• MATERIALS AND METHODS
CHAPTER II

MATERIALS AND METHODS

First part of the chapter describes about the materials and their methods for synthesizing metal (lithium, zinc and iridium) complexes. The second half of the chapter describes different techniques and instrumental methods used for characterization of these metal complexes and organic light emitting devices prepared using these materials.

2.2 Materials

2.1.1 Chemicals

For the synthesis of metal complexes used as emitting layer in OLED’s the metal salts, organic ligands, base solution and various organic solvents are required. The raw materials used in synthetic method are of high purity, because even a small amount of impurity lowers the luminescent intensity. These impurities which suppress the luminescent intensity or lower the luminescent efficiency of OLEDs are known as fluorescent quenchers and the phenomenon of lowering of luminous intensity is known as quenching. Hence the use of high purity raw materials provides better results in the synthesis of metal complexes used as light emitting layer in OLED’s.

All the chemicals used in synthesis procedure were of high purity, at least 99.9% or more [1-7]. High purity metal salts were purchased from Sigma Aldrich. Other chemicals were also of high purity reagent grade and were used as supplied. The ligands were purified with column chromatography. Analytical grade solvents were used as supplied. General chemical procedures were used for the removal of unwanted impurities in the form of metal ion, wherever necessary. The synthesized ligands and metal complexes were purified by column chromatography and sublimation, respectively. To avoid impurities, it was absolutely necessary to clean all the glassware immediately after use with an excess of solvents. After cleaning with solvents, cleaning with distilled water and drying was required.
2.1.2 Requirements of materials used in OLEDs

In general, complexes of metal with organic molecules must contain the following properties to become promising candidates for OLEDs [8-11]

i) Non crystalline behavior

ii) High electrical, chemical and thermal stability (Morphological stability)

iii) Strong photoluminescence, electroluminescence

iv) Easy preparation with high yield

v) Low cost of synthesis and process ability

vi) Possess a suitable ionization potential and electron affinity in order to match energy levels for the injection of charge carriers at electrode/organic material and organic material/organic material interfaces

vii) Permit the formation of a uniform film without pinholes

2.1.3 Properties of the organic ligand

i) The ligand should possess one or more chromophores with high molar extinction coefficient (antenna) and deactivating ligand transitions $S_{1-0}$ (fluorescence) and $T_{1-0}$ (phosphorescence) should be minimal.

ii) The energy of the emitting level of the metal ion should be just below that of the triplet state of the ligand, so that the probability of the transitions from the triplet to emitting level is high, and radiationless transitions of the excited metal ion should be low.

iii) The charge distribution in the chelate ring, the spatial structure and the hydrophobicity of the coordinated ligand determine the efficiency of energy transfer from the ligands to the metal ions. These problems can be overcome by complexing the ion with a suitably designed organic ligand.

2.1.4 Purification of ligands and metal complexes

Ligand purification:
**Column chromatography:** Column chromatography in chemistry is a method used to purify individual chemical compounds from mixtures of compounds. To purify the compound, slurry is prepared of the eluent with the stationary phase powder and then carefully poured into the column. Care must be taken to avoid air bubbles. A solution of the organic material is pipetted on top of the stationary phase. This layer is usually topped with a small layer of sand or with cotton or glass wool to protect the shape of the organic layer from the velocity of newly added eluent. Eluent is slowly passed through the column to advance the organic material. Different isomers move with different speed with eluent through the column. The eluent having pure isomeric form of organic compound, then collected in different container. Often a spherical eluent reservoir or an eluent-filled and stoppered separating funnel is put on top of the column.

**Metal complex purification:**

**Recrystallization:**

Synthesized metal complexes are purified with recrystallization. Recrystallization is a most common technique to purify organic and inorganic compounds. In this technique, an impure solid compound is dissolved in a solvent and then allowed to slowly crystallize out as the solution cools. As the compound crystallizes from the solution, the molecules of the other compounds dissolved in solution are excluded from the growing crystal lattice, giving a pure solid.

**Sublimation:**

In sublimation, a solid compound evaporates directly to the gas phase without becoming a liquid. In vacuum sublimation, the sample is placed under reduced pressure, this permits sublimation at lower temperatures (without decomposition). In purification by sublimation, a solid compound is heated and evaporates. The vapors condense on a cold surface to form new crystals. Chemists use sublimation to purify samples of solids that have significant vapor pressures. (If a solid can’t be evaporated, sublimation can’t be used to purify it.) Sublimation is preferable to recrystallization in many cases because solvent is not added to the compound to be purified.
2.1.5 Synthesis methods for metal complexes

The metal complexes to be synthesized have been divided into three classes based upon the metal used.

i) Complexes of lithium with 8-hydroxyquinoline and substituted 8-hydroxyquinoline.

Scratched lithium metal (1 mmol) was added to a solution of ligand (1 mmol) prepared in acetonitrile. After stirring the mixture for ~15 min. at room temperature on a magnetic stirrer, a crude product, which precipitated from the solution, was collected by filtration. The product was purified by washing with acetonitrile, deionised water and then again with acetonitrile. The solid so obtained was dried in vacuum.

ii) Mixed ligand complexes of zinc.

