Charge Injection and Magneto-transport Studies in Small Molecule Organic Light Emitting Diodes

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This thesis is dedicated to
my beloved parents who have done so much to bring me up.
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Declaration

This work has not previously been submitted to satisfy any of other degree requirements at this or any other university. This thesis contains no material published or written by another person except where due reference is made in this thesis itself.

______________________________
Abstract

This thesis presents the results of study of the electronic properties of small molecule/metal interfaces. These interfacial properties are important for the efficient carrier injection in organic light emitting devices. Small organic molecules such as aluminium tris(8-hydroxyquinoline)(Alq₃), gallium tris(8-hydroxyquinoline)(GaQ₃), N,N’-diphenyl-N,N’bis (3-methylphenyl)-(1,1’-biphenyl)-4,4’ diamine(TPD) and lithium quinoline (Liq) are studied with different cathode interfaces such as Al, LiF/Al and Mg:Ag. The results show that a traditional model of a common vacuum level is not applicable at organic/metal interfaces.

The barrier height for electron injection can be lowered by inserting a thin organic material in between the cathode and emission layer. A series of alkaline metal quinolines (Li, Na, K, Rb and Cs) are investigated as electron injection layers for TPD/Alq₃ double layer devices with high work function Al cathodes. It is found that with the insertion of a metal quinoline between the Al cathode and the Alq₃ layer, the work function of the cathode is lowered due to the vacuum level shifts by ~1.0 eV and the barrier height for electron injection is lowered to ~0.3 eV from ~1.3 eV.

The magnetic field effect on the device current or Organic Magnetoresistance (OMR), light output and the efficiency of small molecule OLEDs is studied. The magnetoresistance (∆I/I) of the OLEDs is found to be strongly dependent upon the magnetic field, the device current and the device thickness. Both positive and negative magnetoresistance is observed. The results show that the negative magnetoresistance is due to the diffusion and dissociation of the triplet excitons at the interfaces and the positive OMR is due to the interaction of free carriers with triplet excitons in the presence of a magnetic field. The change in the light output and efficiency is always positive with applied magnetic field which has been attributed to the hyperfine scale mixing of the triplets and singlets. The observations show that the magnetoresistance is excitonic in nature in all the small molecule organic materials studied.
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Chapter 1

Introduction

1.1 Motivations and Thesis Outline

The demand for light-weight and low-cost displays has attracted a significant amount of interest in many different types of technology in the academic as well as industrial sector. In the past 60 years, inorganic semiconductors such as germanium, silicon and gallium arsenide dominated electronics and materials such as GaAsP, AlGaAs, GaPN, AlInGaAs, etc acquired a huge popularity for indoor and outdoor display applications soon after the commercial introduction of GaAsP Light Emitting Diodes in 1962 [1]. To be regarded as satisfactory for practical applications, displays should have a brightness of \( \sim 100 \text{cd/m}^2 \) at operating voltage in between 5 to 15V with efficiency 5lm/W and a continuous operational life time of at least 10,000 hours [2]. Conventional semiconductor materials, however, are not very easily and economically used as large area displays. There is a continuous search for low cost, portable and more efficient materials. Organic materials have recently been introduced due to their advantageous properties over the conventional inorganic semiconductors.

Since the demonstration of organic light emitting diodes (OLEDs) using small molecule organic material by Tang et al. [3] and polymer by Burroughes et al. [4], there has been extensive use of organic semiconductors as an active electroluminescence layer for light-emitting devices. Such organic materials have attracted considerable attention due to their advantageous properties compared to conventional semiconductors. They are especially suitable for large area applications with a low cost without compromising on the device performance and the efficiency. A further advantage is that a wide variety of materials can be designed in order to cover a wide range of the emission wavelengths and increase the luminous efficiency of the material. For example, a wide range of the emission colours from green to red, was obtained simply by doping Coumarins and 4-dicyanomethylene-4H-pyrans (DCMs) into tris(8-Hydroxyquinoline) Aluminium (Alq₃) with different concentrations [5]. Furthermore, a very thin film of only few nanometres is used in the organic devices, which make the devices less bulky as well as more practical as they are easily portable. The processing techniques for the organic materials are either solution processing for polymers or the
vacuum evaporation for the small molecules which are quite simple. In contrast to this, inorganic materials needed a complicated single crystal growth processing techniques and lattice matching which is costly and sophisticated.

The main characteristics needed for light-emitting organic materials are that the material should at least support the injection/transport of one type of the charge carriers. Further it should be fluorescent so that it is capable of emitting light through recombination after the application of the electrical or optical excitation. A reasonable amount of work has been done in this direction in order to improve these features of organic materials [3-14]. In many cases, instead of a single layer device, a multi-layered device structures were preferred [3, 5-7, 15-18]. However, this multilayer device structure posses many challenges as the device comprises of many organic/organic and organic/metal interfaces, which generally do not behave electrically and chemically as a pure material. These interfaces are found to be responsible for injection and transport of the charge carriers and ultimately to the device operating voltage and efficiency. In this thesis, this issue will be addressed in chapter 3 where the electronic properties of such interfaces are investigated in a complete OLED device by monitoring the built-in potential with different metal cathode using saturated photoconductivity method.

Lowering a barrier height for an electron injection at the cathode on a small molecule thin film device is a central key point of today’s research on the optimisation of OLED devices. Much research has been devoted in this direction, for example, the use of low work function materials such as Ba, Ca, Na, Mg, Cs, Rb, Li, etc [19-24]. However, such low work function metals possess a major problem of degradation and delamination of the cathode due to their highly reactive nature. An alternative approach is the use of an insulating layer, such as low work function metal halides, (LiF, NaF, CaF₂), as an electron injection interface layer in cooperation with stable high work function metals [11, 21, 25-32]. Many stable organic compounds such as Sodium Stearate (Nast) [33], Calcium Acetates (Ca (acac)₂) [34], Lithium quinolate (Liq) [35-40], Sodium quinolate (Naq) [38] were recently demonstrated as electron injection interface materials. The result shows that the device performance was improved and comparable to that of conventional LiF/Al cathode. Even though the mechanism of the improvement of efficiency of such devices is attributed to the improved electron injection, the role of such organic interface layers was not yet understood fully. This issue is addressed in chapter 4 of this thesis, with investigation of a series of alkaline metal quinolates as electron injection interface materials.
The effect of magnetic fields on the device current and efficiency of OLEDs has been a subject of interest since the work of Kalinowski et al. [41, 42]. They attributed to the improvement in the light output and efficiency of the device to the mixing of the singlet and triplet electron-hole pair in the magnetic field, while the increase in the device current is due to dissociation of singlet electron-hole pair in the device. In an attempt to explain the mechanism of the increase in the device current in magnetic field, many studies were performed on the small molecules such as Alq₃, pentacene, tris-(2-phenylpyridine) iridium (Ir(ppy)₃), Platinum Octaethylporphyrin (PtOEP) and polymers such as, poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO), polyphenylene ethynylene (PPE) and large efficiency improvement of ~10% was observed on applying only few mT of magnetic field [42-48]. Even though the effect of magnetic field on OLEDs was universal and easily observable for all materials investigated, none of the experiment gave a complete mechanism. There is reasonable amount of confusion as these studies reported many different mechanisms, such as triplet-triplet annihilation (TTA) [49-51], singlet diffusion [41-43], spin-dynamics [47, 52, 53], hole and/or electron transport [44, 54], etc. An extensive study of such effect of magnetic field investigations are carried out in small molecule materials such as Gaq₃, Inq₃ and TPD in the chapters 5 and 6 and the mechanism responsible will be presented.

Furthermore, the trap limited transport has been observed in most of the vacuum deposited organic materials such as in Mq₃ where M is one of the group III metal such as aluminium, gallium and indium and suggests that the device transport properties are heavily altered by presence of the traps. Once bipolar transport occurs, the device current is given by \( j \propto V^{m+1} \), where \( V \) is the voltage across the device and \( m \) can vary from 0 to 8 for Alq₃ [55]. This kind of device current is believed to be due to trapping of charge carriers. Organic materials are regarded as self trapping materials and very little information is available about the trapping nature. This area is not investigated properly as what is the cause of the traps and how their presence in the device affects the operation, especially the transport properties such as mobility of charge carriers. In this thesis, this topic is addressed by studying the operation of the device under the magnetic field. It will be demonstrated that the presence of triplets in the device can change the transport of the free carriers such as electrons and we will show that the triplet states of the material act to slow down free carriers. This will be further addressed in chapter 5 and 6.
The scope of this thesis is to address the issues relating to the charge injection and electronic properties of the small molecule/metal interfaces and the magneto-transport properties of charge carriers in the complete OLED devices. Chapter 1 presents brief overviews of the electronic properties of organic molecule and device physics with existing theories. An account of the interface properties of small molecule/metal interfaces and some of the aspects of magnetoresistance (OMR) of such organic material is also presented. In chapter 2, we present a description of device fabrication method and all the experimental techniques used in the work. In chapter 3, we present the results of the study of the energy level alignment at the organic/metal interfaces. The calculation of the barrier heights for electron injection at these interfaces is also presented. In chapter 4, we will report the effect of thin alkaline metal quinolates as electron injection layers in Alq3 OLEDs on the device performance. Chapter 5 presents a comparison of the magnetoresistance (OMR) of the group III metal quinolates and describes the effect of change of the central atom on OMR. In chapter 6, we will examine whether the conventional hole transporting material N, N’-diphenyl-N,N’ bis (3-methylphenyl)-(1,1’-biphenyl)-4,4’ diamine (TPD) can be realised as a potential blue emitting electroluminescent material. We also use different cathodes in TPD devices to check whether OMR in TPD is excitonic in nature. Lastly, chapter 7 concludes the thesis with possible extension of future works.

### 1.2 Properties of Organic Semiconductors

Organic semiconductor materials are usually \( \pi \)-conjugated carbon compounds. They are insulators as they carry no free charge carriers at room temperature. The band gap of organic materials ranges from 1.5 to 3.5eV depending upon their chemical structures [56, 57]. Organic semiconductors are categorised in two classes, small molecules (with low molecular weight) and polymers (higher molecular weight), depending upon their processing techniques. Small molecule devices are generally fabricated using vacuum evaporation techniques while the polymers are applied by spin-coating, drop casting, screen printing, gravure etc. Well known small molecule organic materials Alq3, TPD and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) are shown in the Figure 1.1.

Organic semiconductor materials, either small molecule or polymers, possess a backbone of alternate single and double carbon-carbon bond as shown in Figure 1.1. As carbon has atomic number 6, its ground state electronic configuration is \( 1s^22s^22p^2 \).
There are four valence electrons and four bonds are possible in the case of formation of a saturated carbon compound. As all four electrons are used to make a bond, the material is a perfect insulator. However, the case is different in unsaturated organic material where not all of four available electrons are used for the bonding. For example, when three of such electrons are used to form a chemical bond in such a way that there are three identical sp² hybridized orbitals. These orbitals are aligned at 120° with each other as shown in Figure 1.2(a) and capable of forming σ-bonds. The excitation energy of the σ-bond is very high and beyond the visible spectral range (~8eV) and the electronic property contributed to the material by the σ-bond is totally insulating in nature.

![Figure 1.1: A chemical structure of small molecule organics Alq₃, TPD and BCP. Alq₃ was used as emission layer (EL), TPD as hole injection and transport layer (HIL and HTL) and BCP as electron injection and hole blocking layer (EIL and HBL) in this work.](image)

The remaining 2s electron can be promoted to the empty pₑ orbital and oriented perpendicular to the orbital of sp² (see Figure 1.2(a)). The π-bond is formed by the electron contribution from two pₑ orbital of the adjacent carbon atoms. This π-bond is very weak and it allows delocalization of the electron in the large portion of the chain, in the case of polymers, or in the closed circle in the case of small molecules. The delocalised electrons (π-electrons) in the material make these organic materials semiconducting in nature and are responsible for the electronic properties of the material. In π-bonds, any addition of extra charge leads to a significant amount of structural relaxations in the molecules. The π-bond is responsible for all essential electronic features of the organic materials such as charge generation and transport, light absorption and emission.
The π-orbitals in organic semiconductors are generally called Molecular orbitals (MO). If a molecular orbital is filled with electrons, then it is called the Highest Occupied Molecular Orbital (HOMO) and if it is empty, then it is called Lowest Unoccupied Molecular Orbital (LUMO). The HOMO and LUMO are similar to the valence and conduction bands in the case of inorganic semiconductors. The HOMO and LUMO separation in the materials is called the band gap or HOMO-LUMO gap. The wavelength of the light emitted in the recombination process depends upon the band gap. By changing the chemical structure of organic material, the band gap can be changed in order to get a desired emission wavelength.

**Figure 1.2:** (a) A schematic representation of sp² hybridized orbital and unhybridized pₓ orbitals in Carbon atom. (b) Formation of σ and π-bonds combining with another c-atom. Three sp² hybridized orbitals form σ-bonds and pₓ orbitals form π-bonds.

When an extra electron is added on the pₓ orbital, it will disturb the double bonding in the system changing the energetics of the molecule. The combination of electron and structurally relaxed molecule is called an electron polaron. Due to the addition of the electron, new electronic states will appear as shown in Figure 1.3(b) in what is otherwise the band gap of the molecule. Similarly when an electron is removed from the molecule, it will form a hole polaron as shown in Figure 1.3(c). There is a coulombic attraction between the hole and electron polaron and due to this attraction, a
bound state can form which is called an exciton. If the exciton is formed by an electron-hole pair on the same molecular unit then it is called a Frenkel exciton. In the case of Frenkel excitons, the distance between the electron and hole is very small, not more than the intermolecular distance. If the electron-hole pair exists at a large distances, such that it is extends over many molecular units, then it is called a Wannier-Mott exciton. The excitons of inorganic semiconductors are of Wannier-Mott type. Usually, in polymers and small molecules, the electron-hole pair interacts to form Frenkel excitons and the exciton is localized on a single repeat unit of the polymer (or a molecule) and strongly bound with a binding energy of order of few hundreds of meV.

**Figure 1.3:** A schematic representation of (a) HOMO and LUMO of a neutral molecule (b) electron polaron and (c) hole polaron

Organic materials can be regarded as insulators in terms of the charge transporting properties because of the very low mobility of charge carriers and the very low free charge carrier densities. Organic materials are highly disordered materials because of the different local environments of the molecules, different molecular geometries imposed by interactions and the nearest neighbours and chemical defects such as break up of bonds and/or conjugations. Due to this kind of disorder, there exists an ensemble of the energy states for both neutral states and charged states. When an electron is added or removed, a strong structural relaxation occurs in a molecule. However, as the electron transfer integrals between neighbouring molecules are not large, the charges in the electronic state of the molecule remain localized on the individual molecule or on the individual conjugated system and the electrical transport occurs by hopping between these localized states in the solid films. The mode of transport in organic semiconductors is hopping of the carrier in the wide distribution of energies. The main
causes of the disorder in the case of the small molecule are molecular orientations and any possible chemical defects. A permanent dipole of the molecule also contributes significantly to the disorder of the material because the different orientation of the dipole moments results a random electric field that modulates the energy level in the film. Due to this, the mobility of small molecule thin films is very low, only about 10^{-4}-10^{-3} \text{cm}^2/\text{V}\text{s}.

Due to the low mobility of the charge carriers in molecules, a single layer OLED device where only same layer of a small molecule material is used as both electron and hole transport layer is found to be inefficient and requires large drive voltage. Hence the idea of a multilayer device is introduced where different materials of high hole and electron mobility are sandwiched. Usually, the diamines such as TPD, N,N’-di(naphthalene-1-yl)-N,N’-diphenyl-benzidine (NPB) are categorized as hole injection and transport layer as these materials offer little resistance to hole transport with the hole mobility ranging up to ~10^{-3} \text{cm}^2/\text{V}\text{s} [58, 59]. Materials such as Alq\textsubscript{3} and other metal chelates are used as electron transport materials. The electron transport in the organic material, however, is harder due to the presence of common impurities such as oxygen and water which introduce more energy states between HOMO and LUMO trapping electrons [60]. For example, in Alq\textsubscript{3}, the electron mobility ~10^{-5} \text{cm}^2/\text{V}\text{s} is achievable only at high field at 10^6\text{V/cm} [58, 61-63]. Moreover, in the case of amorphous films, different types of electron transport were observed depending upon the level of purity of Alq\textsubscript{3} [63]. Nondispersive transport was observed in purified Alq\textsubscript{3} indicating that there is absence of the intrinsic traps while the material “as received” or exposed to air has shown highly dispersive electron transport indicating the impurities and the exposure to air offer major obstacles to efficient transport. In the recent study done on the exposure with different dosages of nitrogen, oxygen and moisture on Alq\textsubscript{3} film, it was shown that water seriously reduces electron transport even at very low dosage [64]. Oxygen was found to interact with Alq\textsubscript{3} only at high dosage and gave highly dispersive transport. In contrast to this, nitrogen being inert has no influence and the transport remains nondispersive even at high dosage. One study of LUMO of water exposed Alq\textsubscript{3}, done by X-ray photoelectron spectroscopy (XPS) has shown that the LUMO was shifted downward by ~0.16eV, which corresponds to the depth of the trap for the electron [60]. Furthermore, the electron mobility in Alq\textsubscript{3} was found to be heavily dependent on the deposition rate during film evaporation [61]. In the study, it was found that an increase in the evaporation rate from 0.2 to 0.7nm/s, caused the drift mobility of
electrons to drop by about two orders of magnitude. This suggests that the film quality is also responsible for electron transport in case of Alq₃, although the mechanism is not clear.

1.3 Device Physics

An organic light-emitting device is a sandwich of one or more semiconducting organic materials between two electrodes. A schematic representation is shown in Figure 1.4. One of the electrodes is a low work function metal which is capable of injecting electrons, the other electrode is a transparent high work function material such as ITO, from which the emitted light can escape. The thickness of the organic material is extremely small, of order of few hundreds of nm. The operation of the device involves the injection of charge carriers from the electrodes and transport towards the emissive layer when the forward bias is applied. The holes and electrons generate an exciton in the emissive layer, which returns to the ground state and emits light.

![Figure 1.4: A schematic representation of a single layer OLED where an organic light emitting material is sandwiched between the high work function transparent ITO, used as the anode and the low work function metal, used as the cathode.](image)

Once a forward bias is applied in the device, the electrons from the cathode have to overcome an energetic barrier and transport to the lowest unoccupied molecular orbital (LUMO) level while the holes from the ITO anode have to overcome hole barrier and transport to the highest unoccupied molecular orbital HOMO of the emissive material. In order to reduce the energetic barriers for the holes and increase the work function of ITO anode, it can be treated with different processes such as Ar, O₂, H₂,
UV-ozone [10, 65-70]. However among such treatments, the oxygen plasma treatment has been reported to be the most efficient in order to increase the work function of the ITO up to 5.2eV [66-69]. Typical low work function metals Li, Ca, Mg and their alloys such as Mg:Ag, are preferred as cathodes. The insertion of a thin insulating layers such as LiF, NaF, MgF₂, CaF₂ between the cathode and emissive layer is widely used to facilitate electron injection [11, 21, 26, 27, 30, 71], although the mechanism responsible for the improved electron injection is not properly understood.

**Figure 1.5:** A schematic of the injection, transport, recombination and light emission in a double layer device under operation. The multilayer device structure offers very low barriers for electrons and holes, while at same time it traps the charge carriers at an organic/organic interface to allow maximum recombination and further prevents the quenching of the excitons at the electrodes.

Generally, the organic materials show intrinsically low mobility. In order to optimise both carrier concentration in the emissive layer and obtain the maximum possible efficiency, a multi layered device is preferred with separate injection/transport layers for each of the carriers [3, 6, 7, 72]. Figure 1.5 shows a simple energy level diagram of a double layer device with a representation of the processes occurring, such as charge injection, transport and recombination in the device. If suitable organic materials are used, the barrier height is lowered for both charge carriers and the charge accumulation occurs at the emissive layer as shown in the figure due to the barrier at the organic/organic interface. A typical example of such multilayer device is the first prototype device structure introduced by Tang [3]. The use of multilayer device structures has additional advantages as some of the layers can act as blocking layers.
against the injection/transport of either holes or electrons from the neighbouring layer and prevent the quenching of excitons through the electrodes. Furthermore, it shifts the recombination zone towards the organic/organic interfaces and ultimately gives maximum recombination. The wavelength of emitted light is dependent on the electronic structure of the organic material i.e. the energy difference between the HOMO and LUMO of the molecule which can be easily tuned by the chemical modification of the material, by the doping of the organic materials or using stacked device structures [5, 12, 14, 73].

1.4 Charge Injection

Since the discovery of the organic light emitting devices, it was realised that charge injection from the metal contact was an important process for the device performance. The large barrier heights observed at the metal/organic contacts limit the efficient charge injection at the contacts. The interface barrier height means the energy offset between the HOMO or LUMO of the organics and the work function of the metal. The large interface barrier at the metal/organic contacts makes the device performance injection-limited, with very small numbers of charge carriers injected in the device. When the contact materials are chosen in such a way that there is a very small barrier height for charge carriers, one of the contacts is referred to as ohmic and able to supply enormous number of charge carriers, then the device performance is limited by the transport properties of the organic material and in such a case, the device is bulk-limited.

The organic semiconductors can hold a maximum current in the device, called the space charge limited current (SCLC), and this is given by the Mott-Gurney equation (1.1).

\[ J_{SCLC} = \frac{9}{8} \mu \varepsilon \frac{V^2}{L^3} \]  

where, \( \mu \) is the mobility of charge carriers in the material, \( \varepsilon \) is the permittivity of the semiconductor \( (\varepsilon = \varepsilon_0 \varepsilon_r) \) and \( V \) is the voltage across the device of thickness \( L \).

The efficiency factor, \( \eta \) which represents the ratio of measured current \( J \) and the SCLC current \( J_{SCLC} \), \( \eta = J/J_{SCLC} \) can be calculated for a given contact. If \( \eta = 1 \), the contact is ohmic, while \( \eta < 1 \), it is injection limited contact. However, theoretically, it is estimated that if the contact barrier \( \Phi_{\text{barrier}} \leq 0.3 \text{eV} \), the current in the device is space charge limited at room temperature and the contact is ohmic in nature [74, 75]. When
If $\Phi_{\text{barrier}} \geq 0.3\text{eV}$, then the contact is unable to provide enough charge and SCLC limit is not achieved, so the contact is injection limited.

Charge carrier injection in organic materials is not straightforward like in inorganic materials, where a simple model like the thermionic model is successfully applied [76]. The injection is influenced by various parameters such as the characteristic of the organic media, charge localization properties, hopping type of transport and polaronic effects so the thermionic emission model does not fit. Due to the low mobility of the charge carriers in the organic material, there is a significant amount of charge accumulation occurring at the interface after injection and the injection current is diffusion limited. At high electric fields, the tunnelling of the charge carriers through the triangular barrier occurs, which is called Fowler-Nordheim tunnelling (FN tunnelling). These classical models, however, do not account the hopping nature of the charge carrier transport in organic semiconductors. Due to this, none of the existing models is strictly applicable and the magnitude of the current predicted by the model differs by many orders of magnitude compared to what is measured in real devices. In a real device, it is realized that due to the low mobility, there is also a significant amount of back flow of the injected charge as a large concentration of charge accumulates at the interface.

Recently, Scott et al. introduced a model which took account of both the back flow of the injected charge carriers and their hopping nature [77]. In the model, they modified an existing classical model by considering the recombination current i.e. current contributed by the back flow. By comparing the cumblic attraction of the image charge (charge left on the metal after electron injection) and the electron with thermal energy, $kT$, it is possible to calculate the distance from the interface of metal/material beyond which the electron escapes from the interface without recombining. Considering the diffusive transport of electrons in the materials with a uniform applied field, the recombination current is calculated. The true current is the difference between the thermionic current and the recombination current. The validity of this model has been already tested experimentally by using a molecular doped polymer PC: TPD with different concentration of TPD in order to vary the mobility and found that the current is proportional to the mobility of the doped system [78]. Lately, the hopping nature of charge carrier transport is introduced in the model of injection considering the thermally assisted tunnelling of the charge carrier from the metal to the organic materials [79].
1.5 Metal/Organic Interfaces

Injection of the charge carrier into organic semiconductors is dependent on the energy barrier at the metal and the semiconductor interface because the barrier controls the carrier concentration which affects the efficiency and operating voltage of the device. In most cases, the barrier height is not just the difference of the work function of the injecting metal and the energy level of the organic material because the chemical and electronic properties of the interface modify the magnitude of the barrier significantly. The barrier height at the interface is found to be dependent on electronic properties such as dipole formation, charge localization, chemical reactions, metal diffusions etc. In this section, such kind of electronic modification of the interfaces is discussed and possible causes are presented.

