical density. Absorbance (A) is a dimensionless quantity defined as the negative of the base-ten logarithm of the transmission (T)$A=-\log_{10}T$. Another quantity of interest is the absorption coefficient (α). The absorption coefficient is given by Beer's Law which relates I to I_o by t. $I = I_o e^{-\alpha t}$ where "t" is the thickness in cm and consequently, absorption coefficient α is in cm^{-1}. As the absorbance is the negative base-ten logarithm of the transmission then α = 2.303A/ t. Absorption spectrometers measure the intensity of the transmitted light as a function of wavelength and compare it to the intensity of the reference at the same wavelength **[41, 42].**

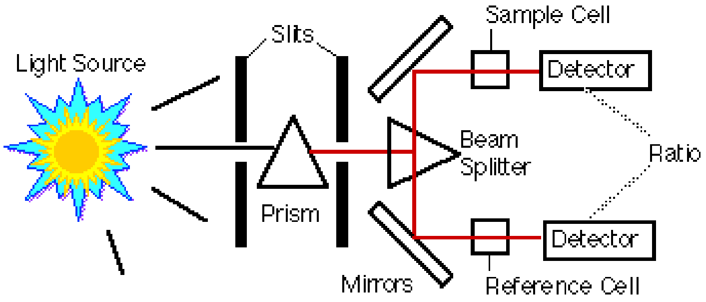


Figure 2.4: Schematic of double beam UV-Visible spectrometer to measure absorption spectra in the wave length range of 200 nm to 900 nm. [43]

For the experimental absorption spectra measurements of polymer, thin films were prepared by spin coating from toluene solution on to a sapphire substrate. The ultraviolet visible spectra (UV-Visible) absorption spectra were measured on a Shimadzu UV 2401 PC UV visible recording spectrometer. The schematic is shown in **Figure (2.4)**.

2.4.2 Photoluminescence Spectroscopy

When light of sufficient energy is incident on a material, photons are absorbed and electronic excitations are created. 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 by emission of light (a radiative process) or via a nonradiative process. If radiative relaxation occurs, the emitted light is called photoluminescence (PL). The energy of the emitted light is related to the difference in energy levels between the two electron states involved in the transition between the emitted states and excited states.

Photoluminescence (PL) is simple, versatile, and nondestructive. The instrumentation that is required for ordinary PL work is modest: an optical source (laser), mirror, collection lenses, optical power meter or spectrophotometer, and a photo detector.

The UV line of an Ar^+ (argon ion) was used in our experiment. There are three lines of wavelength in UV laser 351.4 nm, 351.1 nm, and 363.8 nm respectively. An external prism was used to separate lines. Neutral density filters were used to reduce the intensity of the laser line to avoid heating the sample. The emission spectra were collected using a miniature flexible fiber optic spectrometer USB 2000 detector. For some measurements the 325 nm line of HeCd laser was also used as the excitation source.

2.5 Fourier Transform Infrared Spectroscopy

A molecule absorbs radiation only when the natural frequency of vibration of some part of molecule (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 increase 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 techniques, which offers the possibility over the other usual method of structural analysis (x-ray diffraction, electron spin resonance, etc.) is that it provides useful information about the structure of molecules and binding 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. This device generates Fourier Transform of infra-red spectrum, which is converted in to spectrum itself by a computer. This approach has the advantageous of providing much higher source radiation throughout, increased signal to noise (S/N) ratio and higher wave number accuracy than is possible with a conventional light dispersive spectrometer**.**

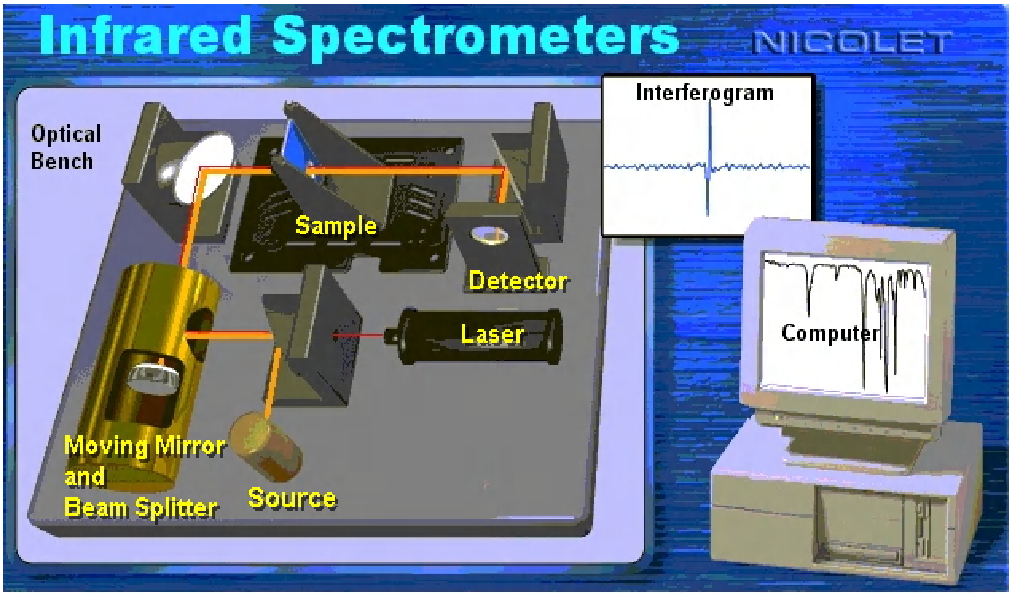


Figure 2.5: Set-up of FT-IR Nicolet 5700 [60]

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 υ, whose unite is cm^{-1}. The relation between velocity c, wavelength λ and frequency υ is as follows;

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

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

2.6 Thermo Gravimetric Analysis

Thermo Gravimetric Analysis (TGA) is a thermal analysis technique **[44]** 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 (non-combustible) 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 tarred 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 no combusted residue at some final temperature, and the temperatures of various sample degradation processes.

2.7 X-ray Powder Diffraction

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.

2.7.1 Fundamental Principles of X-ray Powder Diffraction

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d\sin\theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this.

2.7.2 X-ray Powder Diffraction Instrumentation

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector.