The zinc complexes were obtained by the reaction of the two ligands, 2-(2-hydroxyphenyl)benzoxazole (HPB)/2-(2-hydroxyphenyl)benzothiazole (BTZ) and substituted 8-hydroxyquinolines with zinc acetate (ligands and metal) at 1:1:1 molar ratio in ethyl alcohol. A solution of ligand I (1 mmol) was prepared in 20 ml ethanol and ligand II (1 mmol) in 20 ml of ethanol was added in a 100 ml three neck flask, the reaction mixture was stirred at 60 °C for 2 h. This was allowed to cool to 50 °C and a solution of zinc acetate (1 mmol) in 5 ml of deionized water was added drop wise to the reaction mixture and pH of the reaction mixture was adjusted to 6-7 by adding aqueous solution of base (dilute NaOH). After 2 h of stirring a yellowish precipitate of the complex separated from the reaction mixture which was filtered and dried at 100 °C.

iii) Complexes of Iridium with substituted 1,3,4-oxadiazole.

Iridium complexes were prepared according to the procedure reported by Dedeian et al [12]. The synthetic method used to prepare these complexes involved two steps. In the first step, IrCl₃·3H₂O was allowed to react with an excess of the cyclometalated ligand (2.5 times) to give a chloro-bridged dinuclear complex. The chloro-bridged dinuclear complex could readily be converted to mononuclear complexes by replacing the two bridging chlorine atoms with a bidentate β-diketone, finally producing iridium(III) ion to be octahedrally coordinated by three chelating ligands. The coordination geometry of the “(ButOXD)₂Ir” fragment in the mononuclear complex is the same as that for the dinuclear complexes.
2.2 Instrumentation

In material characterization basically the synthesized materials are characterized by variety of techniques to assure that the appropriate materials with suitable properties are synthesized. Some of the instruments utilized for the characterization of the metal chelate complexes are given below

2.2.1 C H N elemental analysis

Elemental analysis is an experiment that determines the amount in weight percent of an element in a compound. For different elements, there are different experiments to determine elemental composition. The most common type of elemental analysis is for carbon, hydrogen, and nitrogen known as C H N analysis. This type of analysis is especially useful for organic compounds (compounds containing carbon-carbon bonds). The elemental analysis of a compound is particularly useful in determining the empirical formula of the compound. Elemental analysis on carbon, hydrogen and nitrogen is the most essential investigation performed to characterize and/or prove the elemental composition of an organic sample. The Elemental Analyzer performs a fast and accurate analysis of the elements carbon, hydrogen and nitrogen simultaneously.

Principle

The C H N mode is based on the classical Pregl-Dumas method where samples are combusted in a pure oxygen environment, with the resultant combustion gases measured in an automated fashion. In the presence of excess oxygen and combustion reagents, samples are combusted completely and reduced to the elemental gases CO₂, H₂O, NOₓ and SO₂. The combustion products are then passed to the gas control zone. Gases are captured in the mixing chamber of the gas control zone. Here, gases are rapidly mixed and precisely maintained at controlled conditions of pressure, temperature and volume. The result is the thorough homogenization of product gases. After homogenization of product gases, the mixing chamber is depressurized through a column in the separation zone of the instrument.
As the gases elute, they are measured by a thermal conductivity detector in the detection zone of the analyzer.

**Procedure**

The samples must be highly purified, dried and pulverized solids to perform C H N analysis. Carbon-hydrogen-nitrogen (C H N) analysis is performed by burning the homogeneous unknown sample. As a result of the complete combustion of the compound, all of the carbon in the compound is converted to carbon dioxide gas and all of the hydrogen in the compound is converted to water vapor and nitrogen is converted to NO\(_x\). The gas stream first passes through a desiccant, typically Mg(ClO\(_4\))\(_2\), that removes all moisture from the gas stream. Next the gas stream passes through a tube containing NaOH, which removes all carbon dioxide from the gas stream (forming NaHCO\(_3\)). Then, CO\(_2\), H\(_2\)O and NO\(_x\) combustion gases are passed through a reduction tube with helium as the carrier gas for converting the NO\(_x\) nitrogen oxides into N\(_2\) and binding the free oxygen. By weighting the tubes containing Mg(ClO\(_4\))\(_2\) and NaOH before and after the combustion reaction, it is possible to determine the amounts of water and carbon dioxide produced by the combustion reaction and thus the amounts of hydrogen and carbon in the unknown compound. After corresponding absorption of CO\(_2\), H\(_2\)O, the content of the remaining nitrogen is determined by thermal conductivity detection.

**Instrument**

![Elemental Analyzer Perkin Elmer 2400 (CHN) instrument.](image)

CHN elemental analyses (Carbon-Hydrogen-Nitrogen) were performed on Elemental Analyzer Perkin Elmer 2400 C H N instrument

**2.2.2 Fourier transform infra-red (FT-IR) spectroscopy**
A molecule absorbs radiation only when the natural frequency of vibration of some part of molecule (i.e. atom or group of atom 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). It provides useful information about the structure of the molecules and bonding quickly, without tore-some evaluation method. Moreover, IR provides a very faster method of identifying chemical structures especially those of the organic ones. In instrumentation for IR spectroscopy, electromagnetic (EM) radiation with frequencies between 4000 and 400 cm\(^{-1}\) (wave numbers) is concerned with spectroscopy. It is absorption in this region which gives invaluable information about structure determination and verification of organic compounds by making use of the fact that it is absorbed by interatomic bonds in organic compounds. Chemical bonds in different environments will absorb varying intensities and at varying frequencies. Thus IR spectroscopy involves collecting absorption information and analyzing it in the form of a spectrum. The frequencies at which there are absorptions of IR radiation ("peaks" or "signals") can be correlated directly to bonds within the compound. Each interatomic bond may vibrate in several different motions (stretching or bending), individual bonds may absorb at more than one IR frequency. Symmetrical vibrations do not cause absorption of Infra-red radiation. In IR signal intensities are usually denoted by the following abbreviations: w = weak, m = medium, s = strong, v = variable.