1.5.1 Electronic Properties of the Interfaces

Figure 1.6 shows a schematic electronic structure of a typical metal/organic interface.

![Energy Level Diagram](image)

*Figure 1.6: An energy level diagram for the metal/organic interface considering a common vacuum level, $E_{\text{vac}}$ at the interface with no dipole i.e. $\Delta=0$.*

$E_{\text{vac}}$ denotes the vacuum level of the solid which corresponds to 0 eV, above this level an electron can escape easily from the solid or metal. The energy difference
between the HOMO and the vacuum level, $E_{\text{vac}}$ is called as ionisation potential (IE) and the energy difference between the LUMO and the vacuum level, $E_{\text{vac}}$ is an electron affinity (EA) of the organic material. The work function of the metal is $W_{\text{cathode}}$ and the difference between the energy level of LUMO and $W_{\text{cathode}}$ is the barrier height for electron injection ($\Delta \Phi_{\text{electron}}$). The values of the work function for the metal and the HOMO position of the organic material can be determined by ultraviolet photoemission spectroscopy (UPS) or cyclic voltametry (CV). The HOMO and LUMO gap can be measured by the optical absorption spectra of the material and finally the value of EA is estimated from the measured values of HOMO and HOMO-LUMO gap.

**Figure 1.7:** A dipole modified metal/organic interface. The HOMO-LUMO of the organic molecule shifts downward by $\Delta$, making the electron barrier $\Delta \Phi_{\text{electron}}$ smaller than the $\Delta \Phi_{\text{electron}}$ shown in Figure 1.6, which is obtained without a vacuum level shift.

The picture of the metal/organic interface in practice is not simple as shown in the Figure 1.6 because the concept of considering a common vacuum level $E_{\text{vac}}$ at the interface is not valid [80-82]. There can be different processes such as charge transfer from metal to organics and vice versa, redistribution of the electron cloud, rearrangement of the charge, interfacial chemical activity etc. occurring at the interface when two materials make contact, modifying the interface [80]. This causes the new
vacuum level to shift significantly than the previously measured one (obtained in absence of any other material). There are many studies done for different organic materials recently in order to probe the interfacial properties of metal/organic interfaces by UPS [80-91]. All these studies have shown that a concept of a common vacuum level at the interface is not applicable and a dipole of magnitude, \( \Delta \), is formed, shifting the \( E_{\text{vac}} \) and the HOMO-LUMO of the organic materials. The magnitude of the dipole \( \Delta \), however, has been found to be dependent on the work function of metal and nature of the organic material. The real picture of the interface is depicted in Figure 1.7 with a dipole \( \Delta \) at the interface. The formation of the interfacial dipole can modify \( \Delta \Phi_{\text{electron}} \) and the work function of the metal by the same value of the vacuum level shift \( \Delta \). In other word, the work function of the metal is lowered making the barrier height smaller.

### 1.5.2 Origin of Interfacial Dipole

From studies done on wide varieties of organic materials with different metal interfaces, it is concluded that there is a relation between the dipole formation, \( \Delta \) for the organic material and the work function of the metal used [80, 84]. A main trend observed is that there is always a negative vacuum level shift which causes a lowering of the vacuum level. Based upon this trend, the origin of the dipole at the interface and the cause of the vacuum level shift were explained by Ishii et al. and the mechanism was illustrated in Figure 1.8 (adapted from Ref. [80]).

The main cause of the dipole can be electron transfer between the metal and the organic, as shown in Figure 1.8, causing the positive and negative charges to separate across the interface. The origin of the charge separation at the interface (and resulting electric field) is similar to conventional band bending, which also results from the charge transfer across an interface. In the case of the interfacial dipole, however, the electric field is confined to a very narrow region, not more than 1-2nm [92]. This kind of electron transfer occurs for combinations of a strong donor organic-high work function metal as shown in Figure 1.8(a1) or a strong acceptor organic-low work function metal as shown in Figure 1.8(a2).
The second factor responsible for the origin of the dipole may be the image effect or the modification of the surface dipole at the metal surface. It can be due to the polarization of the electron cloud attracted by the image charge formed in the metal surface as shown in Figure 1.8(b). There can be a rearrangement of the electron cloud tailing from the metal due to presence of the molecule at the surface as shown in the Figure 1.8(c). Another factor responsible for the origin of the dipole is chemical interaction as shown in the Figure 1.8(d), when either metal or the organic molecule or both, are chemically very reactive. In such conditions, the presence of organics on the metal surface lead to the formation of new bonds as well as rearrangement of the existing local chemical bonds. In such a case, the direction of the dipole formed depends upon the chemical interaction. The fourth factor contributing to the dipole is the possible existence of an interfacial state, however, the interfacial state of the organic/metal interface can be quite different than that of an inorganic semiconductor. In the case of an inorganic semiconductor, the interfacial state is formed due to its intrinsic and extrinsic origin such as dangling covalent bonds at the crystal structures, surface defects, the metal induced gap states formed by the penetration of metal in to the semiconductor etc. In an organic material, however, the existence of such states is less
likely as they are bonded by weak van der Waals forces. Finally, for a polar organic molecule, which possesses a permanent dipole, the orientation of this dipole can lead to an interfacial dipole as shown in Figure 1.8(f).

1.5.3 Barrier Heights and Dipoles by Monitoring $V_{bi}$

In order to gain the knowledge about injection barriers, usually, the organic material is evaporated in ultra high vacuum on the top of the metal and UPS measurements carried out [31, 80-84, 87, 89, 90]. Recently, Brown et al. introduced an electroabsorption method of monitoring the $V_{bi}$ of the complete polymer device in order to study the electronic energy level line up at the polymer/cathode interfaces [21, 22]. The working principle is described as follows.

The principle of measurement of the interfacial dipole and change of the work function of the cathode just by monitoring the $V_{bi}$ of the complete device is presented in Figure 1.9. In order to minimize the electron and hole injection barriers, it is normal to use a low work function cathode and a high work function anode. Due to the difference in the work functions, in a complete device there is a built-in potential of magnitude $V_{bi}$ across the organic layer due to the equilibrium of the Fermi levels of the electrode when they come in contact. In the absence of intrinsic and extrinsic charge carriers in the organic layer, the electric field in the layer can be considered to be uniform. In such a case, if the HOMO-LUMO gap of the organic is $E_G$, $\Phi_{\text{anode}}$ and $\Phi_{\text{cathode}}$ are the barriers at the anode and cathode respectively, then following equations can be written (see Figure 1.9).

\[
W_{\text{anode}}-W_{\text{cathode}} = eV_{bi}\tag{1.2}
\]

\[
\Phi_{\text{electron}} + \Phi_{\text{hole}} + eV_{bi} = E_G \tag{1.3}
\]

The relation (1.3) shows that if the anode ($W_{\text{anode}}$) and the organic material (the value of $E_G$) are kept constant, a decrease in the cathode work function increases $V_{bi}$ and there will be equal decrease in the barrier height at the cathode. The relation (1.3) modifies to

\[
\Phi_{\text{electron}(1)}-\Phi_{\text{electron}(2)}=e(V_{bi(1)}-V_{bi(2)})
\]

\[
\Delta\Phi_{\text{electron}} = -e \Delta V_{bi}
\]

In case of the interface, however, where there is a dipole $\Delta$ (due to various mechanisms as shown in Figure 1.7), relation (1.2) is not applicable due to the vacuum level shift by $\Delta$. The relation is then modified to
Hence, if relation (1.2) does not hold in the complete device, there is a vacuum level shift due to dipole formation and the magnitude of the dipole can be calculated easily by using relation (1.4), with known values of work function of anode and a measured value of $V_{bi}$. Moreover, if different thin electron injection layers are used in combination with a cathode of standard work function (a metal such as aluminium), then the change in the work function brought by the interface layer and the dipole can be calculated easily. In this case as the change in $\Phi$ (barrier) is calculated from a change in $V_{bi}$, the change in the barrier is independent of the energy levels of the organic material and the work functions of the cathode.

### 1.6 Device Efficiency

The device efficiency of an OLED is generally expressed in terms of the external quantum efficiency $\Phi_{EL}$ which is defined as the number of photons emitted per injected electron. It can be written as

$$\Phi_{EL} = \gamma \Phi_F \eta_r \eta_e$$

**(1.5)**
Where $\gamma$ is charge balance factor, $\Phi_F$ is the fluorescent quantum efficiency, $\eta_r$ is the ratio of total singlet to total number of exciton formed and $\eta_e$ is the coupling factor.

When an electric field is applied in the device, the charge carriers are injected and transported into the organic emissive layer, the carriers meet and form excitons. Not all injected charge carriers, however, recombine to form excitons as exciton formation is dependent on the injection of electrons and holes and their mobility. The efficiency of formation of the excitons is related to the relative number of positive and negative charge carriers. This factor is denoted as $\gamma$ and called the charge balance factor. Ideally, the maximum value of it is achieved by choosing the metal electrodes (ohmic contacts) in such a way that there is no barrier for the charge carriers and the mobility of holes and electrons are identical.

The excitons formed in the device follow the spin statistics rule and two types of excitons are formed namely, singlets and triplets. The main distinction between these two is that the singlets decay radiatively within very short life time while the triplets are long lived and they relax through nonradiative processes. According to spin statistics, there is one singlet formed for every three triplets. The factor $\eta_r$ is introduced in order to account for the ratio of singlets formed to the total exciton numbers. This suggests that the maximum achievable value of $\eta_r$ is $1/4$ [93].

Furthermore, in the material all the singlet excitons formed do not necessarily decay radiatively, due to the intrinsic properties of the material and due to different factors such as defects of the material, exciton quenching processes etc. The factor $\Phi_F$, called as the fluorescent quantum efficiency is used to account for the photoluminescence properties of the material. In the case of organic materials, impurities such as water and oxygen can act as quenching centres. One main process of singlet exciton quenching in the complete device is due to diffusion of the metal into the organic layer. Metals like Ca when used as cathodes can diffuse from the cathode and interact with organic molecules forming $\text{Ca}^{++}$ and the extent of the diffusion and the subsequent quenching is dependent on the thickness of the Ca layer [94].

The efficiency of the device will be maximized if all the light emitted from the recombination process can be extracted out of the device. This is not possible because of total internal reflections at the material, substrate and air interfaces, and some of the emitted light is trapped in the device. The term $\eta_e$, called the coupling factor, or the extraction factor, is used to denote this loss in the efficiency. The value of the $\eta_e$ for small molecule based OLEDs, considering there is no preferential dipole and the light
emission is isotropic, is \(0.5/n^2\) where the factor \(n\) denotes the refractive index of the material. There are many attempts to improve the coupling factor by different modifications in the device architecture including the roughening of the substrate or attaching silica microspheres or microlenses to the substrate or modification of the refractive index of the materials [95].

Furthermore, for simplicity the efficiency of the OLED is expressed in different ways, such as current efficiency (cdA\(^{-1}\)), luminous efficiency (lmW\(^{-1}\)) and power efficiency (dimensionless) or injection efficiency (WA\(^{-1}\)). The injection efficiency \(\eta_i\) is defined as the ratio of the light output per unit area to the current density and is obtained from the slope of the linear characteristics of luminance vs current of the device.

\[
\eta_i = \frac{L(W)}{I(A)} \tag{1.6}
\]

The power efficiency \(\eta_p\) is defined as the ratio of the output power to the input power of the device.

\[
\eta_p = \frac{L(W)}{(V(V) \times I(A))} \tag{1.7}
\]

### 1.7 Organic Magnetoresistance (OMR)

In this section, we address the phenomenon of OMR in organic materials. Before addressing OMR, we first discuss the formation of excitons and intersystem crossing between the different exciton states due to the hyperfine interaction and spin-orbit interactions in absence of an external magnetic field. The effects of a magnetic field in the device operation are then briefly presented with the existing mechanisms.

#### 1.7.1 Exciton Formation

It is already explained in the section 1.2, the injection of electrons and holes in an OLED device can be followed by the formation a bound state of electron-hole pair called excitons. These excitons can take one of two states either singlet or triplet. The main difference between these two states is that the singlet state can relax radiatively whilst for triplet states, the radiative recombination is forbidden; they relax only by non radiative decay process or by being quenched at suitable interfaces. An exciton can have an electron and a hole with either up or down spin \(\frac{1}{2}\) (\(\uparrow\) or \(\downarrow\)) and precess in phase or out of phase. This leads four different configurations as shown in Figure 1.10. These can be
such that when an electron and a hole combine in such a way that the total spin angular momentum is $S=0$, with combination $1/\sqrt{2}(\downarrow\uparrow-\uparrow\downarrow)$, it is called singlet. There can be three possible configurations with total angular momentum $S=1$, with $(\uparrow\uparrow)$, $(\downarrow\downarrow)$ and $1/\sqrt{2}(\downarrow\uparrow+\uparrow\downarrow)$ and these are called triplets. In the triplet states, the Pauli Exclusion principle operates to keep the electron and hole away from each other as they have same spin, due to which the triplet states has a lower energy than the singlet. Figure 1.11 shows the schematics for the ground state with the excited states.

Figure 1.10: A schematic for spin and total angular momentum for singlet and triplet states.

Figure 1.11: A representation of a ground state, singlet and triplet states respectively.
There are two ways to alter the spin of excitons; they are called the hyperfine interaction and spin-orbit coupling. When an electron and a hole interact with the nuclei of an atom in the molecule, the precession frequency can change or spin flip can occur thus converting a singlet into a triplet and vice versa. This process of conversion of the spin state is called the hyperfine interaction. When an electron and hole are in pair states where a bound exciton state not properly formed, the exchange interaction energy is negligible, the spin of singlet state mixes with entire triplet states, changing the concentration of the pair states and the excited states. The radiative and non radiative decay of the molecule can be altered by this process in expense of one another.

Another way to modify the spin of the excited state is by introducing the spin-orbit coupling in the molecule, which causes the energy level of different spin state to splits into different levels, so that the mixing of the all excited states makes much easier. Electron possesses spin angular momentum of magnitude S (given by $S=\sqrt{s(s+1)}\hbar$, where s is spin quantum number and $s=1/2$) and orbital angular momentum L (given by $L=\sqrt{L(L+1)}\hbar$ and L is orbital angular quantum number and $L= 0, 1, 2,\ldots,n$, where n the energy level of electron). When an electron revolves around the nucleus of the atom, due to its orbital motion it sees a nucleus as a source of magnetic field. This magnetic field interact with the spin angular momentum vector S of the electron. The interaction is given by the scalar product of two momentum vectors, S and L (i.e. S.L) and it is called spin-orbit effect. Due to this interaction, the energy level with different spins become degenerate and it gives closely spaced energy levels which causes the mixing of triplet excited states with singlet states easier. This increases the intersystem crossing between the singlet and triplet at zero magnetic field. With an increase in the size of the atom, the effect of the spin-orbit coupling becomes stronger with more splitting of the states, allowing the states to convert from one to another easily. Triplet harvest in small molecules and polymers are example of such spin modulation by adding a heavy atom in the system.

### 1.7.2 A Brief History of OMR

Although the studies on the effect of a magnetic field on the fluorescence properties of organic crystal date back to 1960s, interest in the effects on device current and electroluminescent properties of OLED devices has started relatively recently. In preliminary studies, performed on Alq$_3$ devices, it was demonstrated that an external
magnetic field of \( \sim 100 \) mT could increase the device photocurrent by about 6\% and at high field the effect either saturates or decreases [41]. The authors explained the cause of increase of photocurrent in terms of magnetic field dependent mixing of singlet and triplet electron-hole pair states before charge separation. They stated that the initially formed photo excited Alq3 molecules can either decay with radiative \((k_R)\) or non radiative \((k_n)\) pathways or form a singlet electron-hole pair \( ^1(e\ldots h) \). The schematic they proposed is shown in Figure 1.12. The singlet electron-hole pair \( ^1(e\ldots h) \) interact with surrounding nuclei via hyperfine coupling and acquires a triplet \( ^3(e\ldots h) \) nature with rate constant \( k_{ST} \). Both singlet \( ^1(e\ldots h) \) and triplet \( ^3(e\ldots h) \) can dissociate with different rate constants \( k_1 \) and \( k_3 \), giving a photocurrent in the device. They proposed that the mixing of the singlet and triplet electron hole pair occurs in the magnetic field by hyperfine interaction. There can be hyperfine interaction between the electron and hole with nuclei surrounding them mixing between the singlet \((S)\) and entire triplet states \((T_+, T_0\) and \(T_\pm)\). They suggest that in presence of magnetic field there is splitting of the triplet states in three degenerate states so that mixing of singlet and triplet \( T_0 \) is only possible reducing the value of \( k_{ST} \) and reduction of the photocurrent was observed.

\[
\begin{align*}
  h\nu + \text{Alq}_3 & \rightarrow \text{Alq}_3^* & \rightarrow ^1(e\ldots h) & \rightarrow e + h \\
  k_1 & \rightarrow & k_f + k_n & \rightarrow k_{ST} \\
  \text{Alq}_3 + h\nu_f & \rightarrow ^3(e\ldots h) & \rightarrow e + h
\end{align*}
\]

Figure 1.12: A schematic for the mechanism of increase in the photocurrent proposed by Kalinoswki et. al. The figure is adapted from Ref. [41].

In this study, they assumed that the dissociation constant \( k_1 \) for singlet electron-hole pairs is higher than that of triplet electron-hole pairs, \( k_3 \) and the singlet electron – hole pair contribute to the photocurrent. They however did not explain clearly why singlet electron-hole pairs undergo a dissociation process instead of radiative decay. Further it is also not mentioned why triplet electron-hole pairs do not take part in the dissociation contributing to the current in the device. In their another study of magnetic fields on complete Alq3 OLEDs have shown \( \sim 5\% \) and \( \sim 3\% \) increases in the EL and device current respectively in which the increase in EL is attributed to a magnetic field dependent modulation of the singlet population and the increase in the device current is
due singlets diffusion at the cathode [42]. They used same mechanism proposed in Ref. [41] to explain the observed magnetic field effects.

Davis et al. investigated the magnetic field effect on the EL of light emitting devices with many different electrodes of both magnetic and non magnetic nature [50]. They have shown that magnetic field effects were observed in both types of electrode materials with differing magnitudes. Furthermore they showed that there were two distinct processes occurring at low and high magnetic fields. There was a small percentage change in the EL output at low magnetic fields and this process was found to be insensitive to the temperature and the drive voltage of the device. The high field process, however, was found to be enhanced at low temperature and high current densities [50]. This finding was similar to that of the delayed fluorescence observed in anthracene as described in Ref. [96]. This was attributed to the triplet-triplet annihilation (TTA) process [96, 97]. This is bimolecular process in which two triplets come close enough to form an intermediate pair state \((T_1, T_1)\). They can interact with each other yielding a singlet exciton \(S_i\) which finally decays with an emission of a photon. This process is spin conserving when it goes from \(T_1+T_1\) to \(S_0+S_i\), shown in Figure 1.13. It can be denoted as

\[
T_1+T_1 \leftrightarrow (T_1, \ldots, T_1) \leftrightarrow S_i+S_0 \rightarrow S_0+S_0 + hv
\]

where \(T\) represents the triplet state, \(S_0\) represents a molecule in the singlet ground state and \(S_i\) represents the molecules first excited singlet state. The term \(k_1\) denotes the rate of the pair state formation and determined by the diffusion coefficient of triplet excitons and \(k_1\) is backscattering of the pair state. \(K_2\) represents the rate constant for the triplet annihilation. The luminance obtained by this process is called delayed fluorescence. The emission spectrum of the molecule is similar to the normal PL spectrum as a singlet is involved in a recombination process, however, emission occurs with a reasonable time delay in comparison to normal fluorescence.

A study of the magnetic field dependence of delayed fluorescence of anthracene was performed by Johnson et al. [96]. They observed a small increase in fluorescence at low field, and followed by a decrease as the magnitude of the field increases. When the magnitude of the applied magnetic field is comparable to the spin-orbit and hyperfine field strengths, the electron-hole pair develops singlet nature directly producing a singlet and giving an increase in fluorescence. When the applied magnetic field is large
enough to dominate the field seen by the excitons, the number of singlets is reduced and the fluorescence decreases.

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\[
\frac{\Delta R}{R} = \frac{(R(B) - R(0))}{R(0)} \quad \text{(1.9)}
\]

where \( R \) is the device resistance, \( R(B) \) is the device resistance in presence of magnetic field and \( R(0) \) is the resistance in the absence of the field. They found up to 10% OMR with the application of 10mT field at room temperature and the OMR effect was found to be independent of the direction and the sign of the magnetic field and weakly dependent on temperature.

An OMR study on Alq3 with different cathodes such as Ca, Al and Au by Mermer et al. shows that the magnitude of OMR is heavily dependent on the nature of cathode material [44-46]. This observation was in contrast to the OMR study done on PFO devices where it was heavily dependent on the anode [54]. In the case of Alq3 devices, a Ca cathode shows the smallest drive voltage with the largest value of OMR whereas Au shows the largest value for onset, with the smallest value of OMR. The injection of electrons from the Ca cathode into Alq3 is not injection-limited and this is confirmed by I-V characteristics of the devices which obey a power-law with a space-charge limited current during operation. This shows that the device is bulk-limited. This suggests that OMR of Alq3 is not due to interface resistance but due to the bulk limited magneto-transport. According to them, this phenomenon cannot be explained by existing magnetoresistance theories such as classical magnetoresistance (MR~\( \mu^2 B^2 \), \( \mu \) is mobility of charge carrier), hopping magnetoresistance (the wave function shrinkage with applied B field, leads only to positive MR) or electron-electron interaction (only significant at very low temperature) and needs further investigation.

In order to attempt to explain the mechanism of OMR, we investigated the OMR of Alq3 OLEDs with different cathodes and different Alq3 thickness [98, 99]. These preliminary studies strongly suggest that OMR is excitonic in nature as shown by many previous studies [41, 42, 100, 101]. Our studies further suggest that a magnetic field dependent triplet-carrier interaction is responsible for the existing OMR. These concepts are elaborated with our experimental evidences in chapters 5 and 6.

### 1.7.3 Excitonic Nature of OMR

Our recent observation of OMR measurements on Alq3 OLED structured devices strongly suggests the excitonic nature of OMR [98]. OMR is visible only at voltages where electron injection is occurring in the device. At the same point, the device is
emitting light. This proves that excitons are formed under these conditions. No OMR is seen below the turn-on voltage of the device where the charge transport is unipolar and the formation of the excitons is not possible. This observation suggests that OMR is related to the generation of excitons. The applied magnetic field is acting on the generated excitons to modulate their concentration to change the current and EL.

Further we introduced singlet excitons in Alq3 OLEDs by illumination and observed the effect of the magnetic field [102]. We found that there is OMR even before electron injection and turn-on of the devices, where OMR is not seen on unilluminated devices. This strongly suggests that OMR is due to the magnetic field modulation of the singlet excitons in the illuminated device before bipolar injection occurs. From these observations, our initial studies conclude that OMR is excitonic in nature. We will introduce more examples of excitonic nature of OMR and discuss more in detail in chapters 5 and 6.

In order to explain the mechanism of OMR, Prigodin et al. have also proposed a model based on its excitonic nature [55]. According to this study, OMR in the devices is due to a change in the charge transport in the presence of a magnetic field and the electron-hole pairs can either combine to form singlets and triplets or dissociate into free charge carriers. The magnetic field can change the mixing of the triplets and singlets and the recombination rate for electron-hole pairs which changes the device current. OMR in the device is hence due to a change in the dissociation of electron-hole pairs and their recombination in the presence of a magnetic field. If this is what is happening in the device, then a proportional relationship between the change in the current ($\Delta I/I$) and the change efficiency ($\Delta \eta/\eta$) should be observed, this comes about as change in efficiency (recombination) is due to change in the dissociation of the electron-hole pairs. We will also examine this model further in small organic materials.