Figure 2.6: Bruker's X-ray diffraction D8-Discover instrument. [45]

X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being K_α and K_β. K_α consists, in part, of $K_{\alpha 1}$ and $K_{\alpha 2}$. $K_{\alpha 1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha 2}$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, and Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. $K_{\alpha 1}$ and $K_{\alpha 2}$ are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with CuK_α radiation = 1.5418Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

X-ray powder diffractogram. Peak positions occur where the X-ray beam has been diffracted by the crystal lattice. The unique set of d-spacings derived from this patter can be used to 'fingerprint' the mineral. The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ. The instrument used to maintain the angle and rotate the sample is termed a goniometer. For typical powder patterns, data is collected at 2θ from ~5° to 70°, angles that are preset in the X-ray scan **[45].**

2.8 Device Processing

2.8.1 Substrate Cleaning and Preparation

All substrates were cleaned and prepared prior to use. The preparation method depends on the substrate in question. Substrate cleaning involves the use of chemicals that pose significant health risks, therefore all procedures were performed in a fume hood or glove box while wearing appropriate personal protective equipment as outline on the material safety data sheets.

The plates of ITO coated glass 25 mm X 25 mm X 1.1 mm were patterned by placing strips of scotch tape at approximately 3 mm intervals. The substrate is coated with zinc powder and placed in a 37% HCl and distilled water bath. Through manual abrasion and chemical reaction the ITO in the exposed regions was removed. The etched sample was rinsed thoroughly with water and the tape removed leaving a patterned surface. Following patterning, the substrates were put into a clean teflon holder and sonicated in an acetone bath for 15 min. This was followed by 15 min of sonication in an isopropanol bath. The substrates were then rinsed with fresh isopropanol and blown dry with oil free nitrogen gas. Finally they were placed in an Ultra Violet Ozone Cleaning Systems for 10 min before being transferred to the glove box/thermal evaporation system for use or stored in a covered Petri dish for use clean substrates were essential for obtaining reliable and repeatable experimental data.

Organic surface contaminants may react chemically with the polymer film or electrode material while metallic/insulating particles may contribute to unusual film morphology and device performance.

2.8.2 Device Fabrication Technique

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 aluminum. The term thin film is generally applied to layers that have thicknesses on the order of several micrometers or less. These films may be as thin as a few atomic layers. In many cases, adding atoms or molecules to a substrate surface one at a time forms thin films. Thicker layers are generally called coatings. Although the same processes that are used to form thin films can often form coatings, there are some coating processes that are not applicable to forming thin films. For example, thermal spray coating processes, which melt small particles, accelerate them to high velocities, and splat-cool them on the surfaces, are not applicable to forming thin films. The properties of thin films generally differ from the values for the materials in the bulk form. In many cases, the growth and properties of thin films are affected by the properties of the underlying substrate material. The properties of the film can also be affected by the high surface to volume ratio of the film. Many technique 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.

2.8.3 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 (Figure-3.7) deposition technique consists in heating until evaporation of the material to be deposited. The material vapor finally condenses in form of thin film on the cold substrate surface and on the vacuum chamber walls. Usually low pressures are used (about 10-6 or 10-5 Torr), to avoid reaction between the vapor and atmosphere. At these low pressures, the mean free path of vapor atoms is the same order as the vacuum chamber dimensions, so these particles travel in straight lines from the evaporation source towards the substrate. This originates 'shadowing' phenomena with 3D objects, especially in those regions not directly accessible from the evaporation source (crucible). Besides, in thermal evaporation techniques the average energy of vapor atoms reaching the substrate surface is generally low (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-tocompletion 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.

2.8.4 Fabrication of Organic Light Emitting Diode

The OLED device was fabricated in a configuration ITO (120nm)/α-NPD (50 nm)/Zn(2,2'-BPY)-5,7-dichloro-8HQ (50 nm/LiF(1 nm)/Al(150 nm) as shown in schematic diagram of OLED (Figure-4.3)

Indium-tin oxide (ITO) coated glass substrates with sheet resistance of 20 Ω/squire 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 × 10-5 torr) at a deposition rate of 0.2 - 0.5 Å/sec and LiF at 0.1-0.2 Å/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 50 nm N,N diphenyl-N'N'-bis(1- naphthyl)-1,1'-biphenyl-4,4'-diamine(_-NPD) (Sigma Aldrich) was used as hole transport layer.

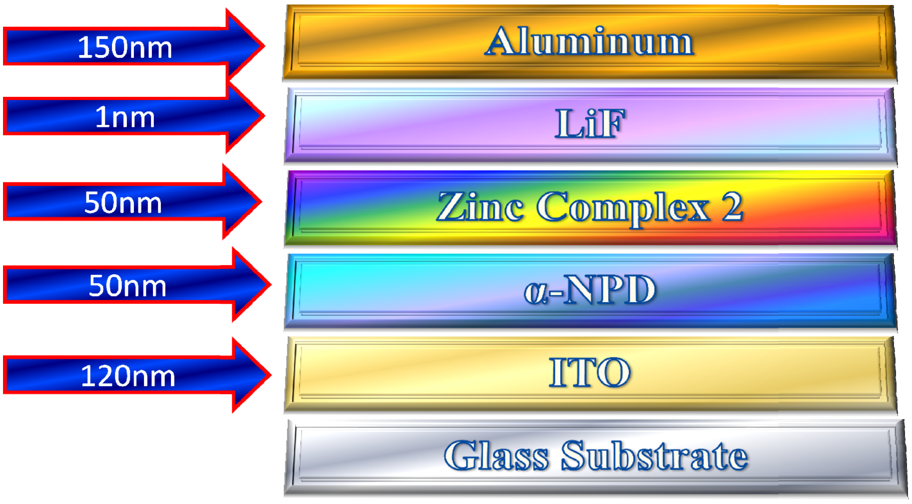


Figure 2.7: Device Configuration

Zinc complex Zn(2,2'-BPY)-5,7-dichloro-8HQ was used as the emitting layer . The electron injection was facilitated using a 1nm thin LiF (Merck, Germany) layer followed by a thick layer of Aluminium. The device area was 5 × 5 mm. The Current–Voltage (I-V) characteristics were measured using a luminance meter and a Keithley 2400 programmable voltage-current digital source meter.

CHAPTER 3

MOTIVATION

Organic semiconducting polymers and organic molecules are gaining a lot of attention of scientific community due to versatility of its applications in organic light emitting diodes, sensors, thin film transistors and solar cells. OLED display is of particular interest as it offers many advantages like low operating voltage, low power consumption, and high contrast etc. Organic molecules have been known to show electroluminescence since early the 1960. The electroluminescence was reported for small organic molecule and conjugated polymer polyphenylene venylene (PPV). Small molecules like Alq_3 have been the materials of choice for organic light emitting (OLED) because of their process ability, relatively high efficiency, and a wide range of colour emission for full colour display. The OLED devices are differ in one aspect from inorganic semiconductor LED devices, due to low carrier concentration in the transport layer, the current voltage characteristics of these devices are injection limited. The balance of electron and hole in the emissive region is very important for fabricating highly efficient OLED. Several investigations have been carried out in fabricate efficient OLED devices.