**Principle**

This 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 \(\bar{\nu}\), whose unite is cm\(^{-1}\).

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 transmittance (T) versus wave number (cm⁻¹) has been plotted.

**Procedure**

The sample to be examined is taken as a liquid film by making solution in suitable absorbing solvent or as a mull in nujol in case of solids not sufficiently soluble in solvents or a pellet obtained by pressing the sample in a hydraulic press. The radiations emitted by source of radiation, a small ceramic rod, made of either silicon carbide or Nernst filament are divided into two beams, one of which passes through the sample and the other functions as reference beam. The reference and the sample beams are then passed alternately into a monochromator at very short intervals by means of a rotating mirror. In the monochromator the emergent beams are sorted out into individual wavelengths by means of a prism which is transparent to infrared radiation. The pulsating single beam emerging through the exit slit is a narrow band consisting of only a very few frequencies. After this dispersion, the beams are focused alternately at each particular wavelength throughout the spectral range. The spectrum which is a measure of the difference in intensities of the reference and sample beams throughout the wavelength range is recorded on a special graph paper.

**Instrument**

Perkin Elmer Model No. 5700 FTIR spectrometer was used to record the IR spectra.

![Perkin Elmer Model No. 5700 FTIR spectrometer](image)

**Fig. 2.2 Perkin Elmer Model No. 5700 FTIR spectrometer**

**2.2.3 ¹H NMR spectroscopy**
The past fifty years nuclear magnetic resonance spectroscopy, commonly referred to as NMR, has become the prominent technique for determining the structure of organic compounds. Of all the spectroscopic methods, it is the only one for which a complete analysis and interpretation of the entire spectrum is normally expected. NMR is non-destructive and good data may be obtained with modern instruments from samples weighing less than a milligram. NMR spectroscopy is a powerful tool for chemists because of the NMR chemical shift. The area under the peak also corresponds to the relative number of each type of proton. The NMR chemical shift is known to be very sensitive to intra- and intermolecular factors. These effects can be vividly seen in gas-phase NMR spectroscopy of small molecules. As one varies the density of the sample in the gas phase, one also sees a variation in the NMR chemical shift, indicating an intermolecular contribution. Furthermore, variable temperature studies and isotopic substitution also lead to variations in the measured NMR chemical shift, indicating an intramolecular effect.

**Principle**

The following features lead to the NMR phenomenon:

1. A spinning charge generates a magnetic field. The resulting spin-magnet has a magnetic moment (μ) proportional to the spin.

2. In the presence of an external magnetic field (B₀), two spin states exist, +1/2 and -1/2. The magnetic moment of the lower energy +1/2 state is aligned with the external field, but that of the higher energy -1/2 spin state is opposed to the external field. Note that the arrow representing the external field points North.

3. The difference in energy between the two spin states is dependent on the external magnetic field strength, and is always very small. The following diagram illustrates that the two spin states have the same energy when the external field is zero, but diverge as the field increases. At a field equal to B₀, a formula for the energy difference is given (remember I = 1/2 and μ is the magnetic moment of the nucleus in the field).
Strong magnetic fields are necessary for NMR spectroscopy. The international unit for magnetic flux is the tesla (T). The earth's magnetic field is not constant, but is approximately $10^{-4}$ T at ground level. Modern NMR spectrometers use powerful magnets having fields of 1 to 20 T. Even with these high fields, the energy difference between the two spin states is less than 0.1 cal/mole. To put this in perspective, recall that infrared transitions involve 1 to 10 kcal/mole and electronic transitions are nearly 100 time greater. For NMR purposes, this small energy difference ($\Delta E$) is usually given as a frequency in units of MHz ($10^6$ Hz), ranging from 20 to 900 Mz, depending on the magnetic field strength and the specific nucleus being studied. Irradiation of a sample with radio frequency (rf) energy corresponding exactly to the spin state separation of a specific set of nuclei will cause excitation of those nuclei in the +1/2 state to the higher -1/2 spin state.

**Procedure**

Sample to be detected is dissolved in a suitable deuterated solvent such as CDCl$_3$, D$_2$O, C$_6$D$_6$ etc. A small amount of tetramethylsilane (TMS), a chemical inert substance, is also added to standardize the spectrum. NMR spectrophotometer makes use of a magnet, a radio-frequency, a detector and an amplifier. The detection system is used to note that energy is being transferred from the radio-frequency beam to the nucleus. The sample under investigation is taken in a glass tube which is placed between the pole faces of a magnet. A radio-frequency source is made to fall on the sample. It can be done by feeding energy (radio-frequency source) into a coil wound round the sample tube. A signal is detected when the nuclei in the sample resonates with the source, i.e., $\Delta E$, energy required to flip the proton is the same as that of the source. Energy is transferred from the source via nuclei to the detector.
coil. The output from the detector can be fed to a cathode ray oscillograph or to a strip chart recorder after amplification etc. Protons being in different electronic environments in a molecule cannot resonate at exact frequency of source. Therefore for practical purposes, radio-frequency source is held steady at the said frequency and field strength is varied by placing small electromagnet to the pole faces of the main magnet. By increasing the current flowing through these electromagnets, the total field strength is increased. As the field strength increases, the precessional frequency of each proton increases until resonance with the radio-frequency source takes place. As a proton (or a set of equivalent protons) comes to the resonance, the signal from the detector produces a peak on the chart paper. The NMR spectrum consists of series of peaks that correspond to different applied field strengths. Each peak means a set of protons.