### 1.7.4 Triplet-Carrier Interaction Model

Before introducing the triplet-carrier interaction model for the origin of OMR in Alq3 devices, it is worth presenting some of the background results from Ref. [98]. Typical magnetic field effects on the current ($\Delta I/I$) and efficiency ($\Delta \eta/\eta$) for Alq3 devices with three different cathodes such as LiF/Al, Al and Mg:Ag are shown in Figure 1.14 (adapted from Ref. [98]). The plots correspond to the maximum $\Delta I/I$ and current density $\sim 0.5 \text{Am}^{-2}$ in each case. A sharp rise in OMR and efficiency is observed at very low magnetic fields up to 50mT. This is attributed to a hyperfine scale interaction
process of mixing of the singlet and triplet states in the magnetic field with an increase in the singlets due to the conversion of triplets into singlets [103, 104]. As the number of singlets is increased by the magnetic field, the efficiency and EL output of the device both increase. A very similar process was seen for the device current. It suggests that the low field change on current is also attributed to the same hyperfine scale interaction process. Our studies confirm that OMR is due to an increase in the singlet population and a decrease in the triplet population.

**Figure 1.14:** A typical example of OMR and differential efficiency of ITO/TPD/Alq3/cathodes devices with varying magnetic field near the turn-on voltage ($V_{on}$ for 2.7V) for LiF/Al (square), ($V_{on}$ for 3.2V) for Mg:Ag (triangle) and ($V_{on}$ for 4.0V) for Al (circle). The current density in the devices is ~0.5Am$^{-2}$ (Adapted from Ref. [98]).

Figure 1.14 also shows clearly that $\Delta I/I$ and $\Delta \eta/\eta$ for three different cathodes are different in magnitude. OMR, $\Delta \eta/\eta$ and $\Delta EL/EL$ follows the same trend with a maximum percentage change for LiF/Al and minimum for Al cathode. This is due to the fact that these electrodes have different electron injection barriers, with the smallest barrier using LiF/Al and the highest barrier when an Al cathode is used (see section 3.3.2). Due to its different electron injecting capacity, the device with the LiF/Al cathode has a larger carrier concentration and shows greater efficiency, which is ~4
times more efficient than that of the Al only cathode. Similarly, the Mg:Ag cathode device is ∼3.6 times more efficient than the Al only cathode device. It is obvious that the LiF/Al cathode provides more electrons and consequently more excitons in the device compared to the others. This results in bigger changes in the current and efficiency upon application of magnetic field. It is worth noting that there is saturation in the efficiency plots at high magnetic fields, after a sharp change in efficiency at low magnetic fields within 50mT (see Figure 1.14). A very similar characteristic was found at all current densities and drive voltages for all three cathode materials. This shows that there is no additional process in all three devices after the low field process. Further, under careful examination, the slope of the change in efficiency with magnetic field is found to be same for all three cathodes and at all drive voltages. This also suggests that the change in efficiency is independent of the exciton concentration in the device. This further indicates that there is no process such as TTA occurring in the device (see relation 1.8).

In order to explain the mechanism of OMR, a schematic diagram in Figure 1.15 is introduced. The schematic represents a normal organic fluorescent molecule raise to its excited state by using either electrical or optical pumping. If the molecule is pumped electrically, due to spin statistics one singlet, \( S_1 \), is formed for every three triplets, \( T_0 \), (\( A = 0.25 \) and \( B = 0.75 \)). If the excitation is introduced by optical means, then \( A = 1 \) and \( B = 0 \), and the excitons are generated solely the singlet \( S_1 \). The decay paths of the excitons are \( k_S \) and \( k_T \) for the singlets and triplets respectively. As radiative recombination of triplets is forbidden, the life time of the triplet (\( \tau_T \)) is many times higher than that of the signet (\( \tau_S \)) so the value of the rate constant of the singlet decay is higher than that of the triplet (\( k_S >> k_T \)). The term \( k_{ISC} \) is introduced to denote the intersystem crossing from singlet to triplet. As there is an energy barrier \( E_A \) to undergo intersystem crossing from triplet to singlet, the intersystem crossing term is modified as \( k_{ISC} \exp (-E_A/kT) \) for finite temperature \( T \). In the system, if there is large population of triplets and the temperature is sufficient to overcome the energetic barrier, a triplet can change into singlet. Similarly, if there are more triplets in the system upon application of the magnetic field, the field may act to increase \( k_{ISC} \) so that more singlets will be produced. This kind of increase of the mixing of singlet and triplet has already been demonstrated in the studies of Groff et al. [103, 104]. The intersystem crossing of singlets and triplets in presence of magnetic field is shown schematically in Figure 1.15(b).
Once bipolar injection starts in the device, there will be more triplets than singlets. The magnetic field changes the rate constant $k_{ISC}$ so that it increases the singlet population. The increase in the singlet population increases the EL output and the efficiency of the device. This process of mixing singlets and triplets is referred to as the hyperfine scale interaction mixing of singlets and triplets throughout the thesis.

**Figure 1.15:** (a) A schematic diagram of the excitation paths (either electrical or optical pumping) and recombination pathways in an organic molecule. (b) A vector diagram illustrating the increased singlet and m=0 triplet state intersystem crossing in presence of the magnetic field (Adapted from Ref. [102]).

Furthermore, increase in the singlet and decrease in the triplet population due to a magnetic field can cause the OMR as shown in Figure 1.15, which resembles the sharp change in EL and efficiency. Under electrical excitation, there is an excess of triplets in the device. Studies have shown that the singlet life time is $\sim$10-20ns and that of the triplet is $\sim$25µs in Alq$_3$ at room temperature [105,106]. Due to the long life time, the
triplets remain in the device for long time and can diffuse and dissociate at the interfaces under favourable conditions such as suitable cathode or anode interfaces. Furthermore these triplets can interact with paramagnetic centres such as injected free carriers as shown by Ern et al. [107]. This can result in scattering of the free carrier (route $k_1$), changing the mobility of free carriers, or quenching of the triplet state (route $k_2$), decreasing the triplet concentration as shown below.

\[ T + D_{\pm 1/2} \xrightarrow{k_1} (T...D_{\pm 1/2}) \xrightarrow{k_2} D_{\pm 1/2} + S_0^* \quad \ldots \ldots \quad (1.10) \]

where $T$ is the triplet state, $D_{\pm 1/2}$ is the spin $\pm 1/2$ paramagnetic centre, $(T...D_{\pm 1/2})$ is a pair state, $S_0^*$ is an excited ground state, and $k_1$ and $k_2$ are the rate constants for back scattering and quenching, respectively.

This process of changing the mobility of the carrier by the interaction (denoted by relation 1.10) is demonstrated in Figure 1.16. When a triplet with same electron or hole spin as that of the free carrier come close, there cannot be any interaction in between them and the triplet has to find some another route to transit in the device and this is called site blocking. The process is shown in Figure 1.16(a). However if the triplet has a correct spin as shown in Figure 1.16(b), then it can interact with the incoming carrier and forms the intermediate state which can undergo either dissociation, yielding the original states (i.e free carrier and triplet) or it can quench the triplet with the formation of an excited ground state with following a spin conservation rule.

Hence, if there is an accumulation of triplets in the device due to electrical injection, the magnetic field decreases their concentration by intersystem crossing, so that there is less trapping of the free carriers, which increases the mobility of the free carriers and gives positive OMR. Similarly if the process follows the route $k_2$, as there is decrease of the triplet number, positive OMR observed. As a free carrier has not suitable spin useful for triplets the scattering is occurred with lowering the mobility of the carrier. Hence, if there is an accumulation of triplets in the device due to electrical injection, the magnetic field decreases their concentration by intersystem crossing, so that there is less interaction of the free carriers with the triplets, which increases the mobility of the free carriers and gives positive OMR.
Figure 1.16: Triple-carrier interaction (a) site blocking (b) lowering of the mobility by scattering and dissociation (Route $k_1$) and (b) quenching of the triplet to the excited ground state (route $k_2$).
It is interesting to note that the OMR of all devices has shown different characteristics to the efficiency plots, after low field process. It is clearly seen that there is a linear increase in OMR with magnetic field and no saturation observed, as in case of efficiency, within the measurement range. It suggests that there is a second process in OMR which is also magnetic field dependent. This suggests that the triplet-carrier interaction has some magnetic field dependence. It could be that the process represented by relation 1.10 has some magnetic field dependence. The magnetic field dependence of $k_1$ and $k_2$, however, not clearly known. In both processes, whether the triplet forms an intermediate state with the free charge carrier or the triplet is quenched by forming an excited singlet, as the spin of the triplet is already involved there must be some spin selection rule applied and some magnetic field dependence is expected. The magnetic field dependence of the triplet-carrier interaction was investigated by Wittmer et al. and they stated that the triplet-carrier pair is influenced by the presence of another free carrier [108]. Upon application of the magnetic field, the dissociation of the triplet-carrier pair is enhanced and hence the value of rate constant $k_1$ is increased. As the dissociation is increased due to the magnetic field, the trapping of the carrier is decreased and the mobility of the carrier increases and gives positive OMR as observed in Figure 1.14. The linear increase in OMR may be due to a magnetic field dependence of $k_1$ however, there may be some magnetic field dependence of $k_2$ as well.

It has become clear that from our preliminary study of OMR in Alq$_3$, there are many important process and parameters which are involved in causing changes in current, efficiency and light output with magnetic field. In addition to the hyperfine scale interaction of the singlet and triplet intersystem crossing at low magnetic fields, the triplet-carrier interaction becomes important at high magnetic fields. In the triplet-carrier interaction process, the trapping and scattering of carriers is found to be magnetic field dependent and this affects the mobility of the free carriers significantly.

### 1.8 References

Chapter 2

Experimental and Measurement Techniques

2.1 Introduction

In this chapter, we present a brief description of synthesis and purification of a series of alkaline metal quinolates (Mqs) where M represents the alkali metal such as Li, Na, K, Rb and Cs. During the experiment, organic materials such as Alq3, BCP and TPD, which are available commercially, are also purified by the train sublimation method or by evaporation in a Kurt J. Lesker SPECTROS. The details of such purification processes are described in section 2.2.2.

The sample preparation and the measurement techniques such as current-voltage-luminance characteristics (J-V-L), photoluminescence (PL), electroluminescence (EL), built-in potential measurement (Vbi), UV-Visible absorption spectra and magnetoresistance (MR) measurements are also described in section 2.4. A description of the newly installed Kurt J. Lesker SPECTROS evaporation system is also presented.

2.2 Synthesis and Purification of Mqs

2.2.1 Synthesis of Mqs

Alkali metal quinolates (Mqs) were synthesised from the dehydration reaction of the corresponding alkali metal hydroxides and 8-hydroxyquinoline (Hq) according to the procedure mentioned in references [1, 2]. All of the alkali metal hydroxides and Hq were purchased and used as obtained from Aldrich. We describe briefly the synthesis of Liq as a representative description of alkali metal quinolates synthesis.

The chemical reaction for the synthesis process of Liq is shown in relation 2.1.

\[
\text{LiOH} + \text{Hq} \rightarrow \text{Liq} + \text{H}_2\text{O} \quad \text{........................................(2.1)}
\]

( at 30°C and in presence of CH\textsubscript{2}Cl\textsubscript{2})

3.4595g (23.83mol) of Hq was dissolved in 80ml of dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}) in a dry conical flask. 1g (23.83mol) of lithium hydroxide (LiOH) was added into it. The solution was kept stirring and heated at a moderate temperature of ~30°C for 24hours. A white precipitate was formed which was then filtered through a sinter funnel. The precipitate was washed three times with dichloromethane in order to get rid of excess...
amounts of Hq. Finally, the sinter, covered with aluminum foil, was left for two days in a fume cupboard to dry. The dry precipitate was then collected and weighed. The yield of dried Liq was about 81.7% (~2.96g) of the theoretical yield. Other Mqs were prepared in similar manner with their respective hydroxides. For all synthesis, the amount of Hq was calculated for 1g of hydroxide salt with a 1:1 stoichiometric ratio of each.

2.2.2 Purification of Organic Materials

Purification of the organic materials is an important process in device fabrication for several reasons. As these materials are synthesized by a wet process in cooperation with suitable solvents such as dichloromethane, methanol, water etc, the final product in general is accompanied by water and other excess parent materials such as Hq, salts and hydroxides. The presence of such materials can cause degradation of the device efficiency and lifetime [3]. The black spot formation on the OLEDs after within few hours of device fabrication has been attributed to the presence of water incorporated within the organics [4]. Furthermore, some of the unwanted impurities may result in poor film formation of the material as well as making the material hard to evaporate and sublime.

In addition, the presence of the contaminants can cause a lowering of the mobility of the charge carriers as they act as defect centers that can capture charge. For example, highly purified Alq3 shows relatively nondispersive transport in time-of-flight mobility measurements in comparison to the unpurified or air-exposed material [5]. Moreover, these defect centers can also act as fluorescence quenching centers and lower PL efficiency. This shows that the purification of the organic material is an essential step prior to device fabrication. We carried out purification of all our materials either via train sublimation in a Pyrex glass tube or sublimation in a Kurt J. Lesker SPECTROS evaporation system. The description of the purification with the experimental set up is presented in section 2.2.2.1.

2.2.2.1 Train sublimation

Figure 2.1 shows the system of train sublimation used for purification of Alq3, Gaq3, Inq3 and Liq. 1g of the organic material to be purified was placed in a glass boat of ~3cm length and 1.5cm inner diameter. A Pyrex glass tube of length ~27cm and ~1.5cm inner diameter was used as an inner tube to collect the pure and sublimed
material. A Pyrex test tube of approximately 31cm length, 1.8cm inner diameter and 2.2cm outer diameter was used as housing for the purification column. One end of the housing was inserted into the furnace tube of *Carbolite Furnace* near to the center. The thermocouple was also inserted inside the furnace to monitor the temperature in the column. A *Turbotronik NT 10* turbo pump and *Trivac* rotary pump attached at the other end of the housing column maintain the vacuum in the system, and a combined *Penning/Pirani gauge* was used to measure the pressure inside. The vacuum in the system was kept at <10^-6 mbar during the evaporation.

**Figure 2.1**: *Train sublimation system for purification of Alq3 (Typically at 325°C and 5.3×10^-7 mbar).*

Initially, the organic material was heated at a fast rate of ~5°C/minute until the temperature reached ~150°C maintaining the constant pressure of <10^-6 mbar in the system. Once the above temperature was attained, the system was left at this temperature for about 6 hours for outgassing. Afterwards the rate of heating was slowed down to ~5-10°C/hour, until evaporation started to occur. The temperature afterwards was kept constant for evaporation and sublimation over several days.

After the completion of sublimation, the heater was switched off and the system was left to cool for at least 5 hours. The pump was then switched off and the sublimation column was taken out. The pure material was stripped from the glass tube and stored in a screw top jar under vacuum. Low-density fluffy material which was usually brown or black in color was left as a residue in the boat. This residue generally weighs less than
1% of starting material and mostly insoluble in solvents such as dichloromethane, methanol, chloroform and acetone. Table 2.1 summarizes the sublimation results for materials Alq₃, Gaq₃, Inq₃ and Liq. Gaq₃ and Inq₃ used were synthesized according to Ref. [6] and references therein. The rest of the Mqs were sublimed in the evaporator (section 2.2.2.2).

Table 2.1: Summary of Zone sublimation for Alq₃, Gaq₃, Inq₃ and Liq. The evaporation temperature presented in column 5 was the temperature at which the deposit was first seen in the cold portion of the sublimation column and that presented in column 6, was that noted in the SPECTROS evaporator under a pressure 10⁻⁷ mbar at a rate ~0.2Å/s (during device fabrication).

<table>
<thead>
<tr>
<th>Material</th>
<th>mass used (g)</th>
<th>mass of yield (g)</th>
<th>Yield (%)</th>
<th>Evap. Temp (°C)</th>
<th>Evap. Temp. (purified mat.) (°C)</th>
<th>Color of purified material</th>
<th>Color of residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq₃</td>
<td>1.3</td>
<td>1.02</td>
<td>78.46</td>
<td>230</td>
<td>185</td>
<td>yellow</td>
<td>brown</td>
</tr>
<tr>
<td>Gaq₃</td>
<td>1.21</td>
<td>0.87</td>
<td>71.90</td>
<td>227</td>
<td>190</td>
<td>yellow</td>
<td>brown</td>
</tr>
<tr>
<td>Inq₃</td>
<td>1.22</td>
<td>1.03</td>
<td>84.4</td>
<td>263</td>
<td>200</td>
<td>dark yellow</td>
<td>brown</td>
</tr>
<tr>
<td>Liq</td>
<td>0.65</td>
<td>0.2</td>
<td>30.77</td>
<td>340</td>
<td>235</td>
<td>pale white</td>
<td>black</td>
</tr>
</tbody>
</table>

2.2.2.2 Sublimation in Kurt J. Lesker SPECTROS Evaporation System

Kurt J. Lesker SPECTROS evaporation system (described in section 2.3.5.1) can be used as a purification system as it provides more flexibility in temperature and pressure than the normal train sublimation system described in section 2.2.2.1. As the system chamber is evacuated by a cryopump, the pressure inside the system is less than 10⁻⁷ mbar. Further it is very quick to recover the vacuum if volatile materials are released during the purification process. This helps to prevent the initial organic material from degradation before evaporation and sublimation. Further, the manual heating system as well as PID control enables us to control the heating power of the source to control the temperature/rate very accurately (within ±5°C/0.2Å/s). A residual gas analyzer (RGA) is also fitted inside the process chamber, which can be used to analyze the impurities coming off during evaporation. This enables us to determine the impurities present in the material.
The organic materials to be purified were heated in one of the crucibles. Instead of the normal lid of the evaporation source, a cleaned glass slide was placed exactly on the top of the crucible using an aluminum holder. The glass slide was thoroughly cleaned as described in section 2.3.1. Once the vacuum pressure was less than about 10\(^{-7}\)mbar, the heater was switched on manually so that the rate of temperature rise was kept at \(~5^\circ\text{C}/\text{minute}\) initially. Near to the evaporation temperature (generally above 100\(^\circ\text{C}\)), heating was slowed down to keep temperature rise \(~1^\circ\text{C}/\text{per minute}\). Once the evaporation occurred the temperature was kept constant for several hours (at least 5hrs). The pure material was sublimed and collected on the glass slide above. Finally the pure material was stripped off the glass slide and stored under vacuum. Table 2.2 summarizes the sublimation results for all Mqs (except Liq) and BCP hole blocking material that we have sublimed in a Kurt J. Lesker SPECTROS evaporation system.

**Table 2.2: Summary of sublimation in a Kurt J. Lesker SPECTROS evaporation system.**

The evaporation temperature presented in column 5 was the temperature at which the deposit was first seen on a glass slide and while that presented in column 6, was that noted in the evaporator under a pressure 10\(^{-7}\)mbar at a rate \(~0.2\text{Å/s}\) (during device fabrication).

<table>
<thead>
<tr>
<th>Material</th>
<th>mass used (g)</th>
<th>mass of yield (g)</th>
<th>Yield (%)</th>
<th>Evap. Temp. (°C)</th>
<th>Evap. Temp. (purified mat.) (°C)</th>
<th>Color of purified material</th>
<th>Color of residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naq</td>
<td>1.08</td>
<td>0.53</td>
<td>49.07</td>
<td>310</td>
<td>250</td>
<td>Yellow</td>
<td>black</td>
</tr>
<tr>
<td>Kq</td>
<td>1.12</td>
<td>0.8</td>
<td>71.43</td>
<td>310</td>
<td>265</td>
<td>Yellow</td>
<td>black</td>
</tr>
<tr>
<td>Rbq</td>
<td>0.8</td>
<td>0.3</td>
<td>37.50</td>
<td>303</td>
<td>256</td>
<td>pale yellow</td>
<td>black</td>
</tr>
<tr>
<td>Csq</td>
<td>1.78</td>
<td>0.7</td>
<td>39.33</td>
<td>258</td>
<td>204</td>
<td>dark yellow</td>
<td>dark brown</td>
</tr>
<tr>
<td>BCP</td>
<td>0.5</td>
<td>0.45</td>
<td>90</td>
<td>150</td>
<td>145</td>
<td>pale white</td>
<td>brown</td>
</tr>
</tbody>
</table>

**2.3 Device Fabrication**

The starting material for device fabrication is an ITO coated (~1250Å) glass substrate purchased from Merck. The substrate size was 20mm×20mm with a sheet resistance of \(~13\Omega/\text{Square}\). Firstly, ITO was made dust and contamination free by scrupulous cleaning. The cleaning was crucial as any failure in the cleaning procedure resulted in poor device performance. The ITO anode was patterned by photolithography and etching before evaporation of the organic materials. The details of cleaning
processes, photolithography, etching and fabrication of the device are presented in sections 2.3.1 to 2.3.5.

2.3.1 Cleaning

The ITO substrate was first wiped by tissue paper dipped in isopropanol. The substrate was then cleaned by rubbing with detergent and water. It was then ultrasonicated in deionized water and detergent for about 20 minutes. Further ultrasonication were done in deionized water three times for 5 minutes each time. After this, the substrate was ultrasonicated in acetone and chloroforms twice each for 5 minutes. Finally it was dried using nitrogen gas.

2.3.2 Spin Coating

The substrate was spin coated with a positive photoresist S 1818 sp16 (purchased from Shipley) in a spin coater. The substrate was put at the center of spin coater with the ITO surface facing upward, as the vacuum generated by a vacuum pump held the substrate securely during the spinning. About 12 drops of photo resist were dropped on it using a disposable pipette and the spin coater was set to a spin rate of 6000 rpm. The substrate initially spun at slow rate about 2000 rpm for 20 secs to make surface wet with photo resist and then accelerated up to the higher rate to form a uniform coat on the surface. The substrate was baked in a pre-heated oven at 90°C for 15 minutes.

2.3.3 Photolithography and Etching

ITO substrates during device fabrication were patterned by photolithography. Photolithography is the process of transferring the images from the mask to the surfaces in order to define areas which form the devices. It is done by using suitable material called a photo resist, on which upon exposure to UV light, the image of the mask is transferred. The UV exposed area becomes soluble in the developer solution. The remaining photoresist protects the underlying device area during etching.

ITO surface with spin-coated photoresist was exposed to UV light using a mask for one minute. UV exposure unit LV 202E was used for this purpose. As the photoresist used was positive, upon exposing it to UV, it was softened and removed from the ITO surface during the development process. A NaOH solution, commercially named as Microposit 351 developer, was used as a developer and the photoresist on the unexposed area remained on the substrate protecting the ITO underneath.
The unwanted ITO (exposed ITO) was removed from the substrate by etching. Etching of ITO was done by dipping it in a mixture of 2% HNO₃ and 48% of HCl in 50% of distilled water heated to 50°C for 2 minutes. Finally the substrate was ultrasonicated three times in deionized water and rinsed in acetone to strip off the remaining photoresist.

**Figure 2.2:** Patterned ITO substrate ready for plasma treatment and device fabrication. The rectangular middle stripe of ITO acts as an anode in the OLED structure while the small square of ITO areas are to assist the cathode contacts.

The substrate once again underwent a rigorous cleaning process as described earlier before plasma treatment and deposition. Figure 2.2 shows the etched substrate ready for plasma treatment. The central strip of ITO on the substrate worked as common anode to all four diodes, while small square ITOs were to assist the cathode contact.

### 2.3.4 Plasma Treatment

To remove any remaining contamination from the patterned ITO and increase the work function of ITO, the surface was exposed to oxygen plasma for a certain time at fixed power and pressure inside a *Diner Electronic Femto plasma system*. The ITO substrate was transferred into the chamber of the plasma treatment system with the ITO facing upwards immediately after cleaning and drying. The system was pumped down to a pressure of ~0.3 mbar using a rotary pump. Oxygen gas was let into the chamber and the flow was controlled by a needle valve. To make sure that the chamber was filled only with oxygen, the gas flow was increased to keep the pressure at ~1.5 mbar for at least 5 minutes. The power of the plasma system and treatment time was adjusted to 30 W and 3 minutes. Once the pressure of the oxygen gas was lowered to ~0.2-0.3 mbar,
the generator was switched on to generate an oxygen plasma and the substrate was treated for the desired time. The substrate was then loaded into the load lock for evaporation.

2.3.5 Deposition of Organic Layers and Cathodes

Organic materials used in the fabrication of OLEDs are sensitive to the air and water present in the atmosphere, so the device fabrication is possible only under vacuum conditions (pressure \(< 10^{-7}\text{mbar}\)). Under such pressure, the influence of such external factors can be reduced and the device quality and lifetime can be controlled and improved. For this purpose, a *Kurt J. Lesker SPECTROS evaporation system* was used (shown in Figures 2.3 and 2.4). A detailed description of the system is presented in section 2.3.5.1.