The charge injection, charge transport and various other modifications are necessary and important for improving the efficiency of OLED devices.

3.1 Literature Review

For the first time in the year 1987 Tang *et al* **[2]** constructed electroluminescent device using organic materials as the emitting elements. It has been found that the Electron-hole recombination and green electroluminescent emission 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^2) has been achieved at a driving voltage below 10 V.

In the year 1996 Hamada *et al* **[50]** reported the studies of small molecules which can form thin films on thermal vapour deposition. Following properties has 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

There is another work reported by Hamada *et al* **[46]** 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 ($BeBq_2$) has been reported as an electron transport layer in OLED devices, with a lifetime (initial luminance: 500 cd/m^2) of more than 3500 h, which is a practical level.

Shao *et al* **[47]** in the year 2000 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 about the device:

(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.

(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 500 cd/m^2.

A better performance has been observed by Shaheen *et al* **[48]** using a triphenyldiamine side-group polymers as hole transport layers in multilayer organic light-emitting diodes using 8-hydroxyquinoline aluminum (Alq_3) as an emission layer.

The comparative study of electroluminescent properties of Tris (8-hydroxyquinoline) gallium Gaq_3 and 8-hydroxyquinoline zinc (Znq_2) has been investigated by Qiu *et al* **[47]** in the year 2000. 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 **[49]**.

Degradation mechanisms in small molecule-based organic light-emitting devices (OLEDs) have been reviewed in the year 2002 by Aziz *et al* **[51].**

In the year 2004 the electrical and optical properties of the NiO films deposited under various conditions has been first characterized by Hong *et al* **[52].** 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 Dinh *et al* **[53]** that the enhancement in both the onset electric field (onset voltage) and the reverse current are due to lowering the workfunction of Al/Alq_3 by the application of the super-thin LiF layer. These enable electrons better inject into the emissive Alq_3 material, consequently one can have higher possibility of emissive recombination of excitons in the devices.

In the year 2006 Jang *et al* **[54]** reported that the electrondonating 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)$_2$) has been synthesized and structurally characterized by Qiao *et al* **[55].** 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_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).

In the recent year 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)$_2$) and [(1,10-phenanthroline)(8-hydroxyquinoline)] Zn(ph)$_q$ has been synthesised by Jong *et al* **[56].** The photoluminescence (PL) spectra of Zn(HPB)$_2$ and Zn(ph)$_q$ has been observed to be blue and yellowish green, respectively.

In the same year zinc complexes (Zn(HPB)$_2$ and Zn(HPB)q) has been synthesized. It has been reported that the ITO/NPB (40 nm)/Alq_3 (60 nm)/Zn(HPB)$_2$ (5 nm)/LiF/Al device showed increased luminance of L = 17000 cd/m^2 compared to L = 12000 cd/m^2 for similar device fabricated without the hole-blocking layer.

Again in the same year Williams *et al* **[57]** 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 Shukla *et al* **[58].** 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 Yu *et al* **[59]** in the year 2007 which exhibited blue emission with a peak at 455 nm and the maximum brightness of 650 cd m^{-2}.

Table: Literature Review

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 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 and Shoko Ichinosawa (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 cd/m^2
S. E. Shaheen and G. E. Jabbourl (2000)	Used triphenyldiamine sidegroup polymers as HTLs in multilayer OLEDs using Alq_3 as an emission layer.	A better performance has been observed.
Yong Qiu and Wenhua Hu (2000)	Comparative study of electroluminescent properties of Tris (8-hydroxyquinoline) gallium Gaq_3 and 8-hydroxyquinoline zinc (Znq_2).	It has been reported that Gaq_3 solid film could yield very strong (PL) and an EL device with Znq_2 could harvest a higher brightness even than Alq_3.

3.2 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. Therefore, the proposed work plan is aimed at-

1. To synthesize and characterize the Zinc based electroluminescent metal complexes for the applications in OLED devices.
2. Thermal spectroscopic study such as TGA has to be carried out for deciding the thermal stability.
3. UV-Visible spectroscopy and Photoluminescence spectroscopy is carried out for determining the band gap and luminescence properties.
4. Study of structural measurement (XRD) of Zinc based electroluminescent organic materials.
5. Device have been fabricated with the structure ITO(120nm)/α-NPD(50 nm)/Zinc(2,2'-BPY)-5,7-dichloro-8-hydroxyquinoline(50nm)/LiF(1nm)/Al(150 nm) by using the synthesized zinc complexes 2 as emissive material.
6. Device shows wide electroluminescent spectra which peaks at 560nm and turn-on voltage is 10V.

CHAPTER 4

RESULTS AND DISSCUSSIONS

4.1 Structural and Thermal Characterization

The thermo gravimetric analysis has been done by using SDTA851e-Metter-Tolledo star system in the temperature range 0-800 °C and measure the change in weight of material as a function of temperature. The infrared absorption spectrum of the material has been studied using a Nicolet 5700 spectrometer. In the present work, the thermo gravimetric analysis and structural characterization of Zinc complexes namely Zinc(2,2'-bipyridine)-5-chloro-8-hydroxyquinoline and Zinc(2,2'-bipyridine)-5-7-dichloro-8-hydroxyquinoline before fabricating the device.

4.1.1 Structural and Thermal Characterisation of Zinc(2,2'-bipyridine)-5-chloro-8-hydroxyquinoline

Following **Figure (4.1)** shows the FT-IR spectrum of the material carried out in powder form. The spectrum shows the characteristic peaks of aromatic ring stretching at 742.6 cm^{-1}, which is due to the existence of quinolinic rings. Aliphatic chloro compounds C-Cl at 781.9 cm^{-1}. Aromatic ring resonance peak of C-N-C at 1249.8 cm^{-1} and 1396.3 cm^{-1}, aromatic C-O stretching at 864.2 cm^{-1} and 883.9 cm^{-1}. The peak at 1491.1 cm^{-1} is indicative peak of C=C aromatic ring stretching.