**Instrument**

$^1$H NMR spectra were recorded on a Bruker Avance 300 spectrometer (300MHz).

![Bruker Avance 300 1HNMR spectrometer](image)

*Fig. 2.3. Bruker Avance 300 $^1$HNMR spectrometer.*

### 2.2.4 Thermogravimetric analysis

Thermal gravimetric analysis (TGA) is a type of testing performed on samples that determines changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can identify the point where weight loss is most apparent. TGA is commonly employed in research and testing to determine characteristics of materials such
as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues.

**Procedure**

Analysis is carried out by raising the temperature of the sample gradually and plotting weight (percentage) against temperature. The temperature in many testing methods routinely reaches 1000 °C or greater. After the data are obtained, curve smoothing and other operations may be done to find the exact points of inflection. A method known as high-resolution TGA is often employed to obtain greater accuracy in areas where the derivative curve peaks. In this method, temperature increase slows as weight loss increases. This is to identify more accurately the exact temperature where a peak occurs. Several modern TGA devices can vent burnoff to an infrared spectrophotometer to analyze composition.

**Instrument**

The analyzer usually consists of a high-precision balance with a pan (generally platinum) loaded with the sample.

![Mettler Toledo TGA/SDTA851e instrument](image)

*Fig. 2.4 Mettler Toledo TGA/SDTA851e instrument*

A different process using a quartz crystal microbalance has been devised for measuring smaller samples on the order of a microgram (versus milligram with conventional TGA). The sample is placed in a small electrically heated oven with a thermocouple to accurately measure the temperature. The atmosphere may be purged with an inert gas to prevent oxidation or other undesired reactions. A computer is used to control the instrument.
2.2.5 Differential scanning calorimetry (DSC)

DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions. DSC may also be used to observe more subtle phase changes, such as glass transitions. It is widely used in industrial settings as a quality control instrument due to its applicability in evaluating sample purity and for studying polymer curing. Differential scanning calorimetry can be used to measure a number of characteristic properties of a sample. Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperatures $T_g$. DSC can also be used to study oxidation, as well as other chemical reactions. Glass transitions may occur as the temperature of an amorphous solid is increased. These transitions appear as a step in the baseline of the recorded DSC signal. This is due to the sample undergoing a change in heat capacity; no formal phase change occurs. As the temperature increases, an amorphous solid becomes less viscous. At some point the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature ($T_c$). This transition from amorphous solid to crystalline solid is an exothermic process, and results in a peak in the DSC signal. As the temperature increases the sample eventually reaches its melting temperature ($T_m$). The melting process results in an endothermic peak in the DSC curve.
The ability to determine transition temperatures and enthalpies makes DSC a valuable tool in producing phase diagrams for various chemical systems. We used Mettler Toledo DSC822e instrument for the determination of glass transition temperature of the materials.

2.2.6 UV-visible absorption spectroscopy

Ultraviolet-visible absorption spectroscopy refers to absorption spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The absorption in the visible range directly affects the perceived color of the materials involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

Principle

In UV-visible absorption spectroscopy, the absorbance of light energy or electromagnetic radiation excites electrons from the ground state to the first singlet excited state of the compound or material. The UV-visible region of energy for the electromagnetic spectrum covers 1.5 - 6.2 eV which relates to a wavelength range of 800 - 200 nm. The Beer-Lambert Law, is the principle behind absorbance spectroscopy. For a single wavelength, A is absorbance (unitless, usually seen as arbitrary units), ε is the molar absorptivity of the compound or molecule in solution (M⁻¹cm⁻¹), l is the path length of the cuvette or sample holder (usually 1 cm), and c is the concentration of the solution (M). The equation leads to A
= εcl, where A be absorbance, ε be the molar absorptivity of the material, c be the concentration and l be the path length of the solution.

**Procedure and Instrument**

The instrument used in ultraviolet-visible spectroscopy is called a UV/Visible spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I₀). The ratio I / I₀ is called the transmittance, and is usually expressed as a percentage (%T). The absorbance, A, is based on the transmittance:

\[ A = -\log(\%T / 100\%) \]

The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction grating in a monochromator or a prism to separate the different wavelengths of light, and a detector. The radiation source is often a tungsten filament (300-2500 nm), a deuterium arc lamp, which is continuous over the ultraviolet region (190-400 nm), xenon arc lamps, which is continuous from 160-2000 nm; or more recently, light emitting diodes (LED) for the visible wavelengths. The detector is typically a photomultiplier tube, a photodiode, a photodiode array or a charge-coupled device (CCD). Single photodiode detectors and photomultiplier tubes are used with scanning monochromators, which filter the light so that only light of a single wavelength reaches the detector at one time.

![Fig. 2.6 Ray diagram of UV-Visible spectrophotometer](image)

The scanning monochromator moves the diffraction grating to "step-through" each wavelength so that it's intensity may be measured as a function of wavelength. Fixed monochromators are used with CCDs and photodiode arrays. As both of these devices consist of many detectors grouped into one or two dimensional arrays, they are able to collect light of different wavelengths on different pixels or groups of pixels simultaneously.
A spectrophotometer can be either single beam or double beam. In a single beam instrument (such as the Spectronic 20), all of the light passes through the sample cell. $I_0$ must be measured by removing the sample. This was the earliest design, but is still in common use in both teaching and industrial labs.