2.3.5.1 Description of Kurt J. Lesker SPECTROS Evaporation System

The *Kurt J. Lesker SPECTROS evaporation system* is a computer controlled evaporator system designed for the evaporation of low temperature organic materials and metals. The system contains two parts, process chamber (PC) and load lock (Figure 2.3). The PC has a cryo pump with a scroll pump as a backing pump to keep the chamber pressure less than \(10^{-7}\text{mbar}\) while the load lock is fitted with a Turbo molecular pump with a scroll backing pump and has an ion gauge to measure the pressure. Both load lock and PC can be vented either automatically or manually and, during the process, nitrogen gas is purged to the respective chambers in order to prevent the chambers being contaminated with water and oxygen from the air. During the venting process of the load lock, an automatic gate valve closes to isolate the PC and vice versa.

There is a sliding front door on the PC, which provides a facility to replace sources, materials and crucibles. The substrate/mask array (cassette) in the main chamber makes mask exchange and substrate loading easy. The cassette box has a Z-shift to vary the substrate position from 20cm to 40cm from the source. The rotation rate of 1-10 rotations per second of the cassette provides more uniformity in the deposition on the substrate. The mask changing, substrate insertion and removal can be done manually. The load lock contains a retractable arm with a fork at the end to hold the substrate holders and the masks. When the gate valve is opened, the arm can be inserted in the PC to load the substrate or/and mask into the respective cassette. There are four
different cassettes (levels) in the cassette box i.e. three different masks and one deposit cassette.

**Figure 2.3:** Kurt J. Lesker SPECTROS evaporation system used in device fabrication. The gate valve isolates the load lock and the process chamber. The retractable arm in the load lock allows loading the substrate and mask holders in the process chamber.

The evaporator system in the PC consists of six organic sources and two metal sources (see Figure 2.4). The organic sources are low temperature organic sources that have the ability to deposit volatile organic materials suitable for OLEDs fabrication. The power for the sources is fed through the power unit programmed by SQS software. The power of the organic sources can be varied in order to change the temperature ranging from 50-500ºC. The organic source has an efficient winding system to give optimum heating of the crucible, which will evenly heat up the material in the crucible and reduces the organic “spitting”. The source can hold an alumina crucible of 2.5cm diameter, 5cm high and 15cc capacity. The base of the crucible is fitted with a thermocouple to measure the temperature. On the top, it has a pneumatically controlled flip shutter, which closes as soon as the desired thickness is achieved on the substrate. A flip shutter can be removed easily while cleaning and exchange of the organic materials and crucibles is carried out. The source is mounted at an angle 5-20degrees to the horizontal to help the plume distribute evenly on to the substrate from the crucible.
Figure 2.4: The process chamber (PC) of a Kurt J. Lesker SPECTROS evaporation system. It contains six organic and two metal sources. The movable cassette, which is an array of mask and substrate holders, is also shown at the top.

The metal evaporation sources are located at the bottom part of the PC chamber (Figure 2.4) shielded by a cylindrical housing and a horizontal shield. The metal sources are resistively heated, and controlled directly by the power unit operated by SQS software. Each metal source has a crucible shutter as well as vertical and horizontal shield that prevent the cross contamination. There is a substrate shutter in between the evaporation unit and the cassette box which prevents deposition of material before the desired rate is set.

The deposition rate of the material is monitored by the quartz crystal monitors, which are capable of measuring the thickness to about 0.5% accuracy. The deposition monitors are programmed for each material to measure the rate accurately by programming a SQS-242 thin film deposition controller. The software requires the density and Z-ratio for each material in order to have accurate thickness. The Z-ratio is the parameter that corrects the frequency change to the thickness transfer function to
account for the acoustic impedance mismatch between the crystal and coated material. As the film thickness monitor is not placed at the same distance from the source as the substrate, it is necessary to account for the flux differences between the deposition monitor and the actual substrate. The correction factor used for this purpose is called a tooling factor or calibration factor and needs to be determined experimentally for each material, source and sensor.

The tooling factor is relative to the position of the monitor. The substrate may receive more or less material according to its position relative to the monitor as in Figure 2.5(a) and (b). The tooling factor for a monitor is more than 100% if it sees less than the substrate as shown in Figure 2.5(a) while it is less than 100% as monitor sees more than the substrate for Figure 2.5(b).

Figure 2.5: (a) Substrate sees more than the monitor and tooling is over 100 % and (b) substrate sees less than the monitor and tooling is less than 100%.

The relation for the calculating the tooling factor is:

$$TF(\%) = TF_{\text{initial}} \times \frac{T_{\text{measured}}}{T_{\text{monitor}}} \text{  \hspace{1cm} (2.2)}$$

Where $TF$ is new tooling factor, $T_{\text{monitor}}$ is the value of thickness displayed on the monitor and $T_{\text{measured}}$ is the measured thickness. Similarly, keeping the tooling factor constant, the density factor can be changed for a given material by:
\[ DF(\%) = DF_{\text{initial}} \times \frac{T_{\text{monitor}}}{T_{\text{measured}}} \] ………… ………(2.3)

Where \(DF\) is new density factor to be used in the place of density of old value, \(T_{\text{monitor}}\) and \(T_{\text{measured}}\) is the values mentioned above.

### 2.3.5.2 Evaporation of Organic Materials

Immediately after plasma treatment, the substrate was transferred onto the substrate holder. Screws were used to hold the substrate at a fixed position in the substrate-space. A picture of the substrate holder and masks is shown in Figure 2.6.

**Figure 2.6**: (a) A substrate holder, (b) an organic mask and (c) a metal mask used for device fabrication in the vacuum system.

The substrate holder was then transferred onto the arm in the load lock and inserted into the deposition cassette just on the top of the square mask (10mm×10mm). For all organic materials, the square mask (Fig 2.6(b)) was used. The cassette was lowered to the deposition position. The system was ready for evaporation of the organic material when the pressure reached less than \(5 \times 10^{-7}\) mbar. The SQS 242 software was used to control the preheating and deposition of organic materials. The organic material was heated with two ramps and two soak powers to give the desired constant rate. Once a reasonable rate was achieved and the deposition phase begun, PID terms of SQS 242 software controlled the power to give a constant rate. Different PID terms can be introduced in the software in order to get a constant evaporation rate of the material. \(P\)
terms stands for the proportional power term, which increases the gain of the loop proportional to the difference between the target temperature and the present temperature of the material. Suitable values of $P$ give a smooth and a constant evaporation rate for long periods. $I$ is the integral term that controls the time response and a small value such as 0.5 to 1, makes the response of the loop smooth. $D$ term is the differential term which causes the loop to respond quickly to changes in the rate. PID terms are chosen so that the rate of evaporation remains constant during the whole deposition period. For organics, an evaporation rate of $\sim 2\text{Å/s}$ was used. Typical example of the evaporation rate variation with temperature for TPD, Alq$_3$ and BCP are shown in Figure 2.7. Thin interface layers of organic materials such as Mqs were deposited at a very low rate $\sim 0.2-0.4\text{Å/s}$. After the deposition of organics was completed, the mask was changed for cathode evaporation.

![Figure 2.7: Typical examples of evaporation rate variation with temperature for TPD, Alq$_3$ and BCP during device fabrication.](image)

### 2.3.5.3 Evaporation of the Cathode

For the cathode, aluminum was evaporated from the thermal source. About 35 pellets of Al were put in a titanium diborate crucible. It was out gassed before evaporation on to devices in order to prevent device heating as well as to prevent contamination from impurities in the Al pellets. Usually, when Al was out gassed, the pressure in the PC dropped to $10^{-5}\text{mbar}$ (or even more) which could cause poor device performance. Hence, every time the Al pellets were topped up, out gassing was done as
a routine procedure. During the out gassing of Al, devices on which organics had already been deposited were kept isolated in the load lock.

![Device Structure Diagram]

**Figure 2.8:** (a) Device structure of an ITO/TPD(500Å)/Alq3(500Å)/Mq(10Å)/Al OLED with Top and side view and (b) one such device under operation at drive voltage of 4V with a current density ~36Am⁻² and a light output of intensity ~0.33Wm⁻². The device area is ~4mm².

The cathode mask (shown in Figure 2.6(c)) was loaded into the deposit cassette. The substrate was then loaded onto the mask and the cassette lowered to the deposition position. As in the case of organic materials, deposition of Al was also done by SQS 242 programming. For ~100Å of Al, the evaporation rate was kept ~1Å/s and then was increased up to 10Å/s for the remaining 900Å. The device was taken out of the PC and kept in the load lock until the measurements were performed on it.
LiF was evaporated at a low rate, ~0.2Å/s for ~10Å and the square mask was used for this purpose, in order to minimize shadowing of the thin LiF layer. The evaporation of Mg and Ag cathodes was done similar to that of the Al cathode. The co evaporation of Mg and Ag was done by evaporation of Mg and Ag using two different sources at a rate of 10 Å/s and 1Å/s respectively.

A typical device structure of an OLED prepared by this procedure is illustrated in Figure 2.8(a), with a fabricated device under operation at 4V in Figure 2.8(b).

2.4 Experimental Methods

2.4.1 Current-Voltage-Luminance (J-V-L) Characteristics Measurement

Measurement of the J-V-L characteristics of the OLEDs was performed immediately after the diode fabrication, always within 2hours. For the J-V-L characteristics, a Keithley 236 voltage/current source measure unit was used to drive the diode and to measure the current. The device was placed into the sample holder, which contained electrical contacts, one common anode for the ITO and four different cathodes which were in turn connected to the source measure unit. In order to measure the light output from the device, an integrating sphere and a Newport 1830-C optical power meter were used. The scattered light from the diode was allowed to fall inside the integrating sphere, which was measured by the calibrated Silicon photo detector of the Newport 1830-C and displayed by the power meter in watts. For the J-V-L characteristics the diode was driven well below its breakdown voltage (less than 15V). The instruments were interfaced to a desktop computer using intensity software written in visual basics.

After measurement, the device area was measured using a traveling microscope with a precision of ±0.01mm. The thickness of the organic layer was measured using a Dektak 3ST profilometer.

2.4.2 Built-in Voltage (V_{bi}) Measurement

Built-in potential (V_{bi}) measurements of PLEDs structures have been already demonstrated by Brown et al. in order to probe the energy level alignment of the cathode with that of the polymer [7, 8]. Simply by measuring the V_{bi} in a completed device, the increase or decrease of the work function of cathode W_{cathode} and the
corresponding decrease or increase in the electron injection barrier height can be calculated. Assuming the work function of the anode and cathode are within the energy gap of the organic and considering no interfacial dipoles at the metal/organic interface, \( V_{bi} \) is simply the difference between the work functions of the cathode and anode:

\[
e V_{bi} = W_{anode} - W_{cathode} \tag{2.4}
\]

Where \( V_{bi} \) is the built-in potential, \( W_{anode} \) is the work function of anode, \( W_{cathode} \) is the work function of cathode.

If there is an interfacial dipole then the relation is modified to

\[
e V_{bi} = W_{anode} - W_{cathode} - \Delta \tag{2.5}
\]

Where \( \Delta \) is the magnitude of the dipole formed at the interface.

The built-in potential is determined easily using saturated photovoltaic measurement techniques in OLEDs [9]. Since the free carrier density in the organics is very small, the current due to the built-in electric field is small. When the OLED is irradiated with light, it generates photocarriers. The carriers drift under the influence of the built-in electric field and give rise to a photocurrent. When a positive voltage applied to the device, the effective voltage across diode is \( V_{applied} - V_{bi} \). At \( V_{applied} = V_{bi} \) the photocurrent goes to zero and it changes sign once \( V_{applied} > V_{bi} \). The applied voltage at which photocurrent goes to zero is the compensation voltage and is equal to the built-in potential of the device.

**Figure 2.9:** A schematic set up for the built-in potential measurement of the OLED devices.

Experimentally it is determined by irradiation of laser light, of wavelength 405 nm with intensity 25mW, on the device. Figure 2.9 shows a schematic setup for the
measurement. To apply the bias and measure J-V characteristics of the devices, a *Keithley 236 voltage/current source measure unit* was used. The voltage applied to the diode was from -2 to +3V. In order to make sure that the device was saturated with the given intensity of incident light, neutral density filters (ND) were introduced between the diode and the laser light. This process is very important to ensure the device is saturated at given intensity because $V_{bi}$ could depend upon the illumination and bias history of the diode, if it was not saturated then the measured built-in voltage may not be reproducible and reliable. For this purpose, the measurements were made with different laser intensities, achieved using ND filters, and $V_{bi}$ was recorded as a function of intensity. The device was made saturated at least two higher intensity levels and the $V_{bi}$ was obtained as the average of these two readings.

Further, the built-in potential measured by J-V was alternatively checked and confirmed by using a *Keithley 236-voltage/current-source measure unit* as a high impedance voltmeter. By setting, $J=0$, it measures the voltage across the device, which is the value of $V_{bi}$, and should be equal to that measured by the first method.

Once the $V_{bi}$ was measured, with the reference of anode work function, the cathode work function was calculated and compared to the standard work function of cathode. The deviation of the calculated value from the literature value, enable us to study the interfacial nature and the barrier height lowering for electrons with respect to control cathode e.g. aluminum in the device.

### 2.4.3 Electroluminescent (EL) and Photoluminscent (PL) Spectra Measurement

For the measurement of EL spectra, the light output of the OLEDs was focused into a *550-traix spectrometer* with the help of focusing lenses. The spectrometer was equipped with a *Thorn EMI 9202B S-20 photomultiplier tube and PerkinElmer 7265 DSP lock-in amplifier* to collect the output. The device was driven by a square pulse obtained from a *TG1010 a programmable DDS function generator*. The same pulse was also used as the reference signal for the lock-in amplifier in order to detect the output signal. All EL spectra were collected at room temperature only.

PL measurements were done using the powder form of the organic materials, which were purified either by train sublimation or in the evaporator. The sample was placed in the cuvette and attached to the sample arm, which then was mounted inside
the cryostat. The material was excited using a 405nm laser. A mechanical chopper was introduced in the path of the laser provided the reference signal for the lock-in amplifier. A suitable filter was used in between the mechanical chopper and the detector, in order to remove the effect of any laser present in the PL output.

After collection of the PL/EL spectra, it was corrected for the system response. For the purpose, a correction curve obtained for the detector (saved in the computer) was used to multiply the collected spectra.

2.4.4 UV-Visible Absorption Spectra Measurement

UV-Visible absorption spectra for all organic materials were measured by using a Hitachi U-3000 spectrophotometer. Organic material was dissolved in a suitable solvent such as chloroform or methanol. A cuvette containing the solvent was placed in the reference beam and one with organic solution was placed in the sample beam to obtain the absorption spectra of the organic material. The obtained absorption spectrum of organic material was automatically corrected in reference to background spectra of the solvent and the system response.

To measure the absorption spectra of TPD, BCP and Alq3, chloroform was used as the solvent, while for alkaline metal quinolates, methanol was used. About 0.5g of substance was dissolved in 50ml of solvent and the absorption spectra were recorded. It is then converted into molar absorbtivity by dividing the concentration by the molecular weight of the material.

2.4.5 Magnetoresistance (MR) Measurement

Figure 2.10 shows a schematic diagram for organic magnetoresistance measurements (OMR) of the devices. An electromagnet was used in combination with a variable power supply to generate the magnetic field. The power supply varies the current through the electromagnet in order to change the magnitude of the magnetic field from 0 to ~300mT. The measurement of magnetic field was taken using a calibrated Hirst GM05 Gauss meter. The light output from the device is measured by a silicon photodiode (Newport 818-SL) in cooperation with a Newport 1830 power meter. The device was placed in between the poles of the electromagnet in such a way that the direction of current flow in the device is perpendicular to the applied magnetic field.

Before the OMR measurement, the calibration curve for the magnet was recorded (i. e. B vs I). For this purpose, the magnet was initially switched off for several hours. A
A Gauss meter was inserted exactly about the middle of the core of the magnet. The gauss meter was kept perpendicular to the magnetic field and value of the B was recorded for different values of current (I) flowing the magnet. The graph of B vs I obtained was used to find the value of B at desired I. The null field current for the magnet was measured by inserting a Gauss meter in a similar way. The current in the magnet was adjusted in order to get the magnetic field to zero in the Gauss meter. The system was left for about a couple of minutes to stabilize the magnetic field. The value of the current that corresponds to the null field was noted. This value of the current was applied to the magnet in order to get null field in subsequent OMR measurements whenever needed. The null field measurement was done at least two times, at the beginning and the end of the experiment. Occasionally, sometimes due to the drift of the magnet, the null field measurements were done several times.

**Figure 2.10:** A schematic set up for the magnetoresistance measurement of the OLEDs. The OLED is placed in the light-tight holder adjacent to the light detector and is placed between the poles of an electromagnet, so that the direction of current flow is perpendicular to the magnetic field.

OMR measurement was done immediately after the J-V-L characterization. The device was placed in a light-tight sample holder with a silicon detector on the top of the surface of the device. The device was kept under a pressure \( \sim 10^{-6} \) mbar with help of a system of vacuum pumps in order to reduce degradation. During the measurement, the
device was operated at constant voltage with the voltage varying from ~1.0V to ~10V. A Keithley 236-voltage/current-source measure unit was used as a voltage source as well as for current measurement. The current measurements were averaged over 32 readings. OMR measurements were done for magnetic fields between 0 and 300mT. The null field current measurements were taken twice, before and after the application of the magnetic field and the average value of this measurement was used as the null field current in the device. This value of null field current was used to calculate the percentage change in current and efficiency in the device after the field measurements were done. The process was developed in order to eliminate any effects due to the device performance drifting, which is normal at high drive voltages. Further, to minimize the device drift and degradation, the drive voltage was applied only when the magnetic field in the device was stable, while the rest of the time the drive voltage switched to zero.

2.5 References

Chapter 3

Energy Level Offsets at Interfaces of Organic Small Molecule and Metal electrodes

3.1 Introduction

Injection mechanisms of charge carriers at metal contacts in multi-layered OLEDs have received considerable attention because such contacts are ultimately responsible for the efficient operation of the device. Since the contacts are responsible for the carrier concentration into the device, they play a major role on determining the device parameters such as power efficiency, turn-on voltage, injection efficiency etc. Thin films of small molecule organic semiconductors, such as Alq3, are found to be most efficient in multilayer device structures [1-5]. The thin multilayer device architecture of OLEDs, however, presents several challenges due to the many organic/organic and organic/metal interfaces which are located within only a few molecular layers of each other and these interfaces have different characteristics than the bulk materials.

Recently, many investigations relating to the interfaces of organics and metals have shown that the traditional model of a common vacuum level is not applicable to organic systems [6-8]. This is due to interface modification at the contacts because of various reasons such as interfacial dipole formation, band bending, interfacial chemical activities, doping etc. As the most widely used emissive material, Alq3 has been extensively studied with many metal interfaces using UPS and XPS [9-16]. The studies found that there is a dipole formation at Alq3/metal interfaces. More recently, Brown et al. introduced the built-in potential measurement by electroabsorption to study the interfaces of a PLED device and successfully demonstrated how the measured value of built-in potential can be used to probe the energy level alignment at the cathodes in their finished polymer devices [17, 18].

In this chapter we investigate the energy level alignment at the interfaces of small molecule organic materials such as TPD, Alq3, Gaq3 and Liq with different cathodes such as Al, LiF/Al, Mg:Ag and Ag by measuring the built-in potential (V_{bi}) by a saturated photoconductivity measurement. Further we demonstrate that our simple built-in potential measurement agrees well with the UPS measurement done by other groups.
for well known materials such as Alq₃ and TPD. Finally an energy level diagram is drawn for each of material/cathode interface to understand the energy level alignment at the interfaces and calculate the charge injection barriers.

### 3.2 Experimental

The $V_{bi}$ measurements were done on a set of single layer TPD devices with Al and LiF/Al cathodes. For each measurement at least two sets of devices with the structure ITO/TPD(1000Å)/Al(1000Å) or LiF(10Å)/Al(1000Å) were fabricated with and without plasma treatment. For the plasma treatment, cleaned ITO substrates were treated for 3 minutes at a pressure of 0.2-0.3mbar and at a r.f. plasma power of 30W. The 3 minute treatment time as well as the pressure and power values was chosen by the previous optimization of devices. The optimization of devices was initially performed by fabricating double layer Alq₃ devices on the plasma treated ITO with different exposure times, varying from 1-6 minutes at same power and pressure.

For $V_{bi}$ measurements, a laser, of wavelength 405nm and power 25mW, was used to generate photocarriers in the device. The current-voltage (J-V) characteristics of the devices were measured under saturated illumination. The saturation of the device was tested by reducing the incident intensity using neutral density filters as described in section 2.4.2. The reproducibility of the devices was tested for at least two different sample batches.

The $V_{bi}$ measurements were done on a set of single and double layer Alq₃ devices with Al and LiF/Al cathodes. For each measurement at least two sets of devices with the structure ITO/Alq₃(1000Å)/Al(1000Å) or LiF(10Å)/Al(1000Å) and ITO/TPD(500 Å)/Alq₃(500Å)/Al(1000Å) or LiF(10Å)/Al(1000Å) were fabricated on plasma treated, cleaned ITO substrates. TPD and Alq₃ deposition was done at a rate of 2.5Å/s immediately after plasma treatment. After fabrication, devices were measured for the built-in voltage $V_{bi}$ as described in section 2.4.2.

Similarly $V_{bi}$ was measured for a set of Gaq₃ and Liq devices with different cathodes such as Al, LiF/Al, Ag and Mg:Ag. The evaporation rate used for Gaq₃ and Liq was ~2.5Å/s.
3.3 Results and discussion

3.3.1 ITO/TPD/Metal Interfaces

Indium tin oxide (ITO) is an excellent material for using as an anode in OLEDs due to its semiconducting and transparent nature. The properties of ITO have been widely studied by many groups [19-22] and the conducting properties such as surface energy, sheet resistance and work function are mostly dependent on its chemical and physical properties [19, 20]. The high work function of ITO is preferred in order to provide the lowest energetic barrier for hole injection in organic materials, especially to the hole transport or injection layer. Many approaches have been made in order to increase the work function using physical processes such as mechanical cleaning [19], plasma treatment in different environments such as Ar, O₂, H₂, UV-ozone [23], and chemical treatments such as acid-base, acid treatments, etc [19, 24].

One of the most widely used methods to increase the work function of ITO is oxygen plasma treatment, as it gives the highest work function, ~4.75eV, and the high work function can be retained for long storage periods [19]. There is much work related to the determination of the work function of plasma treated ITO but the absolute value of it is again dependent on the many experimental parameters and measurement techniques. The literature value of work function for bare ITO is ~4.5±0.1eV while that of plasma treated ITO varies from 4.4 to 5.2eV depending upon the measurement techniques and the variables of the plasma treatment such as power, exposure time and oxygen pressure [23, 25].

As ITO plays vital role in our device optimization, it is very important to study the effect of plasma treated ITO on the device performance and determine the work function at the optimized oxygen plasma treatment (the optimized exposure time at constant pressure and power). In this chapter, we investigate the effect of the oxygen plasma treatment on the device performance by monitoring the built-in potential in single layer TPD devices. With the help of the built-in potential in the devices, the work function of plasma treated ITO is determined. The shift of the work function towards a high value and the corresponding decrease of barrier height for hole injection is also calculated. Finally an energy level diagram for a single layer TPD device is presented.
3.3.1.1 $V_{bi}$ by Saturated Photoconductivity Measurement

Figure 3.1 shows the photocurrent characteristics on a typical device of untreated ITO/TPD/LiF/Al as a function of laser intensity. The photocurrent increases with increasing laser intensity. The photocarriers generated due to irradiation move under the influence of the potential difference between the ITO and cathode. When the bias voltage is applied, the carrier is under the influence of both the applied and the built-in potential. The photocurrent will be zero once the built-in potential is equal to the applied bias. The point $V_{bi}$ is the open circuit voltage when the current under illumination is zero.

![Graph showing photocurrent vs. bias voltage characteristics](image)

**Figure 3.1:** Photocurrent vs. bias voltage characteristics for a device with untreated ITO/TPD/LiF/Al in semi log plot, parametric in intensity (laser wavelength 405nm and maximum intensity 25mW).

The value of $V_{bi}$ obtained from J-V characteristics was compared with that obtained directly by setting $J=0$ in the source measure unit. In this case, the source measure unit acts as a very high impedance voltmeter and measures the potential difference between the two electrodes, yielding $V_{bi}$. The comparison of values of $V_{bi}$, obtained by these two different techniques is shown in Figure 3.2 and a summary is presented in Table 3.1. The values of $V_{bi}$ measured by these two methods are averaged
and used to calculate the work function shift of the cathode, barrier heights for electrons and holes and a vacuum level shifts at the interfaces.