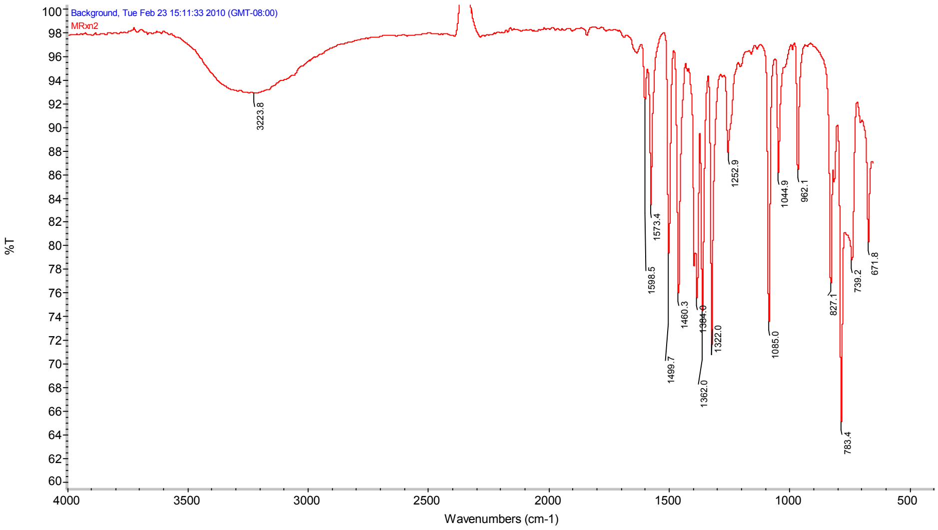


Figure 4.1: FT-IR spectrum of Zinc(2,2'-bipyridine)-5-chloro-8-hydroxyquinoline

TGA of synthesized Zinc(2,2’-bipyridine)-5-chloro-8-hydroxyquinoline was carried out in the temperature range 0-800 ^{0}C as shown in **Figure (4.2)**. The TGA plot of Zinc-5chloro-8 hydroxyquinoline shows a measure large weight loss which starting from 394 ^{0}C indicating thermal degradation. This shows that the compound was stable up to 394 ^{0}C. The high thermal stability in nitrogen, which is attributed to the highly polarized Zn-N bond. The high thermal stability of the material is as an advantage in the fabrication of organic light emitting device for getting greater longevity.

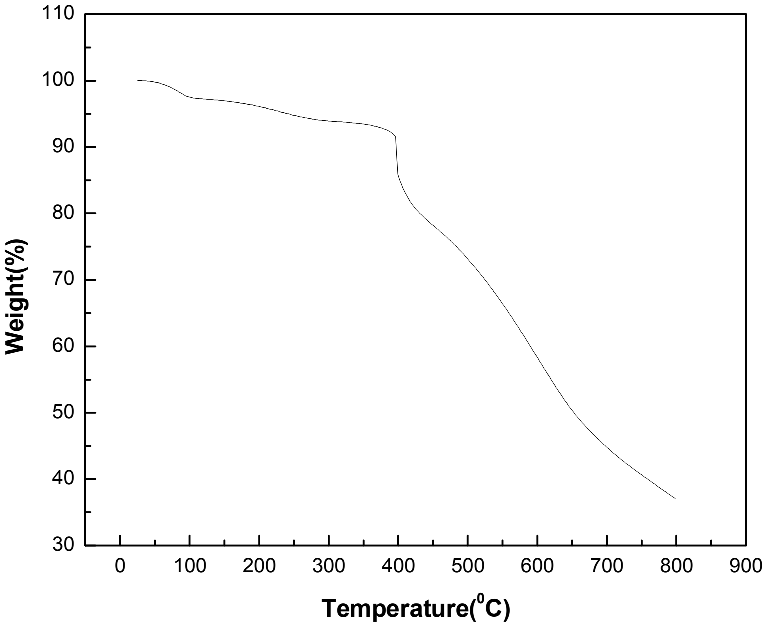


Figure 4.2: TGA of Zinc(2,2’-bipyridine)-5-chloro-8-hydroxyquinoline

4.1.2 Structural Characterisation of Zinc(2,2’-bipyridine)-5-7 dichloro-8-hydroxyquinoline

Following **Figure (4.3)** shows the FT-IR spectrum of the material carried out in powder form. The peak 666.6 cm^{-1} shows aromatic C-H out of plane bending and Trans C-H out of plane bending at 965.5 cm^{-1}. Aromatic primary amines C-N stretching at 1060.1 cm^{-1} and 1250.2 cm^{-1}. Aromatic C-O stretching was observed in the spectrum at 884.3 cm^{-1} and 1113.7 cm^{-1}. The peak shows OH bend at 1362.2 cm^{-1} and 1396.6 cm^{-1}.the group methylene C-H asymmetric and aromatic ring stretching C=C-C at 1491.6 cm^{-1}.

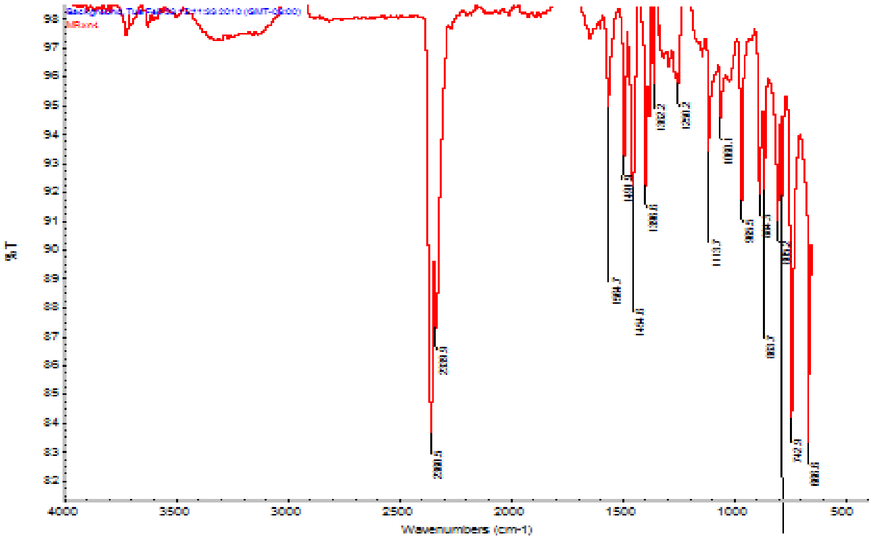


Figure 4.3: FT-IR spectrum of Zinc(2,2'-bipyridine)-5-7-dichloro-8-hydroxyquinoline

4.2 Optical Characterization

UV-visible absorption spectra of the two zinc complexes Zinc(2,2'-bipyridine)-5-chloro-8-hydroxyquinoline and Zinc(2,2'-bipyridine)-5-7-dichloro-8-hydroxyquinoline were recorded on a Shimadzu UV-2401 spectrophotometer. The excitation and emission spectra of a solution of two zinc complexes Zinc(2,2'-bipyridine)-5-chloro-8-hydroxyquinoline and Zinc(2,2'-bipyridine)-5-7-dichloro-8-hydroxyquinoline were recorded with a Fluorolog Spectrofluorometer (Horiba Jobin YVON Fluorolog Model FL 3-11) at room temperature.