![Image](image_url)

Fig. 2.7 Horiba Jobin Yvon spectrophotometer used in our study

In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. The reference beam intensity is taken as 100% Transmission (or 0 Absorbance), and the measurement displayed is the ratio of the two beam intensities. Some double-beam instruments have two detectors (photodiodes), and the sample and reference beam are measured at the same time. In other instruments, the two beams pass through a beam chopper, which blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam in synchronism with the chopper. There may also be one or more dark intervals in the chopper cycle. In this case the measured beam intensities may be corrected by subtracting the intensity measured in the dark interval before the ratio is taken.

Samples for UV/Visible spectrophotometry are most often liquids, although the absorbance of gases and even of solids can also be measured. Samples are typically placed in a transparent cell, known as a cuvette. Cuvettes are typically rectangular in shape, commonly with an internal width of 1 cm. (This width becomes the path length, $L$, in the Beer-Lambert law.). The most widely applicable cuvettes are made of high quality fused silica or quartz glass because these are transparent throughout the UV, visible and near infrared regions.

### 2.2.7 Luminescence spectroscopy (photoluminescence)
Luminescence spectroscopy is the study of luminescence due to spin-allowed transitions in fluorescence and spin-forbidden transitions in phosphorescence, their stimulation and subsequent relaxation. It gives us information about the electronic structure, and also how energy may be dissipated into other modes of molecular motions.

**Principles of luminescence**

i) Fluorescence rarely occurs for excitation wavelength below 250 nm since the energy of these photons is sufficient for dissociation for most organic molecules.

ii) The emission generally is from the lowest electronically excited state with the lowest vibrational state to the electronic ground state at different vibrational levels. Consequently often the spectrum of the fluorescent light is independent of the excitation wavelength.

iii) The most frequently found fluorescence is from low energy $\pi^* \rightarrow \pi$ transitions. This includes aromatic compounds, highly conjugated double bonds and carbonyl structures.

**Procedure**

Photoluminescence (PL) spectra are taken for both in solutions and as powders. The solutions are placed in cleaned quartz cuvetts. PL spectra are taken by exciting the samples with a particular wavelength of light (usually the wavelength of peak absorption). The light source is a xenon arch lamp with broad spectrum emission. A monochromator placed before the sample chamber selects the wavelength used to excite the sample. The luminance of the sample is then passed through another monochromator that scans in 1 nm steps starting 10 nm above the excitation wavelength. The luminance is focused on and detected by a photomultiplier tube. PL is a valuable technique for understanding the nature of photoexcitations in single and multilayer films.

**Instrument used:**

Photoluminescence spectra in the visible region have been recorded on high resolution Ocean Optics fiber optics spectrometer Fluolog Model FL 3-11. This UV/VIS instrument is equipped with a steady state excitation source, an excitation monochromator, an emission monochromator, a microsecond flash lamp and a photomultiplier (200-1100 nm).
2.2.8 Atomic force microscopy (AFM)

Atomic force microscopy (AFM) is a very high-resolution type of scanning probe microscopy, with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. The AFM is one of the foremost tools for imaging, measuring, and manipulating matter at the nanoscale. The information is gathered by "feeling" the surface with a mechanical probe. Piezoelectric elements that facilitate tiny but accurate and precise movements on (electronic) command enable the very precise scanning. In some variations, electric potentials can also be scanned using conducting cantilevers. In newer more advanced versions, currents can even be passed through the tip to probe the electrical conductivity or transport of the underlying surface.

Principle

The AFM consists of a cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Depending on the situation, forces that are measured in AFM include mechanical contact force, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces, solvation forces, etc. Along with force, additional quantities may simultaneously be measured through the use of specialized types of probe (scanning thermal microscopy, scanning joule expansion microscopy, photothermal
microspectroscopy, etc.). Typically, the deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. Other methods that are used include optical interferometry, capacitive sensing or piezoresistive AFM cantilevers. These cantilevers are fabricated with piezoresistive elements that act as a strain gauge. Using a wheatstone bridge, strain in the AFM cantilever due to deflection can be measured, but this method is not as sensitive as laser deflection or interferometry.

If the tip is scanned at a constant height, a risk would exist that the tip collides with the surface, causing damage. Hence, in most cases a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample. Traditionally, the sample is mounted on a piezoelectric tube that can move the sample in the z direction for maintaining a constant force, and the x and y directions for scanning the sample. Alternatively a 'tripod' configuration of three piezo crystals may be employed, with each responsible for scanning in the x, y and z directions. This eliminates some of the distortion effects seen with a tube scanner. In newer designs, the tip is mounted on a vertical piezo scanner while the sample is being scanned in X and Y using another piezo block. The resulting map of the area $z = f(x,y)$ represents the topography of the sample.

The AFM can be operated in a number of modes, depending on the application. In general, possible imaging modes are divided into static (also called contact) modes and a variety of dynamic (or non-contact) modes where the cantilever is vibrated.

**Instrument used:**

*Fig. 2.9 NT-MDT Solver-Pro instrument*
2.2.9 Tristimulus colorimetry

Tristimulus colorimetry is based on three component theory of color vision which states that the eye possesses receptors for three primary colors (red, green, blue) and that all colors are seen as mixture of these primary colors. The most important system used these days is the 1931 Commission International Eclairage (CIE) system [13] shown in fig. 2.10.

![CIE Chromaticity Diagram](image)

*Fig. 2.10 The C.I.E. chromaticity diagram.*

This system consists of the RGB and the XYZ colorimetric systems. The XYZ system, which is explained below, is an extension of the RGB system for practical applications.