From Figure 3.1 and 3.2, it is clearly seen that the device is saturated only above 90% laser intensity. Below this level, even though there is generation of photocarriers, the J-V characteristics show a lower open circuit voltage $V_{bi}$ than the saturation value, depending upon the amount of charge generated and how this charge dissociates at the electrodes. The curves of photocurrent variation with bias voltage are symmetric (see Figure 3.1) for values close to $V_{bi}$ and depend only on the intensity of the light. When $V_{applied} > V_{bi}$, there is a positive voltage drop across the device, injecting the charge carriers from the electrodes and causing the device to turn-on. At this point the current in the device increases and the J-V characteristics become nonsymmetric.

![Figure 3.2: Comparison of $V_{bi}$ obtained from J-V characteristics and with setting $J=0$ with different intensity of incident laser light of wavelength 405nm and intensity of 25mW laser. Different intensity of laser was obtained by using neutral density filters (please note that the scale in X-axis is not equally spaced and linear as shown in the figure).](image)

Even when the device was saturated, at above 90% intensity, there was a slight variation on the $V_{bi}$ measured by either method (shown in Table 3.1). The decrease in the value for $V_{bi}$ measured by J-V compared to $J=0$ may be due to device degradation as $J=0$ measurements were taken after the J-V measurements. The difference between the $V_{bi}$ obtained from J-V and $J=0$, however, is ±0.03V and the batch to batch
reproducibility is ±0.05V. Other built-in measurements in the literature have variations of order of ±0.1V [17, 18, 26-28]. In this experiment, the $V_{bi}$ value is calculated from the average of two $V_{bi}$ values obtained from J-V characteristics and setting J=0 including the device to device and batch to batch variations.

Table 3.1: Summary of $V_{bi}$ obtained from J-V characteristics and with setting J=0 with different illumination level of laser.

<table>
<thead>
<tr>
<th>Intensity of laser (% of 25 mW)</th>
<th>$V_{bi}$ obtained from J-V characteristics</th>
<th>$V_{bi}$ obtained by setting J=0</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.0</td>
<td>1.68</td>
<td>1.66</td>
</tr>
<tr>
<td>93.3</td>
<td>1.66</td>
<td>1.65</td>
</tr>
<tr>
<td>50.0</td>
<td>1.56</td>
<td>1.59</td>
</tr>
<tr>
<td>31.6</td>
<td>1.54</td>
<td>1.53</td>
</tr>
<tr>
<td>10.0</td>
<td>1.31</td>
<td>1.16</td>
</tr>
<tr>
<td>0</td>
<td>0.00</td>
<td>0.02</td>
</tr>
</tbody>
</table>

3.3.1.2 Work Function of Oxygen Plasma Treated ITO

Figure 3.3 shows photocurrent characteristics for the devices ITO/TPD(1000Å)/Al and LiF/Al with and without oxygen plasma treatment. It is clear that there is an increase in $V_{bi}$ due to the oxygen plasma treatment. The average $V_{bi}$ for the devices with an Al cathode, with and without plasma treatment, is ~(0.92±0.03)V and ~(0.60±0.05)V respectively. As the only change between these devices is the plasma treatment of ITO, this change in $V_{bi}$ is solely due to the change in the work function of the ITO induced by the plasma treatment. It is evident that $V_{bi}$ of the device increases by ~(0.32±0.05)V upon plasma treatment resulting in a decrease in hole barrier by the same amount (as $e\Delta V_{bi}=-\Delta \Phi_{\text{hole}}$ (see section 1.5.3)).

We observed similar improvements in the devices with LiF/Al cathodes after plasma treatment. The average $V_{bi}$ increased from ~(1.66±0.03)V for untreated device to ~(1.96±0.04)V for treated one and the decrease in the hole barrier was ~(0.30±0.04)V which is similar to that with the Al cathode, as described above. These results are consistent with the works published by other groups [19, 22]. Moreover, Sugiyama et al. have reported similar improvement of work function (~0.25eV) due to the oxygen plasma treatment by using techniques such as UPS and XPS [23]. In the same paper they have demonstrated that maximum improvement in the work function occurs with
oxygen plasma treatment in comparison to other treatments such as $\text{H}_2\text{O}_2$, $\text{Ar}^+$, $\text{Ne}^+$ sputtering.

The ITO work function measured by different groups using UPS has a consistent value of $(4.5\pm 0.1)\text{eV}$, even though it originates from different suppliers [19, 25, 29]. So it is reasonable to assume the work function of ITO is 4.5eV and that of oxygen plasma treated is 4.8eV (obtained by adding the effect of plasma (0.3 eV) on work function of ITO as discussed above) and this value is used for all the devices in calculations.

Figure 3.3: Photocurrent vs bias voltage in semi log plot for devices ITO/TPD(1000Å)/Al and LiF/Al with and without oxygen plasma treatment.

Figure 3.4: An energy level diagram for a single layer TPD device with and without oxygen plasma treated ITO.
An energy level diagram for plasma treated and untreated devices are shown in Figure 3.4. Considering the HOMO position of TPD to be 5.5eV [30, 31], we calculated the barrier height for holes, $\Delta \Phi_{\text{hole}}$ for plasma treated and untreated ITO devices as 0.70eV and 1.00eV respectively using $W_{\text{ITO(treated)}}= 4.8\text{eV}$ and $W_{\text{ITO(untreated)}} = 4.5\text{eV}$.

It is interesting to note that the calculated value of the hole barrier in the experiment above, is slightly higher than the recently reported value of 0.5eV from Ishii et al. for an ITO/TPD interface which was obtained by UPS [7, 8]. Further, they found a vacuum level shift at the ITO/TPD interface of a magnitude ~0.3eV downward. In our experiment, however, we are unable to see this shift. This can be due to a number of differences between the two experiments, including the nature of the organic material and ITO substrates. Moreover, the TPD used in the experiments has different levels of purity. Different cleaning procedures, oxygen plasma treatment and surface composition can change the interfacial dipole dramatically and give different values of a vacuum level shift and the ITO work function.

### 3.3.1.3 Calculation of Electron Injection Barrier Height, $\Delta \Phi_{\text{electron}}$ at TPD/Cathode Interfaces

We can calculate the barrier height for electrons, $\Delta \Phi_{\text{electron}}$ for Al and LiF/Al cathodes in TPD single layer devices using the energy level diagram in Figure 3.4. Moreover, the effective work function of cathodes can be calculated in individual devices with the help of $V_{\text{bi}}$. All the values are summarized in Table 3.2. The value of the calculated work function of an Al cathode (~3.9eV) that we have obtained here differs from the literature values (~4.3eV) [32-35]. It is, however, interesting to note that the calculated value of the work function of the Al cathode is similar for both plasma treated and untreated ITO within the experimental error (see Table 3.3). This suggests that there is a vacuum level shift at TPD/Al interface. We estimate a vacuum level shift of 0.40eV in our devices which reduces the electron barrier $\Delta \Phi_{\text{electron}}$ to 1.5eV from 1.9eV ($W_{\text{Al-E_LUMO}}= 4.3–2.4 =1.9\text{eV}$). The literature value of 2.4eV for the TPD LUMO was used throughout this work [30, 31].

Recently, the study of the energy level alignments at the interface of the organic material and other solid materials, e.g. cathode metals, has received a lot of attention. The interfacial electronic structure is estimated by lining up the separately observed electronic structure of an organic material and a cathode metal, with the assumption of a common vacuum level at the interface. This assumption is found to be not applicable [6-
Many of the results show that instead of a traditional model of a common vacuum level, there is formation of an interfacial dipole which can modify the vacuum level by \( \Delta \), the vacuum level shift. This modifies the barrier height at the interface by the same amount \( \Delta \). The vacuum level shift of TPD due to the presence of Al on the interface has been measured by UPS and it is \(~0.45\text{eV}\) [6, 36] and references therein. Their value is consistent with the calculated value of \(0.40\pm0.05\text{eV}\) presented here.

Table 3.2: Calculation of \( \Delta \Phi_{\text{electron}} \) by using \( V_{\text{bi}} \) measured in ITO/TPD/Al and LiF/Al devices with and without plasma treatment.

<table>
<thead>
<tr>
<th>Device</th>
<th>Without oxygen plasma ( (V_{\text{bi}}) )</th>
<th>With oxygen plasma ( (V_{\text{bi}}) )</th>
<th>( V_{\text{bi}})(plasma)-( V_{\text{bi}})(without plasma) ( (V) )</th>
<th>( W_{\text{cathode}}\left(W_{\text{ITO}}^{\text{r}}-W_{\text{Al}}^{\text{r}}\right) )</th>
<th>( W_{\text{change}}\left(W_{\text{Al}}^{\text{r}}-W_{\text{cathode}}\right) )</th>
<th>( \Delta \Phi_{\text{electron}}\left(W_{\text{cathode}}-E_{\text{LUMO}}\right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/TPD/Al</td>
<td>(0.60\pm0.05)</td>
<td>------</td>
<td>3.90</td>
<td>(0.40)</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>ITO/TPD/LiF/Al</td>
<td>(1.66\pm0.03)</td>
<td>------</td>
<td>2.84</td>
<td>1.46</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>ITO/TPD/Al</td>
<td>(0.92\pm0.03)</td>
<td>0.32</td>
<td>3.88</td>
<td>(0.42)</td>
<td>1.48</td>
<td></td>
</tr>
<tr>
<td>ITO/TPD/LiF/Al</td>
<td>(1.96\pm0.04)</td>
<td>0.30</td>
<td>2.84</td>
<td>1.46</td>
<td>0.44</td>
<td></td>
</tr>
</tbody>
</table>

3.3.1.4 Energy Level Diagram for TPD/Cathode Interfaces

The pictures developed for TPD/Al and TPD/LiF/Al interfaces, including the vacuum level shift are shown below in Figures 3.5(a) and 3.5(b) respectively. For TPD/LiF/Al interface, the effective cathode work function \( W_{\text{LiF/Al}} \) is \(~2.84\text{eV}\), which is smaller than the effective work function of Al, \( W_{\text{Al}} \) \(~3.90\text{eV}\) shown in Table 3.2. This suggests that there is a greater shift \(~1.46\text{eV}\) in the work function of Al due to presence of LiF, indicating that there is strong interfacial dipole formation at the TPD/LiF/Al interface that shifts the vacuum level more. This is more favorable for electron injection because it brings \( W_{\text{Al}} \) nearer to the LUMO of TPD and the barrier height \( (\Delta \Phi_{\text{electron}}) \) becomes only \(~0.44\text{eV}\). As \( W_{\text{LiF/Al}} \) is not precisely known for the interface TPD/LiF/Al in the literature, it is hard to explain at this moment, how the electron barrier, the vacuum level shift \( \Delta \) and the effective work function \( W_{\text{LiF/Al}} \) calculated from the built-in measurement in our experiment are compared to other experimental values. Comparing the consistent value of a vacuum level shift for the Al cathode calculated here with the values reported by other groups, we can assume that our value for LiF/Al can also be considered accurate.
Figure 3.5: Energy level diagrams with vacuum level shift at (a) TPD/Al and (b) TPD/LiF/Al interfaces with a vacuum level shift \( \sim 0.40\text{eV} \) and \( \sim 1.46\text{eV} \) respectively. The corresponding barrier heights for electron injection are 1.5\text{eV} and 0.44\text{eV} respectively.

Even though the experiment confirms that there is a vacuum level shift at the TPD and cathode interfaces, at present, there is no clear reason to explain the dipole formation. There may be one or many processes, responsible for it such as charge transfer, charge redistribution, chemical reaction, chemical doping, surface contamination, the image-effect, a dipole formation due to polar nature of the molecule as discussed in section 1.5.2 [7, 8]. More investigations are needed in this direction.

3.3.1.5 Summary of TPD/Cathode Interfaces

We demonstrated that the oxygen plasma treatment on ITO improves the work function of the ITO by \( \sim 0.30\text{eV} \) in our devices. Further in the interfaces TPD/Al and TPD/LiF/Al, the traditional model of a common vacuum level is not applicable due to the vacuum level shifts of \( \sim 0.40\text{eV} \) and \( \sim 1.46\text{eV} \) respectively at the interfaces. The vacuum level shift on the TPD/LiF/Al interface is larger than the TPD/Al interface and the electron injection barrier from cathode to the TPD is lowered for LiF/Al cathode.
We also demonstrated that a simple built-in voltage measurement of the device can be useful to measure the barrier height in complete devices where UPS can not be used to study the interfacial electronic structures.

### 3.3.2 Alq3/ Metal Interfaces

There are many studies aimed at understanding the interfacial electronic structure of metal cathodes with Alq3, using UPS and XPS [6-12, 15, 36, 37]. Results on such studies on Alq3 have shown that the electronic structure of metal/Alq3 obtained by just lining up the individual energy level of Alq3 and metal, assuming a common vacuum level at the interface, is not applicable when it comes to practical devices [6-8, 11, 37]. This is because of an abrupt shift of the vacuum level at the interface showing that there is the formation of an interfacial dipole. The magnitude of the dipole for Alq3/Al and Alq3/LiF/Al obtained by UPS is ~1eV and ~1.6eV respectively [6-8, 15, 37].

In this section, we study the interfacial properties of Alq3 with Al and LiF/Al by monitoring Vbi of the devices by a saturated photoconductivity measurement. Further we demonstrate how the obtained value of Vbi of the single and double layer OLED devices is used to study the interfacial structure. Furthermore, we will show the value of a vacuum level shift obtained from our calculations are consistent with the published values in the literature. This will confirm the validity of our Vbi measurement for probing the interfacial electronic structure of the OLED devices and it will allow us to use this technique on the new materials.

#### 3.3.2.1 Single Layer Alq3 Devices

Figure 3.6 shows photocurrent characteristics of single layer device of structures ITO/Alq3(1000Å)/Al(1000Å) or LiF(10Å)/Al(1000Å) and double layer device structures ITO/TPD(500Å)/Alq3(500Å)/Al(1000Å) or LiF(10Å)/Al(1000Å). The anode side of all devices is common being plasma treated ITO, with WITO(treated)=4.8eV (section 3.3.1.2). It is clearly seen that Vbi is different for the devices with different cathodes. The difference in Vbi is solely due to a change in the cathode and an increase in Vbi corresponds to a decrease in the electron injection barrier. The excitation wavelength used for the generation of photocarriers in the Alq3 layer is 405nm which corresponds to photon energy of 3.06eV. According to Ray et al., the photocarrier generation with excitation energy greater than 2.75eV or wavelength smaller than 450nm is sufficient to create the bulk photo generation in Alq3 layer [38].
Figure 3.6: Photocurrent vs bias voltage in semi log plot for Alq3 single and double layer devices with Al and LiF/Al cathodes.

The value of $V_{bi}$ obtained for an Al cathode device is $(1.41 \pm 0.02)\text{V}$. When the Al cathode is replaced by a LiF/Al cathode, the $V_{bi}$ increases to $(1.63 \pm 0.04)\text{V}$. The increase in the $V_{bi}$ clearly proves that $W_{Al}$ is lowered due to the presence of the thin layer of LiF. The increase in $V_{bi}$ is $\sim 0.22\text{V}$ compared to the Al cathode, which is equivalent to the barrier height lowering for electron injection. Average values of $V_{bi}$ for these devices are summarized in Table 3.3. The effective work function of the cathode $W_{cathode}$ is obtained from the difference of $V_{bi}$ and $W_{ITO}$. The work function of the oxygen plasma treated ITO anode is taken as $W_{ITO(\text{treated})} = 4.8\text{eV}$. The literature value of $5.8\text{eV}$ for the Alq3 HOMO was used throughout this work [30, 39-41]. The optical band gap is around $2.8\text{eV}$, calculated from absorption spectra so the estimated value of LUMO of Alq3 is $\sim 3\text{eV}$ [42]. The barrier height for electrons is calculated as a difference of the $W_{cathode}$ and LUMO of Alq3.

From Table 3.3, it is seen that the calculated $W_{Al}$ (column 3) is not the standard literature value mentioned Al cathode ($W_{Al(\text{Lit})} = 4.3\text{eV}$) [32-35]. It is interesting to note that once the Al is deposited on the Alq3 layer, the $W_{Al}$ is lowered by $\sim 0.91\text{eV}$ and the barrier height for electron injection becomes $\sim 0.39\text{eV}$. This lowering of the work function obtained is consistent with the vacuum level shift in the interface in Alq3/Al
~1.0eV measured by many other groups by UPS [6-8, 15, 37]. The barrier height for electrons reported in their work is ~0.5eV for the Alq3/Al interface. Here, it is worth to note that they used their measured value of HOMO and optical band gap to calculate the LUMO as 2.8eV. The LUMO position in our case, however, is taken as 3eV which is calculated from our previously measured optical gap ~2.8eV [42]. These kind of measurements and the estimation of the LUMO position can have several errors. Firstly while calculating the LUMO position we did not take account of the excitonic effect and a real band gap can be larger than the measured optical gap. Further, in the real device, there is relaxation of the electron once injected into LUMO, causing the LUMO to shift downwards and this is neglected in the estimation of LUMO [7].

Upon addition of a thin layer of LiF in between Alq3 and Al, Vbi is increased and the WAl shifts by ~1.13eV. The larger shift of WAl clearly indicates that the barrier height is further reduced. The new barrier height for electron injection due to the insertion of LiF is ~0.17eV. This barrier height is ~0.22eV lower then the barrier height of the Al only cathode.

A vacuum level shift of ~1.6eV at the Alq3/LiF/Al interface due to the presence of thin LiF is reported by Mori et al. and the reduced energetic barrier height for an electron is ~ 0.1eV [15]. This value of electron injection barrier is consistent with our value obtained above, however the shift of vacuum level of amount ~1.6eV is slightly higher than our value of ~1.2eV.

**Table 3.3: Average Vbi and calculation of the barrier height (ΔΦelectron) for electron injection in single and double layer devices with different cathodes.**

<table>
<thead>
<tr>
<th>Device</th>
<th>Vbi (V)</th>
<th>WCathode (WITO-Vbi)</th>
<th>W change (WAl(Lit)-Wcathode)</th>
<th>ΔΦelectron (Wcathode-E_LUMO) (eV)</th>
<th>ΔΦelectron (light.) (eV)</th>
<th>Vbi(double)-Vbi (single) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/Alq3/Al</td>
<td>1.41±0.02</td>
<td>3.39</td>
<td>0.91</td>
<td>0.39</td>
<td>&lt;0.5*</td>
<td>--</td>
</tr>
<tr>
<td>ITO/Alq3/LiF/Al</td>
<td>1.63±0.04</td>
<td>3.17</td>
<td>1.13</td>
<td>0.17</td>
<td>~0.1**</td>
<td>--</td>
</tr>
<tr>
<td>ITO/TPD/Alq3/Al</td>
<td>1.98±0.02</td>
<td>3.52</td>
<td>0.78</td>
<td>0.52</td>
<td>NA</td>
<td>0.57</td>
</tr>
<tr>
<td>ITO/TPD/Alq3/LiF/Al</td>
<td>2.24±0.04</td>
<td>3.26</td>
<td>1.04</td>
<td>0.26</td>
<td>NA</td>
<td>0.61</td>
</tr>
</tbody>
</table>

* see Ref.[15, 32, 34] ,** see Ref. [15]
3.3.2.2 Double Layer Alq3 Devices

The $V_{bi}$ measured for the double layer devices is greater than $V_{bi}$ measured for the single layer devices by $\sim 0.60 \pm 0.04$V using the same cathodes (see column 7 in Table 3.3). The only difference between single and double layer devices with identical cathodes is the TPD layer inserted in between the ITO and the Alq3. So the difference of $V_{bi}$ is due to the introduction of TPD, this increases $V_{bi}$ and decreases the hole barrier at the anode. The increase in $V_{bi}$ is equal to the work function difference between the plasma treated ITO ($W_{ITO}=4.8$eV) and the HOMO of TPD ($E_{HOMO}=5.5$eV [30, 40]) which is 0.7eV. This value is slightly higher than the difference of $V_{bi}$ ($\sim 0.60 \pm 0.04$V) measured experimentally. It indicates that there is $\sim 0.1$eV shift of the vacuum level at either ITO/TPD or TPD/Alq3 interfaces. Further it is conclusive that $V_{bi}$ is measured from the HOMO of TPD instead of $W_{ITO}$ for the double layer devices. Many studies have already demonstrated that the $V_{oc}$ of a solar cell is determined by the HOMO-LUMO of the active layer instead of the work function difference of the electrodes [43] and references therein. Brown et al. have shown that a hole injection layer of PEDOT:PSS, incorporated between the ITO and the polymer, lowers the barrier height for holes and increases $V_{bi}$. Further, once the PEDOT:PSS is coated on the ITO, $V_{bi}$ is determined by the work function difference of the cathode and PEDOT:PSS anode instead of the ITO [17, 44]. This is because of an energy level alignment at the interface of PEDOT:PSS and ITO. Furthermore the energy level alignment at the ITO/PEDOT:PSS interface is also verified by an independent study by Kulger et al. using UPS [45].

For the double layer device, $V_{bi}$ for the Al only cathode is $\sim (1.98 \pm 0.02)$V. Considering the HOMO of TPD to be 5.5eV, the effective $W_{Al}$ cathode is calculated as $\sim 3.52$eV. This indicates there is a vacuum level shift of $\sim 0.78$eV and the electron injection barrier is $\sim 0.52$eV which would otherwise be $\sim 1.3$eV. Once the cathode is replaced by LiF/Al, $V_{bi}$ increases to $\sim (2.24 \pm 0.04)$V and $W_{Al}$ changes by $\sim 1.04$eV reducing the electron injection barrier further to 0.22eV. The increase in $V_{bi}$ due to the insertion of LiF is 0.3V, which is equivalent to the reduction in the electron injection barrier due to LiF.
3.3.2.3 Energy Level Diagram for Alq3/Cathode Interfaces

An energy level diagram drawn for a single layer Alq3 device with the measured value of the vacuum level shift at the cathode interface is shown in Figures 3.7(a) and 3.7(b).

\[ W_{Al} \approx 3.17 \text{ eV} \]

\[ W_{LiF/Al} \approx 3.17 \text{ eV} \]

\[ \Delta \phi \approx 0.39 \text{ eV} \]

\[ \Delta \phi \approx 0.17 \text{ eV} \]

\[ \Delta \phi \approx 0.91 \text{ eV} \]

\[ \Delta \phi \approx 1.13 \text{ eV} \]

**Figure 3.7:** Energy level diagram for Alq3 devices (a) with Al and (b) LiF/Al cathodes with vacuum level shifts of magnitude \( \approx 0.91 \text{eV} \) for Al and \( \approx 1.13 \text{eV} \) for LiF/Al cathode. The corresponding barrier heights for electron injection are \( \approx 0.39 \text{eV} \) and \( \approx 0.17 \text{eV} \) respectively.

A picture developed for Alq3 with Al and LiF/Al cathodes for a single layer device shows conclusively that the calculated \( W_{Al} \) (\( \approx 3.39 \text{eV} \) and \( \approx 3.17 \text{eV} \)) is lower than the literature value (\( W_{Al}=4.3 \text{eV} \)) for both Alq3/Al and Alq3/LiF/Al interface. This shows that there is a vacuum level shift and dipole formation at these interfaces. For an Al cathode, if there is no dipole formation, the barrier height for electron injection becomes 1.3eV, instead of 0.39eV. This proves that the estimation of the electronic structure of the Alq3/metal interfaces by assuming a common vacuum level is not applicable. Since the magnitude of the vacuum level shift at the LiF/Al interface is larger than that of the Al only cathode, there is a stronger dipole formation in the presence of LiF compared to Al, which is responsible lowering the barrier height for electron injection. Further, this
fully supports the previous measured magnitude of the vacuum level shifts obtained for the Alq₃/cathode interface by UPS [6-8, 15, 37].

It is interesting to note that the vacuum level shift at the interface of Alq₃/Al, for single layer and double layer devices is slightly different for both cathodes. At present, the cause of the lower vacuum level shift for the double layer device is not understood and further investigation is needed in this direction. It is, however, worth noting that there may be a vacuum level shift at the ITO/TPD and TPD/Alq₃ interfaces, which is not considered in the calculation.