4.3 Optical Characterization of the Zinc Complexes

The UV-Vis absorption and photoluminescence spectrum were measured in a solution of ethanol. **Figure (4.4, (a) and (b))** shows the UV and PL spectra of the two zinc complexes Zinc(2,2'-bipyridine)-5-chloro-8-hydroxyquinoline and Zinc(2,2'-bipyridine)-5-7-dichloro-8-hydroxyquinoline respectively. The maxima of the UV-Vis absorption peaks of Zinc(2,2'-bipyridine)-5-7-dichloro-8-hydroxyquinoline was observed at 360 nm, which is due to the π-π* transition of aromatic ring. The peak of the PL spectrum of Zinc(2,2'-bipyridine)-5-7-dichloro-8-hydroxyquinoline was observed at 560 nm. This indicates the material emits the yellowish green colour. The maxima of the UV-Vis absorption peaks of Zinc(2,2'-bipyridine)-5-chloro-8-hydroxyquinoline was observed at 360 nm, which is due to the π-π* transition of aromatic ring.

The peak of the PL spectrum of Zinc(2,2’-bipyridine)-5-chloro-8-hydroxyquinoline was observed at 534 nm. This indicates the material emits the yellowish green colour.

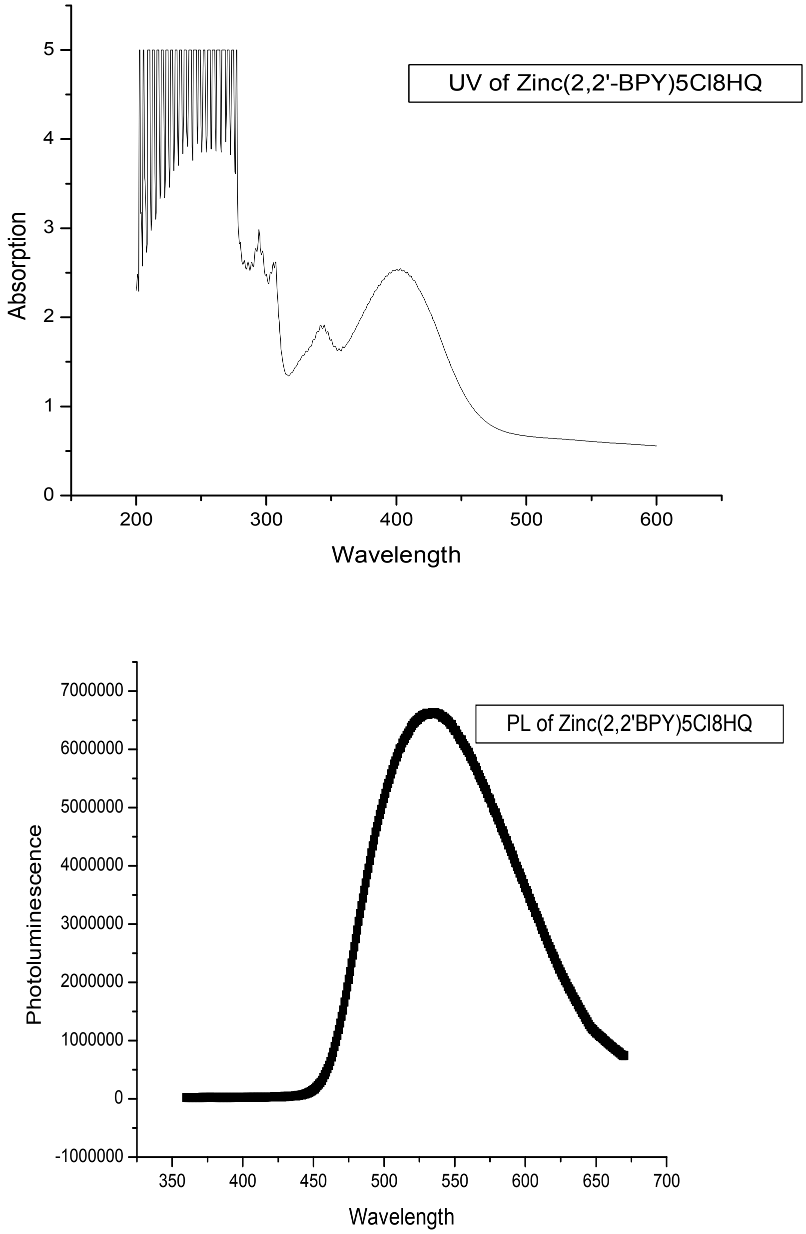
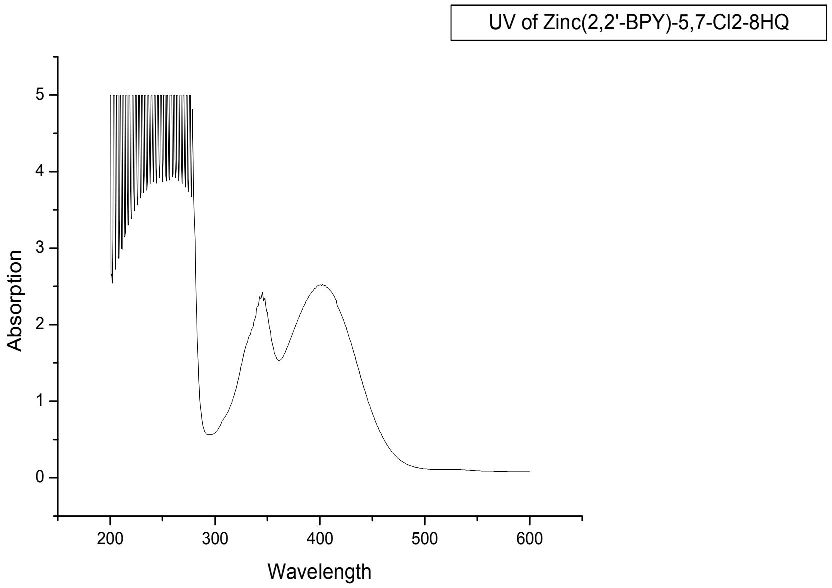