**Principle**

The RGB system is derived from results of psychophysical experiments. In the angular diameter is the angle of arc subtended by the circular field with an angular diameter of $2^\circ$. (The angular diameter is the angle of arc subtended by the circular field at the eye.) The circular color of the two half circles is independently variable. One of the two half circles is used as the reference field and another is used as the test field.

Colors of the reference field are called the reference colors and those of the test field are called the test colors. The reference colors are expressed by monochromatic light of the same intensity at various wavelengths over the entire visible range. The test colors, on the other hand, are composed with a mixture of the three primary colors, red (700 nm), green (546.1 nm), and blue (453.8 nm). The numbers in parentheses show the wavelengths of the respective primary colors.

By varying the mixing ratio of the three primary colors, the observers vary the colors of the test field. In this way, the color of the test field is made to match that of the adjacent reference field. During the observation, it is found that in some wavelength ranges, mixtures of the three primary colors could not match the reference colors. In these wavelength ranges, matches are established if an
amount of one of the three primary colors is added to the monochromatic reference colors. This implies that matches can be established by subtracting one of the primary colors from the mixtures. In other words, there are some wavelength ranges where the stimulus of the primary colors is negative. In this way, the mixture ratios of the primary colors to match all the spectral colors over the entire visible range are obtained. It is assumed, when a catch is established, that the reciprocals of the energy ratio of each primary color of the test field correspond to the relative strength of the stimuli of the respective primary colors at the wavelength of the reference with which the color is matched. Based on the above assumption, three spectral distribution curves of the relative strength of the stimulus for each of the three primary colors (red, green, and blue) over the entire visible range are obtained. The curves are called the spectral tristimulus values or the color matching coefficients. They are \( r(\lambda) \), \( g(\lambda) \), and \( b(\lambda) \), respectively; \( \lambda \) in the parentheses is the wavelength. Since, the sum of the three tristimulus values at each wavelength is always 100\%, the mixture ratio of the three primary colors can be determined by any two of the three tristimulus values. The RGB colorimetric system is based on this and all colors are indicated on the \( r(\lambda) \), and \( g(\lambda) \) coordinates.

To overcome difficulties associated with the negative stimulus of the primary colors, based on the above mentioned color matching experiments, three imaginary reference color stimuli \([X]\), \([Y]\), and \([Z]\) were introduced. By employing the imaginary reference color stimuli, the original tristimulus values were converted mathematically into positive values and all colors could be composed by missing (not subtracting) these three stimuli. This is the basis of the XYZ colorimetric system \( Y \) has been chosen to correspond with the lightness stimulus. Based on the similar idea with that of the RGB colorimetric system, all colors are indicated by these coordinates.

**Specification of light source colours:**

Test light source colours are specified below. The tristimulus values \((X, Y \text{ and } Z)\) for test light source, which has a spectral energy distribution \( P(\lambda) \), are calculated with the following formulae.

\[
\lambda = K \int_{380}^{780} P(\lambda) x(\lambda) d\lambda \quad (1a)
\]

\[
Y = K \int_{380}^{780} P(\lambda) y(\lambda) d\lambda \quad (1b)
\]

\[
Z = K \int_{380}^{780} P(\lambda) z(\lambda) d\lambda \quad (1c)
\]

where

\[
K = \frac{1}{P(\lambda) Y(\lambda) d\lambda}
\]
and $x(\lambda)$, $y(\lambda)$, and $z(\lambda)$ are the spectral stimulus values for $2^\circ$. These quantities are written as $x_{10}(\lambda)$, $y_{10}(\lambda)$, $z_{10}(\lambda)$ for 10.

The chromaticity coordinates of the color of the light sources $x$ and $y$ are calculated with the following formulae.

$$x = \frac{X}{X + Y + Z}$$  \hspace{1cm} (2a)

$$y = \frac{Y}{X + Y + Z}$$  \hspace{1cm} (2b)

The colors of light sources on the XYZ colorimetric system are specified with $Y$ calculated with $x$ and $y$ as given in equation 2a, 2b.

**Specification of the nonluminous object colors.**

The tristimulus values ($X$, $Y$, and $Z$) of the object for which the spectral reflectance (or spectral transmittance) is $\rho(\lambda)$ and $\tau(\lambda)$ are given by:

$$X = \frac{1}{K} \int_{380}^{780} P(\lambda) \rho(\lambda) \bar{x}(\lambda) d\lambda$$  \hspace{1cm} (3a)

$$Y = \frac{1}{K} \int_{380}^{780} P(\lambda) \rho(\lambda) \bar{y}(\lambda) d\lambda$$  \hspace{1cm} (3b)

$$Z = \frac{1}{K} \int_{380}^{780} P(\lambda) \rho(\lambda) \bar{z}(\lambda) d\lambda$$  \hspace{1cm} (3c)

$$K = \int_{380}^{780} P(\lambda) \bar{y}(\lambda) d\lambda$$  \hspace{1cm} (3d)

where $P(\lambda)$ is the spectral power distribution of the light source which illuminates the object, and $x(\lambda), y(\lambda)$ and $z(\lambda)$ are the CIE spectral trichromatic stimuli for fields of $2^\circ$ or $10^\circ$. The chromaticity coordinates of the color of the objects can then be calculated, as with the light source, using Eq. 2a, 2b. CIE co-ordinates are an extremely powerful concept because they facilitate representing an entire luminescent spectrum by two numbers. Furthermore, the simplicity of the visual method for obtaining the color gamut of a set of phosphors is quite attractive. The main drawback to the CIE co-ordinates system is the complexity involved in their calculation. Fortunately, CIE co-ordinates are automatically calculated by most modern spectrophotometers and in the worst case can be calculated by a computer program.