### 3.3.2.4 Summary of Alq₃/Cathode Interfaces

We measured V_{bi} in order to study the electronic structure of Alq₃/Al and Alq₃/LiF/Al interfaces and found that there is a dipole formed at these interfaces which is responsible for the shift of the vacuum level by 0.91eV and 1.13eV for the Al and LiF/Al cathode systems respectively. The shift of the HOMO of Alq₃ toward higher values due to the presence of LiF between the Alq₃ and Al causes the barrier height for electron injection to ~0.17eV. Further we demonstrated successfully that the calculated value of the vacuum level shift and barrier height for electron injection obtained using V_{bi} of the complete Alq₃ OLED devices agreed well with the values obtained by UPS measurements done by others.

### 3.3.3 Gaq₃/Metal Interfaces

Gallium quinoline (Gaq₃) is a small molecule organic material, which can be used as an alternative to the most widely used emitter material Alq₃ as most of its properties such as EL efficiency, emission wavelength and electron transporting are similar to Alq₃. The properties of Gaq₃ have been investigated by many groups for its application as an emitter in OLEDs [46-49]. Even though the PL efficiency of the Gaq₃ is lower than that of Alq₃, the EL efficiency is comparable to Alq₃ [46]. Furthermore, it is experimentally found that the degradation in Gaq₃ devices is much slower than in Alq₃ devices. Recently, Elshner et al. demonstrated that some gallium chelate complexes can be spin coated in order to make the OLED devices which have comparable efficiencies to those of sublimed emitting layers [50].

A study of the interfaces between Gaq₃ and different metal cathodes by using UPS, it is concluded that there is a vacuum level shift at the Gaq₃/metal interfaces due to interfacial dipole formation and/or band bending [51-53]. In this section, we
investigate the interfaces between Gaq$_3$ and different cathodes, such as Al, LiF/Al and Mg:Ag by monitoring the $V_{bi}$ in double layer devices and the electron injection barrier for each cathode is calculated. Finally an energy level diagram is presented.

### 3.3.3.1 Double Layer Gaq$_3$ Devices

Figure 3.8 shows the photocurrent characteristics for the Gaq$_3$ double layer devices with different cathodes. There is an increase in $V_{bi}$ once Al is replaced by LiF/Al and Mg:Ag. The $V_{bi}$ measured for Al only cathode is $\sim(1.86\pm0.03)V$. Insertion of LiF between Gaq$_3$ and Al, increases $V_{bi}$ to $\sim(2.18\pm0.02)V$. Due to the presence of LiF, there is increase in $V_{bi}$ of $\sim0.32eV$, this is equivalent to a lowering of the electronic energy barrier at the Al cathode by the same amount.

![Figure 3.8: Photocurrent vs bias voltage in semi log plot for devices ITO/TPD (500Å)/Gaq$_3$(500 Å /Al, LiF/Al and Mg:Ag cathodes.](image)

A summary of the measured $V_{bi}$ and other calculated quantities are presented in Table 3.4. The anode side of all devices is common, consisting of plasma treated ITO and a TPD layer. As the TPD is deposited on the ITO, the $V_{bi}$ is measured from the HOMO (5.5eV) of the TPD instead of the work function of ITO (4.8eV) (section 3.4.1.2). The work function of the cathode is calculated and presented in column 3. As in the case of TPD and Alq$_3$, the calculated $W_{Al}$ is not the literature value, which
ultimately means that there is a vacuum level shift at the interfaces. The vacuum level shift is ~0.66eV and ~0.98eV for Al and LiF/Al cathodes respectively. The value of the vacuum level shift at the Gaq3/cathode interface is, however, smaller than that in the Alq3/cathode interface obtained in section 3.3.2.2.

The $V_{bi}$ for Mg:Ag cathode is ~(2.06±0.03)V, which is between the values of $V_{bi}$ obtained for the LiF and the Al only cathode. The effective calculated work function of $W_{Mg:Ag}$ is 3.44eV, which differs from the literature value (3.7eV) [14, 32, 34, 54]. Hence there is also a vacuum level shift of 0.26eV at the Gaq3 /Mg:Ag interface. The barrier height for electron injection is calculated from the difference between the LUMO of Gaq3 and the effective calculated work function of cathode (column 3). The literature value of 2.9eV for the Gaq3 LUMO was used [48]. The results of the $V_{bi}$ measurements show that there are vacuum level shifts for all Gaq3/cathodes interfaces.

Table 3.4: Average $V_{bi}$ and calculation of the barrier height ($\Delta\Phi_{\text{electron}}$) for electron injection for double layer Gaq3 devices with Al, LiF/Al and Mg:Ag cathodes.

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{bi}$ (V)</th>
<th>$W_{\text{Cathode}}$ ($W_{ITO-V_{bi}}$)</th>
<th>$W_{\text{change}}$ ($W_{Al(LiF)-W_{cathode}}$)</th>
<th>$\Delta\Phi_{\text{electron}}$ ($W_{cathode-E_{LUMO}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/TPD/Gaq3/Al</td>
<td>1.86±0.03</td>
<td>3.64</td>
<td>0.66</td>
<td>0.74</td>
</tr>
<tr>
<td>ITO/TPD/Gaq3/LiF/Al</td>
<td>2.18±0.02</td>
<td>3.32</td>
<td>0.98</td>
<td>0.42</td>
</tr>
<tr>
<td>ITO/TPD/Gaq3/Mg:Ag</td>
<td>2.06±0.03</td>
<td>3.44</td>
<td>0.26</td>
<td>0.54</td>
</tr>
</tbody>
</table>

3.3.3.2 Energy Level Diagram of Gaq3/Cathode Interfaces

An energy level diagram of Gaq3 with three different cathodes is shown in Figure 3.9. There are vacuum level shifts at all interfaces with ~ 0.66eV for Al, ~0.98eV for LiF/Al and 0.26eV for Mg:Ag. The traditional method of calculating the electronic barrier height, by subtracting the value of work function of the cathode from the value of the LUMO of Gaq3, is not applicable to these interfaces. The maximum vacuum level shift is observed for LiF/Al and the minimum for Mg:Ag. The barrier height for electron injection is the largest for the Al cathode. Even thought there is a larger vacuum level shift observed for the Gaq3/Al interface compared to the Gaq3/Mg:Ag interface, electron injection in a Mg:Ag device is expected to be better than an Al device due to the smaller electron injection barrier.
Figure 3.9: Energy level diagram for Gaq₃ devices with three different cathodes with a vacuum level shifts of magnitude ~0.66eV for Al, ~0.98eV for LiF/Al and ~0.26eV for Mg:Ag cathode. The corresponding barrier heights for electron injection are 0.74eV, 0.42eV and 0.54eV respectively.

### 3.3.3.3 Summary of Gaq₃/Cathode Interfaces

We measured the vacuum level shift for Gaq₃ using different cathode materials and found that the traditional model of a common vacuum level is not applicable, as was found in TPD and Alq₃. The vacuum level shift and a dipole formation at the interface for Gaq₃, however, are smaller in magnitude than that of Alq₃ for corresponding cathodes. Further as in Alq₃, presence of LiF in the device increases the interfacial dipole to ~1eV and reduces the electron injection barrier over the Al only cathode.

### 3.3.4 Liq/ Metal Interfaces

Lithium quinoline (Liq) has been recently demonstrated as an emissive as well as interface material for electron injection by many groups [55-59]. Schmitz et al. studied the improvement of electron injection due to the presence of a thin Liq layer on Alq₃ devices and concluded that the performance improvement on the device due to Liq is similar to that of LiF [55, 56]. Furthermore Liu et al. investigated the Liq layer
thickness dependence of the electron injection properties and the device performance and reported that the thickness dependence is less sensitive than that of LiF [57]. This property makes Liq an interesting interface material for electron injection in cooperation with an Al cathode.

Zheng et al. proposed the mechanism for the improved electron injection as the formation of a dipole at the interface [58], the underlying mechanism of the electron injection due to thin Liq interface material, however, is not yet clear and not properly investigated. Hence it is worth investigating the Liq/cathode interface to find the possible mechanism for a device improvement by understanding the electronic energy level alignment at the Liq/cathodes interfaces. Further in chapter 4, Liq will be used as interface material for electron injection in Alq3 devices and a prior knowledge of the energy level alignment of Liq with different cathodes would be very useful. Hence, in this section, we investigate on the energy level alignment at Liq/cathode interface by measuring $V_{bi}$ in single and double layer devices and calculate the energetic barrier height at these interfaces. An energy level diagram is also presented for a Liq device with different cathodes.

3.3.4.1 Single Layer Liq Devices

Figure 3.10 shows the photocurrent variation with bias voltage in Liq single and double layer devices with different cathode materials.

![Figure 3.10: Photocurrent vs bias voltage in semi log plot for Liq single and double layer devices with different cathodes.](image-url)
It can be clearly seen that the values of $V_{bi}$ obtained for single and double layer Liq devices are different. A summary of $V_{bi}$ measurement and calculations of barrier height for electron injection is presented in Table 3.5. The $V_{bi}$ obtained for the single layer Liq device with Al cathode is $\sim$(1.54±0.03)V while that of LiF/Al is $\sim$(1.59±0.02)V. There is no significant difference in $V_{bi}$ for these two electrodes. This result is quite different to that observed in TPD, Alq3 and Gaq3. The calculated values of the cathode work function are presented in column 3 of Table 3.5. The effective work function of an Al only cathode is 3.26eV, which decreased to 3.21eV upon addition of LiF between the Liq and Al cathode. This proves that there is a very small work function shift in Al and the improvement in the electron injection barrier is due to the LiF. The electron injection barrier presented in column 5 is calculated from the difference between the effective work function of Al (calculated) and the LUMO of Liq. The literature value of 3.15eV for the LUMO of Liq is used [55, 56]. The calculated value of barrier height shows that the LUMO of Liq and the work function of the Al cathode are almost aligned with each other and there is a very small barrier (~0.11eV) for electron injection. As alignment of the Liq LUMO is achieved with the Al and a full reduction of barrier height is made already, there is no further reduction of barrier height observed with LiF/Al. This is supported by the same $V_{bi}$ being measured for Al and LiF/Al cathodes.

**Table 3.5: Average $V_{bi}$ and calculation of the barrier height ($\Delta \Phi_{electr}$) for electron injection in single and double layer Liq devices with different cathodes.**

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{bi}$ (V)</th>
<th>$W_{Cathode}$ $(W_{ITO}-V_{bi})$</th>
<th>$W_{change}$ $(W_{Al(LiF)}-W_{cathode})$</th>
<th>$\Delta \Phi_{electr}$ $(W_{cathode}-E_{LUMO})$</th>
<th>$V_{bi}$ (double)-$V_{bi}$ (single) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/Liq/Al</td>
<td>1.54±0.03</td>
<td>3.26</td>
<td>1.04</td>
<td>0.11</td>
<td>------</td>
</tr>
<tr>
<td>ITO/Liq/LiF/Al</td>
<td>1.59±0.02</td>
<td>3.21</td>
<td>1.09</td>
<td>0.06</td>
<td>------</td>
</tr>
<tr>
<td>ITO/TPD/Liq/Al</td>
<td>2.35±0.03</td>
<td>3.15</td>
<td>1.15</td>
<td>0.00</td>
<td>0.81</td>
</tr>
<tr>
<td>ITO/TPD/Liq/LiF/Al</td>
<td>2.43±0.03</td>
<td>3.07</td>
<td>1.23</td>
<td>-0.08</td>
<td>0.84</td>
</tr>
<tr>
<td>ITO/TPD/Liq/Mg:Ag</td>
<td>2.59±0.06</td>
<td>2.91</td>
<td>0.79</td>
<td>0.24</td>
<td>------</td>
</tr>
<tr>
<td>ITO/TPD/Liq/Ag</td>
<td>1.58±0.06</td>
<td>3.92</td>
<td>0.58</td>
<td>0.77</td>
<td>------</td>
</tr>
</tbody>
</table>
3.3.4.2 Double Layer Liq Devices

The $V_{bi}$ measured for double layer Liq devices with different cathodes is shown in Table 3.5. As in the case of Alq$_3$, the $V_{bi}$ of the double layer devices is greater than that of the single layer devices. When the $V_{bi}$ of single layer Liq devices are compared with double layer Liq devices for Al and LiF/Al cathodes, there is a difference of about $\sim(0.81\pm0.03)eV$. This is due to the introduction of TPD between ITO and Liq. It is already demonstrated that once TPD is placed on to the ITO, the $V_{bi}$ is measured from the HOMO of the TPD, not from the work function of ITO (section 3.4.1.2). This value, however, is slightly greater than the measured work function shift between oxygen plasma treated ITO ($W_{ITO}=4.8eV$) and the HOMO of the TPD ($E_{HOMO}=5.5eV$) which is 0.7eV. This indicates that there is a $\sim0.1eV$ shift of the vacuum level at either the ITO/TPD or TPD/Liq interfaces.

The smallest $V_{bi}$ measured for a Liq double layer device is using Ag cathode which is $\sim(1.58\pm0.06)eV$. The effective work function calculation is shown in column 3 in Table 3.5. Using the literature value for the work function of Ag ($W_{Ag}=4.5eV$), the Ag work function shift is only $\sim0.58eV$ and the barrier height for electron injection is $\sim0.77eV$. The $V_{bi}$ of double layer devices with Al and LiF/Al cathodes is $\sim(2.35\pm0.03)eV$ and $\sim(2.43\pm0.03)eV$ respectively. The work function lowering of the Al cathode is more than 1eV and the calculation shows that there is no barrier height for electron injection. This observation is consistent with the barrier height obtained for single layer devices in section 3.3.4.1. The $V_{bi}$ for Mg:Ag cathode is $\sim(2.59\pm0.06)eV$ with the effective work function $W_{Mg:Ag}$ of $2.91eV$. There is a work function shift of $\sim0.79eV$, (using the $W_{Mg:Ag}=3.7eV$) and the barrier height for electron injection is $\sim0.24eV$. The observations show that the biggest change in work function occurs at the Liq/Al and Liq/LiF/Al interfaces and the smallest at Liq/Ag interface. The work function shifts are indication of interfacial dipole formation.

3.3.4.3 Energy Level Diagram for Liq/Cathode Interfaces

An energy level diagram of a Liq single layer device is shown in Figure 3.11 with Al and LiF/Al cathodes. There are vacuum level shifts of $\sim1.1eV$ at the interface for both cathodes. Due to this vacuum level shift, $W_{Al}$ and the LUMO of Liq are almost aligned making the electron injection barrier almost zero (see Figure 3.11). The traditional method of calculating the electronic barrier height by subtracting the value of work function of the cathode from the value of the LUMO of Liq is not applicable to
these cathodes. Similarly, there are vacuum level shifts at the Liq/Mg:Ag and Liq/Ag interfaces with smaller magnitude of ~0.79eV and ~0.58eV respectively.

Figure 3.11: Energy level diagram for Liq devices with different cathodes showing a vacuum level shift of ~1.04eV for Al and ~1.09eV for LiF/Al. The corresponding barrier height for electron injection is negligible as the Al work function and the LUMO of Liq are aligned due to a vacuum level shift.

### 3.3.4.4 Summary of Liq/Cathode Interfaces

V\textsubscript{bi} for Liq single and double layer devices is measured for different cathodes. As in the case of other small molecule organic materials, the traditional model of a common vacuum level is not applicable in Liq and cathodes interfaces. A vacuum level shift of ~1.1eV is observed for Liq/Al and Liq/LiF/Al interfaces. This indicates that there is a strong interfacial dipole formed in these interfaces. Due to the larger interfacial dipole, the barrier height for electron injection becomes negligible and the LUMO of Liq is aligned to the work function of Al. Due to this, even if LiF is inserted between the Liq and the Al cathode, the V\textsubscript{bi}, effective cathode work function and barrier height for electron injection remains virtually unaffected. There is, however, a weaker dipole formed at the Liq/Mg:Ag and Liq/Ag interfaces, with a barrier height for electron injection of ~ 0.24 and ~0.77eV respectively.
3.4 Conclusion

We successfully demonstrated that in all small organic molecules used in this chapter, there is a vacuum level shift at the organic/cathode interface and the traditional way of calculating an electron injection barrier, just by the difference of the work function of metal and the LUMO of the organic, is not valid in these systems. Further, the $V_{bi}$ monitoring in the OLED device is a useful tool, which can give information about the electronic structure of the organic/cathode interfaces. The experimental values obtained for the prototype material Alq$_3$ are closely matched to other experimental values obtained by UPS and XPS, which shows this technique, is capable of studying the interfacial structure and the relative band positions in complete devices. We have to rely on the UPS and XPS, however, to find the absolute band positions. Further, this technique adds more flexibility as a complete device structure can be used for the interfacial study, whereas the UPS and XPS rely on an interface only.

We found that there are vacuum level shifts of $\sim$0.40eV and $\sim$1.46eV at the TPD/Al and TPD/LiF/Al interfaces respectively. Due to this, the barrier height for electron injection is reduced to $\sim$1.5eV for the Al cathode which is otherwise $\sim$1.9eV. The addition of LiF between the TPD and Al increases the built-in potential and reduces the barrier height further to $\sim$0.44eV. Furthermore, we observed a $\sim$0.3eV increase in the work function of ITO due to oxygen plasma treatment. This indicates that the hole barrier is reduced over untreated ITO by the same amount.

We measured the vacuum level shifts at Alq$_3$/Al and Alq$_3$/LiF/Al interfaces and found that they are $\sim$0.91eV and $\sim$1.13eV shifts respectively. Due to these shifts, the electron injection barrier becomes $\sim$0.39eV for Al cathode. There would be a higher electron injection barrier ($\sim$1.3eV) if there was no vacuum level shift at the Alq$_3$/Al interface and the device performance would be much worse. As there is a greater shift at the Alq$_3$/LiF/Al interface, the electron barrier height is reduced to $\sim$0.17eV. Further we have successfully demonstrated that the energy level diagram obtained on $V_{bi}$ studies agreed with other well established measurements.

There is a vacuum level shift at Gaq$_3$/metal interfaces as in the case of TPD and Alq$_3$. The vacuum level shift and a dipole formation for Gaq$_3$ interfaces, however, are smaller in magnitude than in Alq$_3$ for corresponding cathodes. The vacuum level shift for the Gaq$_3$/Al interface is $\sim$0.66eV with an electron injection barrier of $\sim$0.74eV. Further the presence of LiF in the device increases the interfacial dipole to $\sim$0.98 eV, further reducing the electron barrier height to $\sim$0.42eV. However there is a very small
vacuum level shift ~0.26eV at the Gaq3/Mg:Ag interface and the barrier height for electron injection is ~0.54eV.

As in other organics, a traditional model of a common vacuum level is not applicable in Liq/cathode interfaces. There is a ~1.1eV vacuum level shift for Liq/Al and Liq/LiF/Al interfaces and a barrier height of ~0.11eV. This indicates that there is a strong interfacial dipole formed at the Liq/Al interface and, due to lowering of work function of the Al cathode, it is aligned with the Liq LUMO. Because of this, insertion of LiF, between Liq and Al, does not increase the magnitude of the interfacial dipole. This finding is quite different to what we observed in other organics such as TPD, Alq3 and Gaq3. A weaker dipole, however, is formed at Liq/Mg:Ag and Liq/Ag interfaces, with a barrier height for electron injection of ~ 0.24eV and ~0.77eV respectively.

The reason of the dipole formation at these interfaces is not known as the technique used does not allow us to investigate this. Further investigations are required to explain the mechanism responsible for it.

### 3.5 References

Chapter 4

Enhanced Performance of Alq₃ OLEDs with a thin Mqs (M=Li, Na, K, Rb and Cs) Electron Injection Interface Layer

4.1 Introduction

Alq₃ is widely used as an electroluminescent organic material due to its high luminescent and transport properties and its thermal stability [1-3]. To achieve excellent performance in Alq₃ OLED devices, it is essential to have a high work function anode and a low work function cathode to match the HOMO and LUMO energy levels of organic material and inject holes and electrons with the lowest energetic barrier. Low work function metals such as Ca, Li, Mg, Cs, Sm and metal alloys such as Mg:Ag [4], Li:Al [5], etc. are suitable candidates for electron injection. The sensitive nature of the low work function material, however, is a major obstacle due to their high reactivity and low stability.

Aluminium (Al) and silver (Ag) are less reactive, relatively high work function metals used as cathodes for device stability, at the cost of high driving voltage and lower efficiency. To overcome this problem, Hung et al. first used an insulating layer of LiF between the Alq₃ and the Al and reported an improvement of device performance over Al only cathode devices [6]. Since then, low work function metal compounds such as CsF [7], NaF [8], CaF₂ [9, 10], MgF₂ [10], BaF₂ [10], etc. have been investigated extensively as electron injection layers. Recently low work function metal compounds such as NaCl [11], NaOH [12], sodium stearate (NaSt) [13], calcium acetate (Ca(acac)₂) [14] have been demonstrated as efficient interface layers for Al cathode.

More recently, a small molecule compound, Liq, has been introduced as an excellent interface layer for electron injection by many groups [15-19]. A thin layer of Liq is as efficient as an insulating LiF interface for electron injection with an additional advantage of being less sensitive to thickness than LiF. The mechanism behind the improved electron injection, however, is still not clear. Furthermore, there is a strong possibility that all alkaline metal quinolates can be good candidates for interface layers as Liq is. With this in view, we investigate a series of alkaline metal quinolates (Liq,
Naq, Kq, Rbq and Csq) as electron injection layers in cooperation with an Al cathode and their OLED device performances are compared with those of Al and LiF/Al cathodes.

Furthermore, we systematically varied the thickness of all the quinolates to optimise the thin injection layer of Mqs. In order to understand the mechanism of improved electron injection, different cathode materials such as Ag, Mg, Ag/Al, Mg/Al, Mg:Ag and LiF/Al were studied with an optimised thin metal quinolate injection layer in double layer devices. We monitor the built-in voltage ($V_{bi}$) of the devices with different injection layers in a single and a double layer device structure. This provides us with information about the energetic barriers resulting from different interface layers at the cathode, from which we can interpret the mechanism of improved electron injection and device efficiency.

### 4.2 Experiment

A set of samples with a device structure of ITO/TPD(500Å)/Alq$_3$(500Å)/Mq(X Å)/Al (M is Li, Na, K, Rb and Cs) and X represents the film thickness (5 to 40Å), were fabricated to achieve optimised device performance. The ITO was plasma treated as described in section 2.3.4. TPD and Alq$_3$ were evaporated at a rate of 2Å/s while the thin layer of metal quinolate (Mqs) was evaporated at a rate of 0.2-0.4Å/s. J-V-L characteristics of devices were measured as described in section 2.4.1. To compare the device performance of the different alkaline metal quinolates as electron injection layers, the devices with the structure of ITO/TPD(500Å)/Alq$_3$(500Å)/Mq(10Å)/Al were fabricated. The 10Å thickness of Mqs was found to be the optimised injection layer for improved electron injection. Furthermore, double layer devices with different cathodes such as LiF/Al, Ag, Mg, Ag/Al, Mg/Al and Mg:Ag were also fabricated with thin Liq and Csq interface layers.

The EL spectra and $V_{bi}$ were recorded for all optimised devices. PL spectra were also measured on the purified material, in the form of powder as described in section 2.4.3. Absorption spectra for all Mqs were taken in methanol solution as described in section 2.4.4.
4.3 Results and discussion

4.3.1 Absorption Spectra of Mqs

Figure 4.1 shows the absorption spectra for all Mqs (chemical structure in inset). If the long wavelength cut-off of the absorption is considered as the HOMO-LUMO gap in the unexcited molecule, then all Mqs have an identical gap, corresponding to 356nm or 3.48eV. Our measured value for the HOMO-LUMO gap for Liq is very similar to that reported in the literature (~3.40eV) [15, 16]. The absorption for Alq₃ is shown in the inset which shows that the long wavelength cut-off for is about 440nm which is equivalent to 2.8eV [20]. This shows that the HOMO-LUMO gap for Mqs is larger than that of Alq₃.

Figure 4.1: Absorption Spectra for Mqs (chemical structure of Mqs and the absorption spectra of Alq₃ in inset).
4.3.2 Photoluminescence (PL) Spectra of Mqs

Figure 4.2 shows the PL spectra of pure Mqs. Mqs were purified either by zone sublimation or in the Kurt J. Lesker SPECTROS evaporation system as described in section 2.2.2. A summary of the data obtained is shown in the Table 4.1. The PL peak shifts towards high wavelengths with an increase in the atomic number of the alkaline metal atom attached to the quinoline, however, Rbq in the series does not follow this trend. In the same table, the full width of the half maximum (FWHM) is also presented which shows that Naq has the broadest emission spectra among them. The PL peak obtained for Liq is similar to the previously reported value ~485nm, measured on a thin film of Liq made by vacuum deposition [15, 16].