Figure 4.4: (a) UV-Visible and Photoluminescence spectrum of Zinc(2,2’-bipyridine)-5-chloro-8-hydroxyquinoline



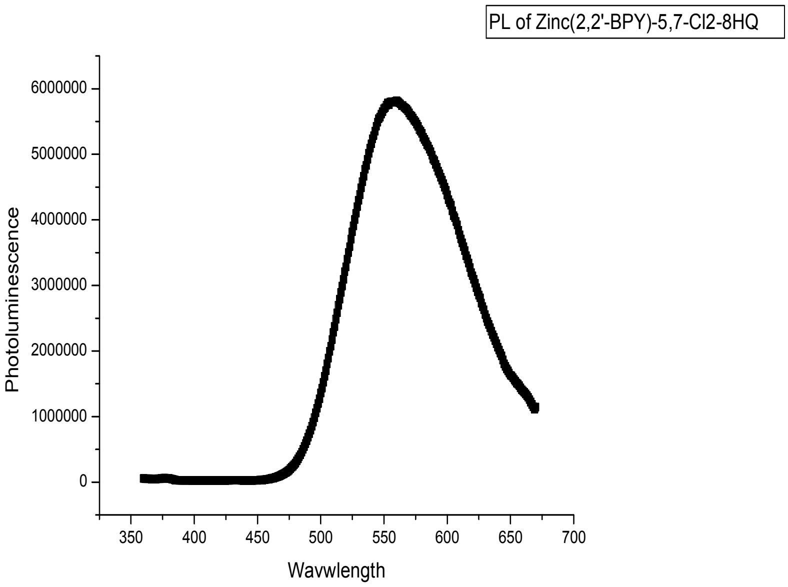
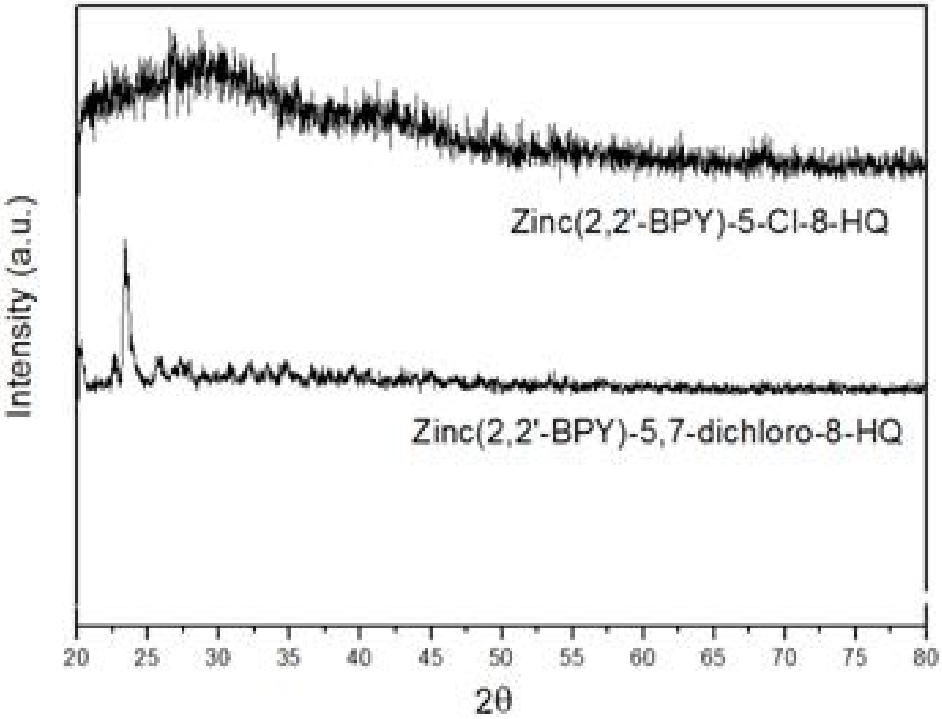


Figure 4.4: (b) UV-Visible and Photoluminescence spectrum of Zinc(2,2'-bipyridine)-5,7-dichloro-8-hydroxyquinoline

4.4 X-ray Diffraction Mesurement of the Materials

The x-ray diffraction analysis of the materials Zinc(2,2'-bipyridine)-5-chloro-8-hydroxyquinoline and Zinc(2,2'-bipyridine)-5,7-dichloro-8-hydroxyquinoline have been studied, which shown below in **Figure [4.5].** The result shows the first material is amorphous in nature and second one shows some crystalline nature at an angle 2θ=23.455, The crystallite size at 2θ=23.455, is 168.6nm.



4.5: x-ray diffraction pattern of Zinc complexes

4.5 Device Fabrication and Characterization:

Organic light emitting Diode have been fabricated with the structure ITO(120nm)/α-NPD(50 nm)/Zinc(2,2'-BPY)-5,7-dichloro-8-HQ(50nm)/LiF(1nm)/Al(150 nm) by using the synthesized zinc complex, Zinc(2,2'-BPY)-5,7-dichloro-8-HQ as emissive material. Device shows wide electroluminescent spectra which peaks at 560nm and turn-on voltage is 9V. The electroluminescence and I-V characteristics of the device are given below.