**Instrument used:**

A High-Resolution USB Fiber Optic spectrometer Model HR2000 was used for the characterization of color co-ordinates of organic light emitting materials.
2.2.10 Device preparation and characterization

The details of OLED preparation are given below. Testing of devices occurred immediately after they were made. If this was not possible the devices were placed in the vacuum chamber until testing could be performed. Several properties of the OLEDs were studied to determine the quality of the devices. These properties include electroluminescence (EL), current-voltage, CIE color coordinates and brightness.

Fabrication of organic light emitting devices needs a pure deposition of organic material on a cleaned substrate. Moisture may degrade the device during fabrication and hence care has to be taken during device fabrication [14]. General techniques for device fabrications are given below.

- **Vacuum deposition or vacuum thermal evaporation (VTE)** – Small molecules are deposited through this process by coating a substance to form thin films. The evaporation process results in parallel surface, important for lifetime of device. Good uniformity and purity is achieved by sputtering process. Organic material is sputtered as thin film on the substrate by bombardment of ions which ejects atoms & molecules from organic solution into a vacuum chamber. These atoms and molecules will form a thin film at the substrate.

- **Organic vapor phase depositions (OVPD)** – High quality organic films with better performance and at lower cost than conventional vacuum thermal evaporation (VTE) process are deposited by OVPD. In OVPD an inert gas carrier is used to transfer organic films onto a cooled substrate in a low-pressure, hot-walled reactor chamber. The organic materials are stored in external, separate, thermally-controlled cells. The materials evaporated from these heated cells are entrained and transported by an inert carrier gas such as nitrogen, using gas flow rate, pressure and temperature as process control variables. The materials deposit down onto the cooled substrate.

- **Inkjet printing** – 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-inches screens or electronic billboards.

- **Dip-coating**: In dip coating method the substrate is slowly dipped into the polymer resulting in a cover of polymers at both sides.
• Spin-coating: - In spin coating method a drop of polymer solution placed onto a rotated plate where the polymer solution is spread out to form a uniform thin film at room temperature. Drops formed may result in non-smooth and non-parallel surfaces and causing degradation of device because of different distances between the electrodes.

In the present work we used vacuum deposition technique for the preparation of the devices because in this study we used metal complexes of small molecules which are having quite good range of thermal stability.

![Image](image_url)

Fig. 2.11 Thermal deposition system (HIND HIVAC)

To study the various optical and electrical behaviors of the synthesized metal complexes, thin film devices containing metal complexes were fabricated by using thermal evaporation technique. Indium–tin oxide (ITO) coated glass substrate with a sheet resistance 20 Ω/cm² was used as anode which was patterned and cleaned using deionized water, acetone, trichloroethylene and isopropyl alcohol sequentially for 20 min using an ultrasonic bath and dried in vacuum oven. The hole transport layer and the emitting layers were deposited on the substrate sequentially under high vacuum (1×10⁻³ torr) at a deposition rate of 0.1 Å/s. The thickness of the deposited film was monitored in-situ by quartz crystal. N,N-diphenyl-N,N-bis(1- naphthyl)-1,1-biphenyl-4,4-diamine (α-NPD) as the hole transporting layer was deposited maintaining a thickness of 300 Å; Metal complexes as the emitting layer with a layer thickness of 350 Å; 2,9-dimethyl 4,7-diphenyl-1, 10-phenanthroline (BCP) as a hole and exciton blocking layer (HBL) maintaining a layer thickness of 60 Å, electron transporting layer
with a layer thickness of 280 Å as electron transport layer and a cathode comprised of 10 Å lithium fluoride (as electron injection) and 1000 Å aluminum were sequentially deposited onto the substrate to complete the device structure. Electroluminescent devices of these complexes finally had a structure ITO/HTL/EML/HBL/ETL/EIL/Al.

α-NPD was used as HTL material because of its high hole mobility ($5.56 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{Sec}^{-1}$) as compare to other hole transport materials [15]. Similarly BCP was used as good hole blocking layer because its HOMO lies quite below (6.5 eV) but its LUMO (2.9 eV) is almost matching with common electron transport materials. Hence BCP layer acts as good hole blocking layer.

Alq3 was used as ETL material because of its good electron mobility ($2.8 \times 10^{-6} \text{ cm}^2\text{V}^{-1}\text{sec}^{-1}$) as compare to other electron transport materials [16-17].

The use of dielectric LiF as an interface material in OLED is reported in literature [18]. The problem with the use of LiF as an injecting material in OLED is that, being dielectric in nature slight increase in LiF layer thickness results the high resistivity of the device. Hence the thickness of LiF layer should not be greater than 10-15 Å.

Basically two main properties of the OLED display make them better technology over the others are; i) low operating voltage and ii) high luminescence efficiency.

Operating voltages of these displays are quite low because the total thickness of the device lies in the range of 100-140 nm only. Decrease in the thickness below 100 nm increase the probability of device shortening and greater thickness increase the operating voltage of the device.

Charge balancing in the emissive layer determined the efficiency of the device. Better charge balancing leads to greater luminescence at low current values, means greater efficiency and vice-versa. The charge mobility of charge carriers in various layers is different. Hence for better charge balancing and better efficiency, optimized thickness of different layers are used in the devices. The optimization of the different layer thickness values have been done by the set of experiments and chose the best value for layer thickness.