![Photoluminescence Spectra](image)

**Figure 4.2:** Photoluminescence (PL) spectra for purified Mqs measured with an excitation of laser light of wavelength 405nm and intensity 25mW.

**Table 4.1:** Data obtained from PL spectra for different Mqs.

<table>
<thead>
<tr>
<th>Mqs</th>
<th>PL peak (nm)</th>
<th>FWHM (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liq</td>
<td>488</td>
<td>0.47</td>
</tr>
<tr>
<td>Naq</td>
<td>528</td>
<td>0.57</td>
</tr>
<tr>
<td>Kq</td>
<td>530</td>
<td>0.50</td>
</tr>
<tr>
<td>Rbq</td>
<td>504</td>
<td>0.54</td>
</tr>
<tr>
<td>Csq</td>
<td>550</td>
<td>0.47</td>
</tr>
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</table>
4.3.3 Thickness Optimisation of Liq as an Electron Injection Layer

We first investigated Liq as an electron injection layer inserted between the emitter Alq₃ and the Al cathode in the device structure ITO/TPD/Alq₃/Al. A series of devices with a varying thickness of Liq (5-40Å) were studied in J-V-L (Figures 4.3(a) and 4.3(b)). Devices without Liq, but with Al or LiF/Al electrode are also shown for comparison. All the devices with a thin Liq layer have low turn-on voltage and high current density at the same driving voltage compared to those without Liq. The turn-on voltage ($V_{on}$) is defined as the voltage when light output is first detected by the measurement system in the experiment. The devices without Liq have turn-on voltages of 3.5V and 2.5V for Al and LiF/Al cathodes respectively. All Liq devices, however, with thickness ranging from 10-30Å exhibit a similar turn-on voltage (2.4V). Even a device with 5Å of Liq showed better injection than the LiF/Al device (see Figure 4.3(a)). At Liq thicknesses greater than 30Å, the turn-on voltage is slightly increased (2.5V) which may be due to excess voltage drop across the thicker Liq layer. From the J-V characteristics, it is clear that the current density is much larger for the Liq devices compared to the device with an Al only cathode. The increase in the current density with thin Liq layers can be related to improvements in either electron injection or the bulk transport properties of the device. As the interfacial layer of Liq is very thin, however, it is unlikely to significantly change the bulk transport properties of the device. This therefore indicates that the cause of the increased current density is due to improved electron injection caused by the insertion of the Liq layer in the device.

All devices with thin Liq injection layers have nearly identical J-V characteristics with saturation at high voltage. The J-V plots for these devices are parallel to the J-V characteristics of the LiF/Al and Al devices after $V_{drive}>6V$. The current saturation in the high voltage range may be due to transport properties in the device. This effect, however, is reproducible for all thicknesses of Liq, which indicates that it is not due to the thickness of Liq or on the transport within the Liq layer. It indicates it is related to the bulk transport properties of the device and this needs further investigation.

All devices with thin Liq have shown lower drive voltages ($V_{drive}$) than devices with Al or LiF/Al cathodes. $V_{drive}$ is operating voltage of the device at certain current density. For example, for current density $J=100\, \text{Am}^{-2}$, the devices with thin Liq require $V_{drive} \approx 4.7-4.8V$, while those of Al and LiF/Al require $\approx 6.7V$ and $\approx 5.5V$ respectively. At the same current density, the light output is $\approx 1\, \text{Wm}^{-2}$ for thin Liq devices, $0.25\, \text{Wm}^{-2}$ for
Al and 0.92 Wm\(^{-2}\) for LiF/Al devices. So Liq interface layer devices emit nearly 4 times more light than the Al only device at the same current density.

**Figure 4.3:** (a) Current-voltage characteristics (J-V) and (b) Luminance-voltage characteristics (L-V) for devices ITO/TPD(500Å)/Alq3(500Å)/Liq(XÅ)/Al. Devices using Al and LiF/Al cathodes are also shown for comparison.
The L-V characteristics in Figure 4.3(b) show the effect of the Liq injection layer on the light output of the devices. The light output of the devices incorporating a Liq thin layer is higher throughout the whole drive voltage range compared to the devices without Liq. This indicates that there is more recombination in the devices with Liq layers at the same drive voltage. This is proof of the improved electron injection and increased carrier density in the device.

The variation of power efficiency with current density is shown in Figure 4.4(a). It can be seen that the device with the Al only cathode exhibits very poor performance with peak power efficiency \( \sim 3.5 \times 10^{-2}\% \) at \( J=150\text{Am}^{-2} \) with \( V=7\text{V} \). Devices with 10-40Å of Liq, show a maximum power efficiency \( \sim 3.2 \times 10^{-1}\% \) at \( J=2\text{Am}^{-2} (V=3\text{V}) \), while the device with the LiF/Al cathode has only \( \sim 2.2 \times 10^{-1}\% \) maximum power efficiency at \( J=2.4\text{Am}^{-2} (V=3.6\text{V}) \). The device with 5Å of Liq exhibits better power efficiency than the Al only device thought it is slightly worse than the LiF/Al device. It is worth noting here that the J-V performance of the 5Å of Liq device is better than that of the LiF/Al.

Figure 4.4(b) shows the electroluminescence output of these devices as a function of the current density. The luminance of the device is proportional to the current density in the entire range measured for all devices. This linearity of the J-L characteristics gives a slope, which is called the injection efficiency (W/A) of the device. The injection efficiency is found to increase with increasing thickness of the Liq. For example, the device with 10Å of Liq has an injection efficiency of \( \sim 1.0 \times 10^{-2}\text{W/A} \), which increases to \( \sim 1.2 \times 10^{-2}\text{W/A} \) for 40Å Liq. While the injection efficiency using Al and LiF/Al cathodes is \( \sim 2.65 \times 10^{-3}\text{W/A} \) and \( \sim 7.57 \times 10^{-3}\text{W/A} \) respectively. The increase in injection efficiency with increasing thickness Liq suggests that in the thicker Liq devices more recombination occurs than the thinner ones, even though the thickness of the Alq3 (emissive layer) is the same. This also indicates that there is better electron injection and recombination in thick Liq injection layer devices, which may be due to increased lowering of the barrier height in the thick devices compared to thin devices. The barrier height variation with injection layer thickness measurement, however, should be performed to confirm this.

Even though thicker (30-40Å) Liq devices have better injection and power efficiency (Figures 4.4(a) and 4.4(b)), they require higher drive voltages. So a thickness (10-20)Å of Liq was chosen as the optimised thickness and this thickness is used later in the study. This optimised Liq thickness is similar to the study by Lui et al.[19] where
they found that the Liq thickness can be increased to about 50Å without significantly compromising the EL characteristics.

**Figure 4.4:** (a) Power efficiency-current density and (b) Luminance-current density characteristics (L-J) for devices ITO/TPD(500Å)/Alq₃(500Å)/Liq(X)/Al. Devices using Al and LiF/Al cathodes are also shown for comparison.
It is interesting to note that this optimised thickness is quite different to the findings of Zheng et al. where they obtained ~5Å as an optimised thickness for Liq [18]. They have shown that the device efficiency decreases sharply upon increase of the thickness beyond 5Å. This kind of decrease in the efficiency due to increased Liq thickness is not observed in our study. The power efficiency variations are less than 10% for all Liq devices except the 5Å device in our study. Further, the performance of Liq and LiF in their study is nearly identical, which is in contrast to ours. Liq thin layer devices studied here have better performance than LiF/Al devices. The differences observed in these studies might be due to the different processing of the Liq devices (e.g. Liq preparation, Liq purity, device fabrication and measurement process). Further, in our study, the thickness of the Liq injection layer can be changed from 10-30Å without a significant decrease in the EL output or increase in V_{on} and V_{drive}. This may be because Liq is an electron transporting material and increasing the thickness of Liq does not impede electron transport [15]. However there is no reported value of electron mobility in Liq in the literature. In contrast to this, as LiF is an insulating material, the EL output and device performance decrease sharply once the thickness is increased beyond the ultra thin optimised thickness, of ~10Å. The less sensitive nature of device performance on interfacial layer thickness makes Liq an alternative to conventional insulating cathodes such as LiF and CsF where the thickness control needs to be very accurate.

4.3.4 Thickness optimisation of Mqs as Electron Injection Layers

All alkaline metal quinolates have shown similar thickness dependence of the J-V-L characteristics as the Liq presented in section 4.3.3. The thickness variation of Mqs on the V_{on}, injection efficiency, power efficiency and V_{drive} at 100Am^{-2} are summarized in Figures 4.5(a)-4.5(d).

For all Mqs, 10-20Å is found to be the optimised thickness in cooperation with an Al cathode for device performance. The power efficiency for all devices saturates 0.2% (at 100Am^{-2}) above 10Å thickness irrespective of material (Figure 4.5(d)), V_{drive} increases slightly as thickness increases from 20-40Å for Csq and Kq (Figure 4.5(b)). This increase in the drive voltage suggests an additional voltage drop across the thicker Mqs layer.
Figure 4.5: (a) Variation of the turn-on voltage, \( V_{on} \), (b) drive voltage, \( V_{drive} \) (at 100 Am\(^{-2}\)), (c) injection efficiency and (d) power efficiency (at 100 Am\(^{-2}\)) for devices with Mq layer thickness varying from 0 to 40 Å. The device structure is ITO/TPD(500 Å)/Alq\(_{3}(500 \text{Å})/\text{Mq(\text{X} Å)}/\text{Al}.

### 4.3.5 Performance Comparison of Optimised Thin Mq\(_{s}\) Devices

Figures 4.6(a) and 4.6(b) show the J-V and L-V characteristics for optimised devices ITO/TPD(500 Å)/Alq\(_{3}(500 \text{Å})/\text{Mq(10Å)}/\text{Al} with \text{Mq(10Å)} as an electron injection layer. All devices incorporating the Mq layer show improved electron injection in comparison to devices with Al and LiF/Al only cathodes by lowering \( V_{on} \) and increasing current density and luminance. The \( V_{on} \) for all devices with thin Mq injection layer is equal to 2.4 V. The lowering of \( V_{on} \) corresponds to a lowering of the electron injection barrier due to the presence of the thin Mq. Further \( V_{drive} \) for devices with thin Mq layers is reduced to \( \sim 4.7-4.9 \text{V} \text{ at 100 Am}^{-2} \). The J-V and L-V characteristics for all Mq devices...
are identical while they are quite different to the LiF/Al and Al cathode devices. Similar values of $V_{on}$ and identical J-V-L characteristics for all different Mqs, suggest that there is a similar barrier height for the electron injection into Alq$_3$.

In Figure 4.6(a), the current density at low-voltages (leakage current) varies significantly between Mq devices and the magnitude of this current is considerably lower than in Al and LiF/Al devices. The device with Al cathode only has a leakage current of $\sim 10^{-2}$A$m^{-2}$. The Liq injection layer device has the lowest leakage current ($\sim 10^{-5}$A$m^{-2}$) whilst that of Csqa has the maximum $\sim 10^{-4}$A$m^{-2}$. The rest of the quinolates of Na, K and Rb have leakage current in between. Due to the lowest work function ($W=1.9$eV) of Cs, there is a strong possibility of reactive interface formation at the Csqa/Al boundary. This reactive interface might be responsible for the high leakage current. Further, the high leakage current in Csqa devices may be due to the more hygroscopic nature of Csqa in comparison to other Mqs.

Although the J-V characteristics are almost identical to each other for thin Mqs devices, the magnitude of J at low voltage decreases in the series from Csqa to Liq. Further J-V characteristics for thin Mqs devices are quite different than that of Liq at low-voltage (just after the device turn-on). J-V characteristics for thin Mqs devices are parallel to the J-V of LiF/Al and Al cathode devices in the high voltage regime, especially after $V_{drive} > 6V$. As all of the devices incorporating Mqs display the saturation in the device current, there is an indication that Mqs are not responsible for the saturation. It suggests that the J-V characteristics are restricted by either carrier injection and/or transport property which becomes apparent at high voltages, in all devices irrespective of the interface/cathode. This suggests that the devices are approaching towards the space charge limited region at the high voltages, where the charge injecting contacts of the device become ohmic and space charge accumulated in the device does not allow to increase the current in the device even voltage is increased. This region is well studied in many literatures [21-23].

The light output variation with bias voltage of the devices is shown in Figure 4.6(b). It shows that all L-V characteristics are approximately parallel at high voltage including the LiF/Al and Al cathodes. For thin Mq devices, there is a slight variation in the L-V curves (\~15\%) at the point where the device turns-on (\~2.4V) and this follows the sequence Liq to Csqa from high output to low output. There are very small variations at high drive voltages in the L-V characteristics. The maximum light output observed is \~0.94Wm\-2 for Al, \~12.27Wm\-2 for LiF/Al and \~30Wm\-2 for Mqs (at V= 8V). Similarly,
at a current density, \( J = 100 \text{Am}^{-2} \), the devices with Mqs show a light output of \( \sim 1 \text{Wm}^{-2} \) at \( (V \sim 4.7-4.8 \text{V}) \) whilst for the LiF/Al device it is \( \sim 0.92 \text{Wm}^{-2} \) \((V=5.5 \text{V})\) and the Al cathode device is the worst with only \( 0.25 \text{Wm}^{-2} \) light output at \((V=6.7 \text{V})\).

**Figure 4.6:** (a) Current-Voltage characteristics (J-V) and (b) Luminance-Voltage characteristics (L-V) for devices ITO/TPD(500Å)/Alq₃(500Å)/Mq(10Å)/Al (with M= Li, Na, K, Rb and Cs). The characteristics for Al and LiF/Al cathode devices are also shown for comparison.
The injection and power efficiency variation with current density for different Mqs is shown in Figures 4.7(a) and 4.7(b) respectively. The injection efficiency for Al and LiF/Al devices is $2.65 \times 10^{-3}$ W/A and $\sim 7.57 \times 10^{-3}$ W/A. Injection efficiencies for Mqs are $\sim 5$ and 1.3 times higher than the injection efficiencies of Al and LiF/Al devices respectively. Electron injection layers Rbq, Csq and Kq show slightly higher injection efficiencies ($\sim 1.13 \times 10^{-2}$ W/A) than Liq and Naq ($\sim 1 \times 10^{-2}$ W/A). This further suggests that with an increase in the atomic mass of the metallic atom attached to quinoline, there is increase in the injection efficiency. This result is consistent with finding of Endo et al. [17] in which they compared the current injection efficiency of different ligand materials with different central metal ions and found that Naq to be more efficient than Liq. Further Chen et al. found that with an increase in the atomic size in the complexes, the orbital energy of the central atom and ligand become larger and the chemical bond becomes weaker [24]. This may result an increase in the charge transport/injection properties and may be responsible for better injection efficiency with increasing atomic number of the central alkali metal.

As the devices with 10Å Mqs interface layer have higher injection efficiencies compared to LiF/Al devices, more recombination occurs in the Mqs devices. This proves there is a higher electron concentration. An increase in the electron injection is obvious, from the observation of the improved J-V characteristics and lower $V_{on}$ values. Another possibility is that all Mqs may be acting as a hole blocking layers. The observation of a larger absorption gap for Mqs compared to Alq₃ (section 4.3.1) suggests that these Mqs may act as hole blocking layers.

All thin Mqs interface devices show improved efficiency compared to devices with Al or LiF/Al cathodes at all current densities (see Figure 4.7(b)). For devices with Al only cathodes, the light output can be obtained at a current density of $\sim 0.2$ Am$^{-2}$. While for a LiF device it is $\sim 0.04$ Am$^{-2}$ and for rest of the Mq interface layer devices, it is $\sim 0.01$ Am$^{-2}$. This indicates that despite the low current density in thin Mqs devices, the electron concentration is higher. The improvement of the luminance, even at lower ($\sim 4$ times) current densities than those in LiF/Al cathode devices may be due to the improved electron injection property of the interface and balancing the hole and electron density in the emissive layer.
Figure 4.7: (a) Luminance-Current density characteristics (L-J) and (b) Power efficiency-Current density for devices ITO/TPD(500Å)/Alq₃(500Å)/Mq(10Å)/Al. The characteristics for devices with Al and LiF/Al cathode are also shown for comparison.
Figure 4.8: Power efficiency (left axis) at 100 Am^{-2} and Injection efficiency (right axis) for devices ITO/TPD(500Å)/Alq_3(500Å)/Mq(10Å)/Al. The efficiencies for devices with Al and LiF/Al cathode are also shown for comparison.

The summary of injection and power (at J=100Am^{-2}) efficiencies for Mqs interface layer devices is presented in Figure 4.8. For all interfaces, the device performance is better than the LiF/Al cathode device and the power and injection efficiency increases with an increase in atomic number and a decrease in the work function of the central atom. This is consistent with the earlier work reported by Oyamada et al. when they used ultra thin layers of the same series of low work function metals as cathodes (capped by Al) [25]. They found that improved device performance corresponds to the decreased work function (with Cs most efficient and Li least and the rest intermediate between them). However there is a slight decrease in the efficiency with Csq interface layer which could be due to the very sensitive nature of Csq thin film under ambient conditions. It is clearly seen that black spot formation and degradation of the device starts after a few hours of device operation during the experiment, which could be due to the reaction of Csq with water molecules present in air. The rest of the Mqs are found to be fairly stable.

The EL spectra for the devices with Mqs as electron injection layer are presented and discussed in section 4.3.7.
4.3.6 Liq and Csq as Electron Injection Layers Using Different Electrodes

In order to have insight on the mechanism responsible for the improved electron injection in the devices with thin Liq and Csq interface layers, devices were fabricated using different cathodes such as Ag(1000Å), Mg(1000Å), Ag(100Å)/Al(900Å), Mg(100Å)/Al(900Å), Mg(90%):Ag(10%) and LiF(10Å)/Al(1000Å) with work functions ranging from 3.6-4.5eV [26-28]. It is already shown in section 4.3.5 that the improvement of the electron injection using different Mqs is quite similar despite having different chemical reactivity of the alkaline metal atoms attached to the quinoline ligand. Here, two extreme metal quinolates, in terms of reactivity, Liq and Csq, are chosen.

Figures 4.9(a) and 4.9(b) show the J-V characteristics of devices with a Liq and Csq injection layer using different cathodes. The J-V characteristics of an Ag cathode (with an interface layer) devices are worse than that of an Al only cathode device. For example, when Ag is used as a cathode, in both Liq and Csq interfaces, the drive voltage at which electron injection increase to 3.5V and 3.1V respectively while it is 2.4V for the Al cathode. For Ag/Al cathode, it is 2.5V for both interfaces.

The Ag cathodes are found to be worse than the conventional LiF/Al cathode for electron injection even in combination with Liq and Csq layers (see Figures 4.9(a) and 4.9(b)). This indicates that there is only a small effect of the injection layer when Ag cathodes are used. The rest of the cathodes have improved electron injection in combination with either Liq or Csq and the J-V characteristics are nearly identical after the device turn-on. It has been found from the J-V characteristics, the Liq with Al is the best interface for higher current densities and Liq with LiF/Al is the worst interface. Csq with LiF/Al and Mg/Al are the best interfaces with higher current densities compared to other cathode materials. The most active cathode material used here is Mg, which has intermediate current densities in both interfaces. This shows that there does not appear to be a relationship between the increase in the current density and the reactivity of the metallic cathode used. This also suggests that there is no release of Li or Cs from corresponding metal complexes upon deposition of the metallic cathode materials.
Figure 4.9: Current density-voltage (J-V) characteristics of devices with (a) Liq and (b) Csq interfacial layers. The device structure is ITO/TPD(500Å)/Alq₃(500Å)/Liq or Csq(10Å)/cathodes. Devices without interface layer using Al and LiF/Al cathodes are also shown. The cathode materials used are Al, LiF/Al, Mg, Ag, Mg:Ag and Ag and Mg capped with Al with Liq and Csq interface layer.
Figure 4.10: Luminance-current density (L-J) characteristics for (a) Liq and (b) Csq interfaces using different cathode materials. The device structure is ITO/TPD(500Å)/Alq3(500Å)/Liq or Csq(10Å)/cathodes. Devices without interface layer using Al and LiF/Al cathodes are also shown. The cathode materials used are Al, LiF/Al, Mg, Ag, Mg:Ag and Ag and Mg capped with Al with Liq and Csq interface layer.
The luminance variation with current density is shown in Figures 4.10(a) and 4.10(b) for Liq and Csq interfaces respectively. All interface and cathode combinations show improved light output compared to LiF/Al and Al cathodes at all current densities. There is a linear dependence of L on J for all devices and they show similar injection efficiencies. The maximum injection efficiency is observed using Mg:Ag cathodes for both Liq and Csq interfaces. The minimum improvement in injection efficiency is obtained with the Ag cathode. Even though the injection efficiency is similar for all other interfaces and cathode combinations, Ag and Ag/Al have shown a different behaviour compared to other cathodes. Injection efficiency of the Csq/Ag and Csq/Ag/Al cathode is lower than that of Liq/Ag and Liq/Ag/Al. They are still, however better than the LiF/Al and Al cathode devices. The injection efficiency for a Mg:Ag cathode for both interfaces is $\sim 1.12 \times 10^{-2}$W/A while it is $\sim 1 \times 10^{-2}$W/A for Liq with Ag and Ag/Al cathodes and $\sim 9 \times 10^{-3}$W/A for Csq with Ag and Ag/Al cathodes. As the injection efficiency is still better than the LiF/Al and Al cathodes, it again suggests that the Liq and Csq layers may be acting as hole blocking layers at the cathode interface.

Figures 4.11(a) and 4.11(b) show the power efficiency variation with current density for devices with Liq and Csq interfaces. It can be clearly seen that devices with Mg, Mg:Ag, Mg/Al, LiF/Al and Al have comparable power efficiencies, which are greater than the LiF/Al cathode devices for both interfaces. It is interesting to note that at higher current densities, they all converge to same efficiency value. When Ag is used as cathode, in both interfaces, the power efficiency is found to be lower than the LiF/Al cathode but it is greater than plain Al cathode. Further, the devices with Ag cathodes have very low power efficiencies at low current densities. This is probably because these devices have higher hole currents (see Figures 4.9(a) and 4.9(b)) which do not contribute to the recombination process. Even though Liq and Csq show hole blocking property as described previously, these devices are less efficient due to the low concentration of electrons.

In contrast to this, Ag/Al cathodes show remarkable improvement, as efficient as LiF/Al cathodes for both interfaces. The light output is observed at a current density $\sim 0.1$A/m$^2$ for the Ag cathode and $\sim 0.05$A/m$^2$ for the Ag/Al cathode for both interfaces. For the rest of the cathode, it is $\sim 0.010$A/m$^2$. At present, the different nature of Ag and Ag/Al cathodes is not understood. It could be related to the fact that Ag does not stick to the organics very well and due to this, there may be a formation of a patchy layer, with some regions consisting of just Al, in the case of the Ag/Al cathode. We also noticed
that the power efficiency variation with current density is almost identical for Liq and Csq with Ag and Ag/Al cathodes in Figures 4.11(a) and 4.11(b). This strongly suggests that the mechanism behind the improved efficiency using Ag cathodes with both interfaces should be the same. There is no significant difference between Mg, Mg/Al, Mg:Ag, LiF/Al and Al cathodes with both interfaces in terms of power efficiency.

![Power efficiency variation with current density for devices with (a) Liq and (b) Csq interfacial layers. The device structure is ITO/TPD(500Å)/Alq3(500Å)/Liq or Csq(10Å)/cathodes.](image)

**Figure 4.11:** Power efficiency variation with current density for devices with (a) Liq and (b) Csq interfacial layers. The device structure is ITO/TPD(500Å)/Alq3(500Å)/Liq or Csq(10Å)/cathodes.
Figure 4.12: Luminance variation with drive voltage (a) Liq and (b) Csq interfacial layers. The device structure is ITO/TPD(500Å)/Alq3(500Å)/Liq or Csq(10Å)/cathodes. Devices without interface layer using Al and LiF/Al cathode are also shown. The cathode materials used are Al, LiF/Al, Mg, Ag, Mg:Ag and Ag and Mg capped with Al with Liq and Csq interface layer.