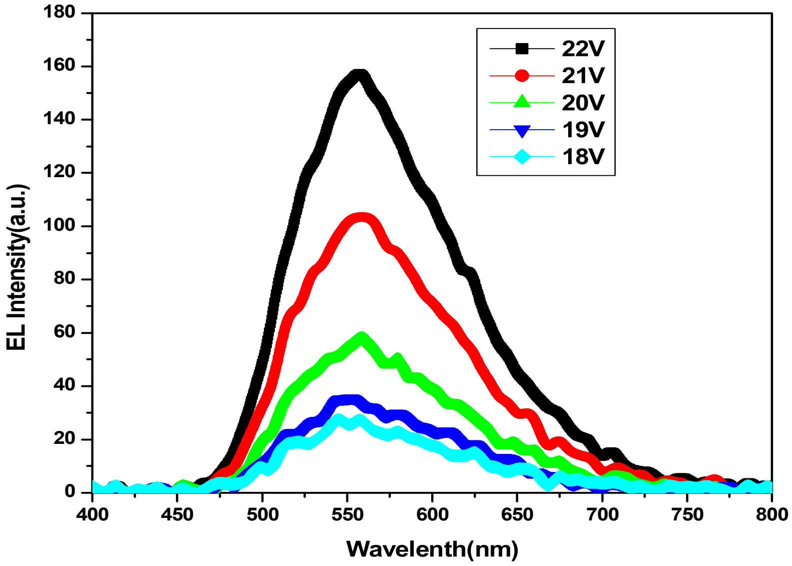


Figure 4.6: Electroluminescence of the device

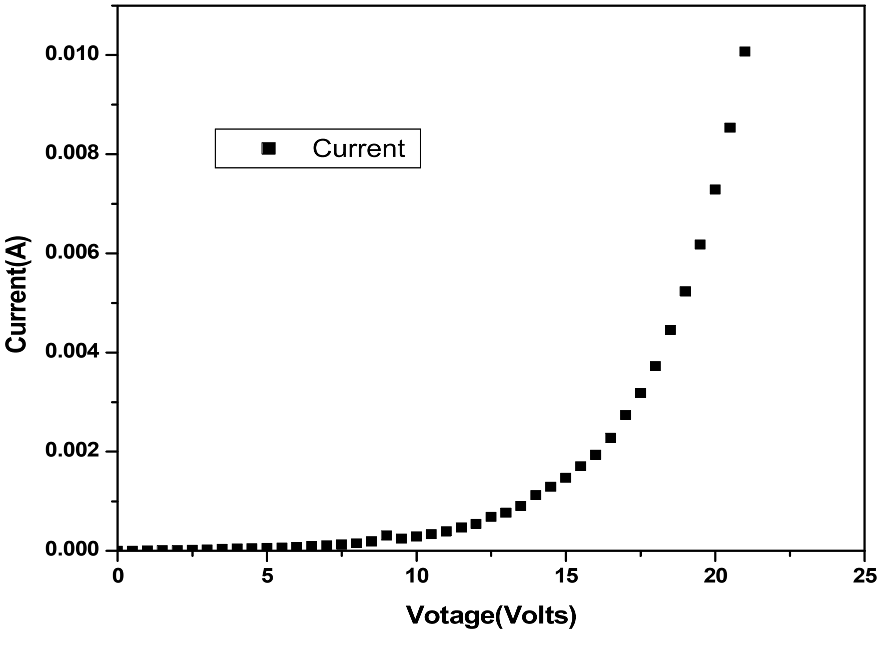


Figure 4.7: I-V Characteristics of the device

CHAPTER 5

SUMMARY AND FUTURE SCOPE

5.1 Summary

We can say that "necessity is the mother of invention" in case of organic electronics. One of the most exciting opportunities in optoelectronics currently is device based on organic materials. These have many advantages, primarily: lower-technology processing with less sensitivity to processing environment, flexibility and the opportunity to apply the enormous power of organic synthesis to tailoring the properties of the materials to specific applications. Furthermore, organics can emit light directly as do conventional cathode-ray-tube and plasma display panels, rather than relying on backlighting systems such as are used in liquid-crystal displays. One can imagine these technologies leading to poster size televisions which can be rolled up and stored in mailing tubes, or unrolled and thumb-tacked to a wall. The materials are already being applied in compact light weight, power efficient light emitting device in small areas such as cell-phone displays. The primary problem with all organic devices is stability. When carriers are injected in these materials, sometimes a molecule falls apart.

The important conclusions of the present study have been summarized as follows:

Zinc(2,2'-bipyridine)-5-chloro-8-hydroxyquinoline and Zinc(2,2'-bipyridine)-5,7-dichloro-8-hydroxyquinoline as the novel electroluminescence materials for OLED applications have been synthesized and characterized using different spectroscopic techniques.. The materials were structurally characterized by FTIR, TGA and optically characterised by UV Visible absorption spectra, Photoluminescence spectra. The Photoluminescence properties Zinc(2,2'-bipyridine)-5-chloro-8-hydroxyquinoline shows maximum absorption at 360 nm, Photoluminescence peak at 534 nm and that of Zinc(2,2'- bipyridine)-5,7-dichloro-8-hydroxyquinoline shows maximum absorption at 360 nm, Photoluminescence peak at 560 nm. The decomposition temperature was observed at 350 ^{0}C for Zinc(2,2'-BPY)-5-chloro-8-hydroxyquinoline .

We can fabricate Organic light emitting diode with the structure ITO/αNPD(40 nm)/Zinc complex(35 nm)/BCP(6 nm)/Alq_3(30 nm)/LiF(1nm)/Al(100 nm) by using the synthesized zinc complexes as emissive material.

5.2 Future Scope

The studies presented in thesis further suggest that there are areas of academic and technological interest. Some of the areas are mentioned as follows-

1. In the present work, the synthesized electroluminescent Zinc complexes can be used as emissive layer in fabricating the OLED devices to obtain good electroluminescence properties. The effect of attachment of different groups and different ligands to the some other metal complexes (Al, Cd, Be, B, Pt) and other rare earth elements could be tried for optimizing quantum efficiency, brightness and operating voltages.
2. Temperature dependent photoluminescence could also be carried out in order to get information about the variation of the traps, excitonic vibrations etc.
3. Temperature dependent transport studies could be performed deeply for getting the information about the conduction mechanism i.e. Injection limited conduction and bulk limited conduction , since it pave the way for better device fabrication.
4. Another possible area of future research work will be to reduce the interface defects which form during OLED fabrication in order to increase current densities which will eventually improves the device efficiency.
5. Photons reflected at the interfaces to the air may be redirected to the OLED surface by using scattering films on the viewer's side of the substrate (70% light emission).
6. For small area displays using ordered structures at the interfaces of air like microspheres and lenses and photonic crystal structure inside the device may be good choice.