2.2.11 Electroluminescence
Electroluminescence (EL) is the emission of light by a substance under the action of electric field or current. Electroluminescence in organic materials involves formation of excited molecules (excitons) followed by their recombination. This recombination may give rise to either light or heat emission. Electroluminescence may also result in either fluorescence or phosphorescence, or involve both mechanisms.

Procedure

The sample is mounted in a sample holder and placed in the sample chamber. The excitation is provided by the Xenon lamp CVI monochromator combination. The device is positioned so that the emitted light passes through a collection lens and focused on the photomultiplier tube (PMT). The proper positioning is determined by running a time based scan and moving the sample until the emission is maximized. Once the device is aligned the scan is run at either constant voltage or constant current. If the devices are bright then scans are run with a short integration time (0.1 second); however, for very dim devices the integration time is increased to 1 second to try and reduce the noise in the signal. Scans are typically run from 350 nm to 750 nm.

Instrument used:

Electroluminescence spectra were taken on a high resolution USB Fiber Optic spectrometer Ocean Optics Model HR2000.

Fig. 2.12. Ocean Optics Model HR2000 Spectrofluorometer setup.

2.2.12 Current-Voltage (I-V) characteristic

Procedure
A sourcemeter is used to apply a DC voltage to the device and to measure the resulting current. A multimeter is used to monitor the voltage output by the sourcemeter. The current output from the sourcemeter and the voltage reading from the multimeter are recorded by a computer. Both, the voltage output of the device and the monitoring of the meter outputs are controlled by a Lab View program. The program allows the user to specify the voltage range to be scanned, the step size of the voltage and the amount of time each voltage is applied to the device. Data is written to a file for later analysis and is also plotted on the screen to determine if any problem occurred during the scan. The I-V curves are often taken at the same time as and when brightness measurements are made.

![Sourcemeter Image](image)

**Fig. 2.13. Keithley Model 2400 sourcemeter.**

**Instrument used:**

Current-voltage (I-V) characteristics were measured using a Keithley 2400 Sourcemeter.

2.2.13 **Brightness**

To characterize an OLED accurately, it is necessary to measure the brightness of the device. Brightness is a photometric (luminous) value, which means the value is adjusted for the way the human eye perceives the color. Since the eye is most responsive to green light, a green light always appears brighter than a blue or red LED.

**Principle**

To determine the brightness of a device a distinction must be made between photometric quantities and radiant quantities. Radiant quantities, such as radiant flux ($\Phi_e$), irradiance ($E_e$), and radiance ($L_e$), are all physical characteristics of a device that are measurable in a laboratory. All of the radiant quantities have corresponding photometric quantities luminous flux ($\Phi_l$), illuminance ($E_l$) and luminance ($L_l$), respectively. Brightness refers to the luminance of a device and is typically measured
in lumen/m^2 steradian or candela (Cd)/m^2. To convert from a radiant quantity, Qe (\(\lambda\)), to a photometric quantity, Qv, using the eyes luminous efficiency V (\(\lambda\)) the following relationship is used [42],

\[
Q_v = 683 \int Q_e(\lambda)V(\lambda)d\lambda
\]

**Instrument used:**

The brightness was measured simultaneously with luminance-current-voltage (L-I-V) characteristics were measured using a luminance meter (L-I-V) Model LMT RS 232.

*Fig. 2.14. Luminance meter Model LMT RS 232.*

### 2.2.14 Determination of electron mobility using transient EL

To calculate the charge mobility inside a molecule, transient electroluminescence is one of the techniques. With transient electroluminescence (EL) we mean the time resolved EL after applying a square voltage pulse over the sample. After a delay time (\(t_{\text{del}}\)) the EL starts to rise, which was thought to depend on the charge carrier transient time inside the film. The delay time is observed on the time scale of tens of microseconds.

In our studies, for the time resolved electroluminescence (EL) measurements, the bilayer OLEDs were fabricated on indium-tin-oxide (ITO) coated glass substrates having a sheet resistance of 20 \(\Omega/cm^2\) and a thickness of 120 nm. OLEDs have device structure ITO (120 nm)/ 0.4 wt % Fe-TCNQ doped \(\alpha\)-NPD (50 nm)/ our synthesized complexes (70 nm)/Al (120 nm). The transient EL setup consisted of a pulse generator, a fast photo detector (photo multiplier tube (PMT)) and a fast storage oscilloscope. Fabricated OLED was electrically excited by applying a fast square electrical pulse from a 15 MHz function generator HAMEG HM8131-2 with accurate repetition, rise and decay time. To study the EL rise time at different voltages the pulses with a frequency of 1 KHz, duty of 50% were
applied. The time-resolved EL response of the device was measured using the PMT detector. Along with the input pulse, the detector’s output was coupled to one of the input channels of a HAMEG Analog-Digital Scope HM1507-3, where the input pulse and the output EL response of the device were recorded simultaneously. By the overlapping of the input voltage pulse and the transient EL response of device, a delay in the onset of EL was clearly seen.

The delay time between the electrical and optical pulse was measured using a digital oscilloscope. This delay time is a direct measure of the transit time of the fastest carrier (electrons) towards the recombination zone. This transit time has been measured for all the devices at different electric fields. Charge carrier mobility has been calculated from the transit time by using the expression

\[ \mu = \frac{d^2}{t_{tr} \times V} \]

*Fig. 2.15 Block diagram of the experimental setup for the transient EL measurements*

REFERENCES
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