References

1. G. G. Malliaras and R.H. Friend, Physics Today. **58**, 53 (2005).
2. C. W. Tang and S.A. Van Slyke, Appl. Phys. Lett. **51**, 913 (1987).
3. Y. Sato, S. Ichinosawa, and H. Kanai, IEEE J. Quant. Elect. **4**, 1 (1998).
4. C.W. Tang, S.A. Van Slyke and C.H. Chen, J. Appl. Phys. **65**, 3611 (1989).
5. J. Kovac, L. Peternai and O. Lengyel, Thin Solid Films. **433**, 22 (2003).
6. Organic light emitting diode, http://www.wikipedia.com.
7. A. Bernanose, M. Comte and P. Vouaux, J. Chem. Phys. **50**, 64 (1953).
8. A. Bernanose and P. Vouaux, J. Chem. Phys. **52**, 396 (1955).
9. H. Kallmann and M. Pope, J. Chem. Phys. **32**, 300 (1960).
10. H. Kallmann and M. Pope, Nature. **186**, 31 (1960).
11. M. Peter and H. Wolfgang. J. Appl. Phys. **33**, 205 (1962).
12. M. Pope, H. P. Kallmann and P. Magnante, J. Chem. Phys. **38**, 2042 (1963).
13. S. Mizuka, P. Martin and K. Hartmut, J. Chem. Phys. **43**, 2920 (1965).
14. W. Helfrich and W. Schneider, Phys. Rev. Lett. **14**, 229 (1965).
15. D. M. Pai, J. Chem. Phys. D **3**, 151 (1970).
16. E. Gurnee and R. Fernandez, U.S. Patent. **3**, 172, 862 (1965).
17. R. Partridge, Polymer. **24**, 733 (1983).
18. J. H. Burroughes, D. D. C. Bradley and A. R. Brown, Nature. **347**, 539 (1990).
19. S. Kappaun, C. Slugovc and E. J. W. List, Int. J. Mol. Sci. **9**, 1527 (2008).
20. http://media.wiley.com/CurrentProtocols/ET/et0204/et0204-fig-0001-1-full.jpg.
21. H. Sirringhaus, N. Tessler and R. H. Friend, Science. **280**, 1741 (1998).
22. M. G. Kaplunov, High Eng. Chem. **42**, 64 (2008).
23. Y. Hamada., T. Sano, M. Fujita, T. Fujii, Y. Nishio and K. Shibata, Jpn. J. Appl. Phys. **324A**, 514 (1993).
24. S. A, Carter, M. Angelopoulos, S. Karg, P. J. Brock and J. C. Scott, Appl. Phys. Lett. **70**, 2067 (1997).
25. S. Wang, Coord. Chem. Rev. **215**, 79 (2001).
26. V. K. Rai, R. Srivastava, G. Chauhan , K. Saxena, R.K. Bharadwaj, S. Chand, and M. N. Kamalasanan, Mater. Lett. **62**, 2561 (2008).

27. I. M. Chan and F. C. Hong, Thin Solid Films. **450**, 304 (2004).

28. J. Kido, K. Hongawa, K. Okuyama and K. Nagai, Appl. Phys. Lett. **64**, 815 (1994).

29. S. F. Liu, Q. Wu, H. L. Schmider, H. Aziz, N.X Hu, Z. Popovic and S. Wang, J Am. Chem. Soc., **122**, 3671 (2000).

30. Q. Wu, J. A. Lavigne and S. Wang, Inorg. Chem. **39**, 5248 (2000).

31. G. G. Malliaras and J. C. Scott, J. Appl. Phys. **83**, 5399 (1998).

32. H. Aziz and Z. D. Popovic, Chem. Mater. **16**, 4522 (2004).

33. J. C. Scott, G. G. Malliaras, J. R. Salem, P. J. Brock, L. Bozano and S. A. Carter, SPIE Proc. **3476**, 111 (1998).

34. L. S. Hung and C. H. Chen, Mater. Sci. Eng. R **39**, 143 (2002).

35. A. Curioni and W. Andreoni, J. Am. Chem. Soc. **121**, 8216 (1999).

36. M. K. Wei, C. W. Lin, C. C. Yang and Y. W. Kiang Int. J. Mol. Sci. **11**, 1527 (2010).

37. K. Sugiyama, H. Ishii, Y. Ouchi and K. J. Seki, Appl. Phys. **87**, 295 (2000).

38. N. Donze, P. Pechy, M. Gratzel, M. Schaer and L. Zuppiroli, Chem Phys. Lett. **315**, 405 (1999).

39. A. Sharma, D. Singh, J. K. Makrandi, M. N. Kamalashanan, R. Srivastava, and I. Singh, Mat. Lett. **61**, 4614 (2007).

40. www.physicscourses.okstate.edu

41. T. R. Hebner, C. C. Wu, D. Marcy, M. H. Lu and J. C. Sturm, Appl. Phys. Lett. **72**, 519 (1998).

42. G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri and A. J. Heeger, Nature. **357**, 477 (1992).

43. http://www.boomer.org/c/p4/c24/Fig05.gif.

44. http://www.impactanalytical.com/tga.html

45. http://www.bama.ua.edu/~chem/seminars/student_seminars/fall05/papers-f05/xu-sem.pdf.

46. Y. Hamada, IEEE Trans. Elec. Dev. **44**, 1208 (1997).

47. Y. Shao, Y. Qiu, W. Hu and X. Hong, Adv. Mater. Opt. Elect. **10**, 288 (2000).

48. S. E. Shaheen and G. E. Jabbour, B. Kippelen, and N. Peyghambarian, Appl. Phys. Lett. **74**, 21 (1999).

49. T. Sano, Y. Nishio, Y. Hamada, H. Takahashi, T. Usuki and K. Sibata, J. Mater. Chem. **10**, 157 (2000).

50. Y. Hamada , T. Sano, H. Fujii, Y. Nishio, H Takahashi and K. Shibata, Jpn J. Appl. Phys. **35**, 1339 (1996).

51. Z. D. Popovic and H. Aziz, IEEE J. Quant. Elect. **8**, 2 (2002).

52. I. G. Hill, A. Rajagopal, A. Kahn and Y. Hu, Appl. Phys. Lett. **73**, 662 (1998).

53. A.N. Du, Q. Me and M. Lu, Synth. Metals. **149**, 193 (2005).

54. Y. K. Jang, D. E. Kim, O. K. Kwon, and Y.S Kwon, J. Korean Phys Soc. **47**, 1057 (2006).

55. J. Xie, J. Qiao, L. Wang, and Y. Qiu, Inorg. Chim. Acta. **358**, 4451 (2005).

56. K. W. Sam, Y. J. Min, L. B. Jong, J. Y. Ki, and K. D. Eun, J. Nanosc. and Nanotech. **6**, 3637 (2006).

57. C. Williams, Appl. Phys. Lett. **88**, 183104 (2006).

58. V.K. Shukla , S. Kumar and D. Deva, J. Luminescence. **121**, 132 (2006).

59. T. Yu, W. Su, W. Li, Z. Hong, R. Hua and B. L. Thin Solid Films. **512**, 4080 (2007).

60. http://www.forumsci.co.il/HPLC/FTIR_inst.jpg.