Figures 4.12(a) and 4.12(b) show the luminance variation with drive voltage. The values of $V_{on}$ are higher for devices using Ag or Ag/Al cathodes compared to the plain
LiF/Al cathode. The plain Al cathode device turns-on at ~3.5V and \( V_{on} \) decreases to 2.4V upon insertion of thin Liq and Csq layers. The devices with plain LiF/Al turn-on at 2.5V while the devices with both interfacial layers using Ag cathode turn-on at ~2.7V.

**Figure 4.13:** A summary of the drive voltage, \( V_{drive} \) (at 100Am\(^{-2}\)) for devices with Liq and Csq interfacial using different cathodes. The \( V_{drive} \) without interface layer using Al and LiF/Al cathodes are also shown.

Figure 4.13 shows a summary of \( V_{drive} \) at 100Am\(^{-2}\) for Liq and Csq interfaces using different cathodes. It is interesting to note that most of the cathodes performed very well, with \( V_{drive} \) as low as ~4.7V for either interface irrespective of the cathode metals used. Remarkably, the work function of the cathodes has little effect on \( V_{drive} \) once the thin layer of Liq or Csq is deposited. It is also worth noting that \( V_{drive} \) for these devices at 100Am\(^{-2}\) is still lower than that of the conventional LiF/Al cathode except for the Ag and Ag/Al cathodes. This indicates that thin interface layers of Liq and Csq are more efficient at high voltages compared to LiF. Furthermore when a Csq interface layer is incorporated with Mg, the device drive voltage increases in comparison to the Liq devices.
A summary of injection and power efficiency, extracted from J-V-L characteristics at J=100Am^2, is presented in Figures 4.14(a) and 4.14(b). The injection efficiency for
both interfaces is higher than that of the plain LiF/Al cathode. Even though the Ag and Ag/Al cathode has good injection efficiency compared to LiF/Al, it has a very high $V_{on}$ and so the power efficiency is poor. This shows that all the metals used, irrespective of their work function, have a tendency to increase the injection efficiency of the device when incorporated with Liq or Csq. It also suggests that this effect may not be due to the release of free Li or Cs from the corresponding metal quinolates because Ag is chemically less active than other cathode materials used here, and hence is less likely to react with the Liq and Csq to release the free metals. Furthermore the injection and power efficiencies are better for Ag cathodes than for the plain Al cathode. Even though Ag is regarded as a poor cathode material for electron injection, it can be very useful in combination with suitable interface materials such as Liq and Csq. Further there could be some possible improvements on the device performance as no optimisation was performed for the Liq or Csq thickness using the Ag cathode.

4.3.7 EL Spectra of OLEDs with Thin Mqs as Interfacial Layer

The EL spectra for the devices with Mqs as electron injection layer are presented in Figure 4.15. The spectra are collected at current density $\sim 100\text{Am}^{-2}$ for all devices.

**Figure 4.15:** EL spectra of devices ITO/TPD(500Å)/Alq3(500Å)/Mq(10Å)/Al layer. EL spectra using plain Al and LiF/Al cathodes are also shown.
All the devices with thin electron injection layers show similar EL to that of the Al and the LiF/Al only cathode devices, with a peak emission at 530nm which is the characteristic peak of the PL of Alq3.

4.3.8 Vbi Measurement for OLEDs

T.M. Brown et al. [7, 29] have shown that the built-in voltage $V_{bi}$ measurement is a useful technique to monitor the energy level line up for the PLEDs with different cathode materials. In previous chapter 3, it is already shown that the energy level diagram obtained from the $V_{bi}$ measurement by monitoring the photocurrent of the devices agreed well with UPS measurements. In this chapter, the same technique is used to determine the $V_{bi}$ of the devices with different interfaces using Al cathode in single and double layer structures. In the experiment, only the interfacial layer at the cathode is changed keeping the anode constant. It will provide the opportunity to find the change in $V_{bi}$ that corresponds directly to the change in the cathode work function due to interface material and the corresponding decrease in a barrier height for electron injection. For this, the single layer, ITO/Alq3(1000Å)/Mq(10Å)/cathode and double layer, ITO/TPD(500Å)/Alq3(500Å)/Mq(10Å)/cathode devices are fabricated and studied. Figure 4.16 shows photocurrent of such single and double layer devices.

4.3.8.1 Single Layer Devices

For the single layer devices, the anode side is common being plasma treated ITO with work function 4.8eV (Section 3.3.1.2). It is clearly seen that $V_{bi}$ is different for these devices using different interfaces to the Al cathode. The difference in $V_{bi}$ is solely due to the change in the interface at the cathode and the increase in $V_{bi}$ corresponds to a decrease in the electron injection barrier.

It is already shown that $V_{bi}$ of Alq3, single layer device is $\sim(1.41\pm0.02)V$ in section 3.4.1.1 with Al cathode. The effective work function of Al, $W_{Al}$ is 3.39eV. The value of $V_{bi}$ obtained is $(1.63\pm0.03)V$ using a Liq interface. The increase in $V_{bi}$ due to the introduction of the Liq is $\sim0.22V$. This indicates that due to introduction of the Liq, the effective $W_{Al}$ becomes 3.17eV. There is a lowering of the Al work function by $\sim1.13eV$ compared to the literature value. The increase in $V_{bi}$ ($\sim0.22V$) over an Al only cathode is equivalent to the lowering of the barrier height for electron injection due to Liq. This lowering of barrier height obtained here is similar to that of the LiF/Al cathode, in section 3.4.1.1. The influence of the Csq interface layer is slightly bigger
and $V_{bi}$ obtained is $(1.69\pm0.03)V$. Upon addition of thin layer of Csq, the $W_{Al}$ shifts by ~1.19 eV. The improvement of $V_{bi}$ or the decrease in $W_{Al}$ due to the Csq is ~0.28V over the Al cathode. The average value of $V_{bi}$ for different devices is summarised in Table 4.2. The effective work function of the cathode $W_{cathode}$ is obtained from the difference of $V_{bi}$ and $W_{ITO}$. The literature value of 5.8eV for the Alq3 HOMO was used throughout this work [30-33]. The absorption spectra measured shows that the optical band gap is around 2.8eV so the estimated value of the LUMO of Alq3 is ~3eV. The barrier height for an electron is calculated as a difference of the $W_{cathode}$ and LUMO of Alq3.

![Photocurrent characteristics for single and double Alq3 devices with Liq or Csq as the interfacial layers in a semi logarithmic plot.](image)

**Figure 4.16:** Photocurrent characteristics for single and double Alq3 devices with Liq or Csq as the interfacial layers in a semi logarithmic plot.

From Table 4.2, it is seen that the calculated $W_{Al}$ is not the standard literature value mentioned for bare Al ($W_{Al(Lit)}$=4.3eV) [25-28, 34]. Larger shifts of $W_{Al}$ due to the presence of Liq or Csq, here clearly indicate that the barrier height is reduced more compared to Al only cathode (see Table 4.2). The new barrier height for thin Liq or Csq is ~0.17eV. This barrier height is lower by ~0.22eV over the barrier height of the Al only cathode. A vacuum level shift at the Alq3/LiF/Al interface due to the presence of thin LiF is studied by Mori et al. and that showed a ~1.6eV shift [35]. The vacuum level shift observed in our case (using Liq or Csq) is slightly lower ~1.2eV. They
reported the reduced energetic barrier height for electron as ~0.1eV [35]. This value of electron injection barrier is consistent with our value obtained using thin Liq or Csq injection layers. This shows that the amount of improvement due to Liq and Csq interface layer is similar to that of LiF.

Table 4.2: Average $V_{bi}$ and calculation of the barrier height ($\Delta \Phi_{\text{electron}}$) for electron injection in single and double layer devices using different interfaces/cathodes.

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{bi}$ (V)</th>
<th>$W_{\text{Cathode}}$ ($W_{ITO}$ - $V_{bi}$)</th>
<th>$W_{\text{change}}$ ($W_{Al(Lit)}$ - $W_{\text{cathode}}$)</th>
<th>$\Delta \Phi_{\text{electron}}$ ($W_{\text{cathode}}$ - $E_{\text{LUMO}}$)</th>
<th>$V_{bi}$(double)-$V_{bi}$(single) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/Alq$_3$/Liq/Al</td>
<td>1.63±0.03</td>
<td>3.17</td>
<td>1.13</td>
<td>0.17</td>
<td>-------</td>
</tr>
<tr>
<td>ITO/Alq$_3$/Csq/Al</td>
<td>1.69±0.03</td>
<td>3.11</td>
<td>1.19</td>
<td>0.11</td>
<td>-------</td>
</tr>
<tr>
<td>ITO/TPD/Alq$_3$/Liq/Al</td>
<td>2.26±0.02</td>
<td>3.24</td>
<td>1.06</td>
<td>0.24</td>
<td>0.63</td>
</tr>
<tr>
<td>ITO/TPD/Alq$_3$/Csq/Al</td>
<td>2.28±0.02</td>
<td>3.22</td>
<td>1.08</td>
<td>0.22</td>
<td>0.59</td>
</tr>
</tbody>
</table>

4.3.8.2 Double Layer Devices

The average value of $V_{bi}$ measured for double layer devices is presented in Table 4.2. The $V_{bi}$ measured for the double layer device is greater than $V_{bi}$ measured for the single layer devices by ~0.61±0.02V when compared to devices with the same electrode (see column 6 in Table 4.2). It is already shown in Section 3.4.1.2, that once TPD is inserted in between the ITO and Alq$_3$, the $V_{bi}$ is measured from the HOMO of the TPD instead of $W_{ITO}$. The increase in $V_{bi}$ (~0.61eV) here is slightly lower than the difference between the HOMO of TPD (5.5eV) and $W_{ITO}$ (4.8eV), which may be due to a small vacuum level shift at the ITO/TPD or TPD/Alq$_3$ interface.

It is already shown that $V_{bi}$ of the double layer device with an Al only cathode is ~1.98±0.02V (section 3.4.1.2). Due to this, the effective $W_{Al}$ cathode becomes ~3.52eV due to a vacuum level shift of ~0.78eV at the Alq$_3$/Al interface. The new electron injection barrier is ~0.52eV which is otherwise ~1.3eV (if no vacuum levels shift). When thin Liq or Csq is inserted, $V_{bi}$ increases to ~2.26±0.02V, which shows the effective $W_{Al}$ cathode is further lowered to ~3.22eV. This is due to a vacuum level shift of ~1.06eV causing the barrier height for electron injection to be ~0.22eV. This vacuum level shift (~1.06eV) is similar to a vacuum level shift of (~1.04eV) obtained using a LiF/Al cathode. Like LiF, Liq and Csq introduce a lowering of the barrier height by ~0.3eV. There is no essential difference between Liq or Csq and LiF in terms of the
barrier height. Further despite being different in the electrical property of these materials, the mechanism of the electron improvement looks similar, they all lower the barrier height for electron injection by shifting the vacuum level for Alq3 down.

Further it is interesting to note that the vacuum level shift at the interface of Alq3/Al in single layer and double layer devices is slightly different for both interface/cathodes ($\Delta_{\text{single}} \approx 1.19\text{eV}$ and $\Delta_{\text{double}} \approx 1.06\text{eV}$). At present, the cause of this smaller magnitude of vacuum level shift for the double layer devices is not understood and further investigation is needed in this direction. It is, however worth noting that there may be a vacuum level shift at the ITO/TPD and TPD/Alq3 layer which is not considered in the calculation.

4.4 Possible Mechanism for Improved Electron Injection

A simple energy level diagram for a complete device is obtained by combining the individual energy levels together. This kind of energy level diagram fail to explain the mechanism behind the improved electron injection, because in a real device, the energy levels do not align at the organic/cathode interfaces according to the traditional model of a common vacuum level [36-38]. In chapter 3, we also demonstrated this experimentally for different organic/metal interfaces and shown that there are large vacuum level shifts at these interfaces, which result in the significant amount of barrier height reduction for electrons. In order to explain the mechanism of improved electron injection due to Mqs, the $V_{bi}$ measured in section 4.3.8 can be used to calculate an effective $W_{Al}$ and draw a complete energy level diagram of the device.

All the experimental data obtained in the measurement of $V_{bi}$ in section 4.3.8, have shown that the effect of using a thin layer of Mqs in Alq3 devices increases $V_{bi}$. This results from the changes in the interfacial structure at Alq3/Mq/Al interfaces that lower the energetic barrier for electrons. This gives direct evidence of lowering of the barrier height due to an increased dipole at the interfaces. Figure 4.17 below shows the relative energy level positions of devices with and without an interface layer, obtained by measurement of $V_{bi}$ and calculating $W_{Al}$.

In our Al device, $V_{bi}$ measured (Table 3.4 & 4.2) is not the difference of the work function of plasma treated ITO and that of Al, and equation (2.3) is not applicable. Clearly the $W_{Al}$ changes due to the interfacial activity which brings the effective work function $W_{Al}$ down to $\sim 3.39\text{eV}$ instead of $4.3\text{eV}$, the literature value of $W_{Al}$. This is not
unusual because in most of the organic layers the vacuum levels do not align when charge transfer occurs at the interfaces and there is dipole formation of magnitude $\Delta$. In such cases, equation (2.4) is applied instead of equation (2.3). The difference of the two values of $W_{Al}$ in our case is due to a dipole formation of magnitude $\Delta \sim 0.91$eV, according to equation (2.4) which is responsible for lowering $W_{Al}$, decreasing the electron injection barrier to $\sim 0.39$eV (which is otherwise 1.3eV).

![Energy Level Diagram](image)

**Figure 4.17: An energy level diagram for a single layer Alq$_3$ device with different interface/cathodes combinations.**

Upon using a LiF thin layer between the Alq$_3$ and the Al, there is an increase in $V_{bi}$. It shows that there is a dipole with a magnitude $\sim 1.13$eV and a corresponding decrease of $W_{Al}$ to 3.17eV (barrier height $\sim 0.17$eV). Similar improvement is observed in the case of thin Liq. Csq is more efficient in producing a bigger dipole as it lowers $W_{Al}$ to $\sim 3.11$eV with an interfacial dipole of magnitude $\sim 1.19$eV (electron barrier height $\sim 0.11$eV). This suggests that the magnitude of the interfacial dipole increases in the series of Mqs if one goes from Liq to Csq. The increase in device performance from Liq to Csq devices is most probably due to this dipole, which shifts the vacuum level and Alq$_3$ HOMO-LUMO downward by $\Delta$. As the work function of the central alkaline atom
decreases in the series, there is evidence that atomic size or work function play a role on the magnitude of the dipole formed at the interface.

As already mentioned in section 4.3.3 studies, the experimental data leads to the conclusion that thin layer of Mqs are acting as a hole blocking layers. The optical absorption gap for Mqs measured in our experiment is larger than that of Alq3, which may responsible for its blocking nature. Further, a shift of the HOMO-LUMO and a vacuum level downward may be another cause of the hole blocking nature as it makes harder for holes to enter the cathode. The large value of the dipole observed using Csq shows that it moves the HOMO-LUMO more and blocks holes more efficiently than Liq. This may be responsible for better injection efficiency of Csq compared to Liq. Furthermore, in the experimental data it has been observed that injection efficiency increases with an increase in the atomic size of the substituent and decreases with increasing work function of the alkaline atom in Mqs.

The performance of Mqs modified devices is related to the thickness of the interface layer. Thinner layers of Mqs are not as efficient as the optimised thickness of 10Å. This can be due to incomplete coverage of the organic layer. This thickness dependence observed is similar to the studies related to LiF and CsF [7, 30, 39-41]. Shaheen et al., using UPS, and Heil et al., using Kelvin Probe, found that the lowering of $W_{Al}$ is dependent on the thickness of LiF and after optimisation (thickness=10Å) the effective $W_{Al}$ remains constant. The observation of improved injection due to 5Å thin layers of Mqs in our experiment shows better performance than an Al only cathode, but due to incomplete coverage on the organic layer, $W_{Al}$ may not be effectively reduced to its lowest value. Once the thickness of Mqs becomes 10Å, $W_{Al}$ is fully lowered and there is no further reduction on increasing the thickness up to 40Å. The same turn-on voltage observed in 10-40Å Mqs devices is evidence that the device performance is already saturated after 10Å. We can conclude that 10Å of Mqs is the thickness that corresponds to the complete coverage of Alq3 layers as well as maximising the lowering of $W_{Al}$ and the dipole formation at the interface.

There is a proposed theory of Li liberation from Liq, due to the thermal evaporation of Al, as a possible mechanism of electron injection as in case of LiF. Liu et al. examined this by using different metals such as Al, Mg, Ca and Ag with Liq interfaces [19]. They found that the performance of the devices is similar for all three metals except Ag. They believed the mechanism of improved electron injection is the release of low work function metal Li from Liq on evaporation of Al, doping Alq3 with
Li. As Ag is less reactive than those metals, it cannot sufficiently release Li metal and results in poor electron injection. There is no other evidence of Li liberation in their study. All alkaline Mqs are stable, and it is difficult to release low work function (highly reactive) metals such as Li, Na, K, Rb, Cs etc. by high work function (less reactive) metals such as Al and Ag from the corresponding stable compounds. Further the performance of the devices obtained in this study are identical, even though the reactivity of the metals used (Al, Mg, Mg:Ag, LiF/Al) is quite different. This leads to the conclusion that it is unlikely that the release of the Li metal from Liq is the cause of the effects observed.

Low work function metal halides such as CsF, CaF2, MgF2, BaF2, etc. are widely used for lowering the electron injection barrier in devices [10, 18]. All these molecules are strongly polar and the introduction of a thin layer of such molecules can generate the dipole on the interface decreasing the surface potential and thus lowering the electron barrier [18]. During the formation process of Mqs, there is the transfer of an electron from the alkali metal atom to the quinolate ligand forming highly polar Mq molecules. It is expected that there is strong dipole formation at the interface due to the strong polarity in the Mq molecules. Moreover, the dipole formed at the interface is strongly linked to the chemisorbed water [42] and this process may be responsible for the strong dipole at the interfaces as all Mqs are highly hygroscopic. Experimentally, it is found that all Mqs are highly sensitive to the environment and a thin film can absorb water very quickly, within a few hours of evaporation resulting in a patchy film. Similarly, the OLED performance of the devices degrades faster than that of LiF/Al cathode devices, probably due to absorbed water at the interface even though Al was capped onto it.

High work function cathode materials such as Ag, also show an improvement of the device efficiency once a thin Mqs interface layer is used, where the reaction of the Ag metal with Mqs is less likely. In the experiment, when thin Liq or Csq is used as an interface layer, the device efficiency and the turn-on voltage of the device are found to be independent of work function of electrode materials such as Ag, Al, LiF, Mg, Mg:Ag, etc. This strongly suggests the formation of a strong dipole at the interface.

4.5 Conclusions

We have demonstrated that a series of alkaline metal quinolates (Liq, Naq, Kq, Rbq and Csq) act as efficient electron injection layers and improve the performance of
Alq3 based OLEDs in cooperation with high work function metals such as Al and Ag. These injection layers are similar to the well-established low-work function cathodes such as LiF/Al in terms of turn-on voltage, power and injection efficiencies. The improved device performance is due to better electron injection in the devices. Further the study of the thickness dependence on the device performance shows that devices are less sensitive to the interface layer thickness as it can be varied from 10-30Å without decreasing the efficiency and increasing the drive voltage significantly. This is additional advantage of Mqs over LiF interface layer, which provides more flexibility in device fabrication.

Comparisons of the performance of different Mq interfacial layer devices have shown very similar improvement in electron injection with the turn-on voltage ~2.4V. The injection efficiency, however, decreases from low work function (Cs) to high work function (Li). This is may be due to a decrease in the energetic barrier at cathode when one goes from Li to Cs.

The measurement of Vbi of the single and double layer devices using Mqs interface layers has shown an increase in Vbi and a corresponding decrease in the electron injection barrier compared to devices without interface layer devices. The Vbi obtained for the Alq3/Mq/Al devices is similar to that of Alq3/LiF/Al. There is an increase of Vbi~0.28eV for the interfacial layer devices (Vbi ~1.69 eV) over the plain Al (~1.41eV) device. This shows that there is more vacuum level shift (~1.19eV) at Alq3/Mq/Al interface and the electronic energy barrier is reduced to ~0.1eV. A shift of the vacuum level obtained from Vbi measurement has conclusively shown that there is a strong dipole formation with lowering the barrier height at Alq3/Mq/Al interfaces which is responsible for better electron injection and device performance.

Study of different metal cathodes has shown that there is no effect of the work function of the metallic cathodes on the device performance once Mq interfacial layer is inserted at cathode. All metal cathodes such as, Mg, Ag/Al, Al, LiF/Al and Mg:Ag cathodes show very similar device performance despite having very different work functions. Since the device performance observed is independent of the reactivity of the metal cathodes used, this strongly suggests that there is no releasing of the low work function alkaline metals from their corresponding Mqs. Even high work function metal Ag performs better than plain Al cathode. It suggests that the interfacial dipole is responsible for improved electron injection. The highly polar and hygroscopic nature of Mqs may be responsible for the strong dipole formation at the interface.
4.6 References


Chapter 5

Magnetoresistance of Group III tris (8-hydroxyquinoline) Organic Light Emitting Diodes

5.1 Introduction

Since the discovery of organic magnetoresistance (OMR) in nonmagnetic organic small molecules such as Alq₃, a lot of effort has been devoted to explain the mechanism responsible for it. Some of the OMR studies show that OMR is excitonic in nature. Kalinowski et al, in an early study, observed an increase in the photocurrent in a thin film of Alq₃ due to a magnetic field [1]. This was attributed to a hyperfine scale mixing of singlet and triplet electron-hole pair before charge separation. In the study, the mechanism of the increase in the current was explained by the formation of an excited Alq₃ molecule which undergoes either a decay path or forms a singlet electron-hole pair. The singlet electron-hole pairs can change into the triplet electron-hole pair by hyperfine interaction with the surrounding nuclei. These singlet and triplet electron-hole pairs can dissociate into a free charge carrier giving a photocurrent. It is further assumed that the dissociation of the singlet electron-hole pair is stronger than that of the triplet electron-hole pair due to the “ionic” nature of singlet electron-hole pair and the overall increase in the current is due to dissociation of singlet electron-hole pairs. This study however does not explained why a photo excited Alq₃ molecule undergoes such conversion and dissociation process instead of proceeding much easier radiative decay route. In a similar study in Alq₃ based OLED devices, the same group observed an increase in light output and current density upon application of a magnetic field [2]. They again explained the change in the current as due to the magnetic field modulation of the population of the singlet excitons and their diffusion to the cathode (as in Ref. [1]). The increase in the light output is attributed to modulation of the concentration of the singlet excitons by the hyperfine scale magnetic field dependent mixing of singlets and triplets [2].

Davis et al. proposed the spin dependent triplet-triplet annihilation (TTA) as a potential mechanism of OMR in their study [3, 4]. In this study, they assumed there is a bimolecular reaction in the material, consuming two triplets to form a singlet, which on
recombination gives increase in light output. The TTA process is already described in the section 1.7.2. in chapter 1. Their recent publication shows that TTA cannot be responsible for a large increase observed in EL at low bias and low magnetic fields, where the triplet concentration is very low [5]. In this study, however, they explained the increase in the EL in the magnetic field as due to the magnetic field induced charge transfer state forming singlet excitons in a similar manner to Ref. [1].

Prigodin et al. furthermore have proposed the excitonic model of OMR in which the magnetic field modulates the spin of the electron-hole pair. In the presence of a magnetic field, there can be only mixing of singlet and T0 triplet and this will change the recombination rate and the current in the device [6]. Another consideration made in this study, is that an electron-hole pair can dissociate back into the free charge carriers. If there is mixing of the singlet and T0 triplet states only in a magnetic field, according to the model, then there will be a decrease in recombination and an increase in dissociation current. They are able to derive the mathematical model for the proposed mechanism and have shown that there is maximum of -50% OMR achievable at high temperatures. Such a high value of OMR, however is not reported yet.

There are some disagreements to the excitonic nature of OMR [7-9]. Some of the studies have shown that there is OMR in “hole-only” devices. Francis et al. found that OMR is independent of cathode material while dependent only on anode material for poly(9,9-dioctylfluorenyl-2,7-diyl)(PFO) devices. They attributed OMR in PFO to the hole transport and concluded that it is not related to the electron transport and electron-hole recombination process [7]. However for their “hole only” devices, OMR was only observed at very high voltages (> 40V) where “weak electroluminescence” was also seen. This demonstrates that excitons must have been present in the regime where OMR was observed, however, this fact was not addressed in their study. Further they found that the OMR in Alq3 is dependent on cathode material and reached the conclusion that none of the existing models can explain their Alq3 OMR results [8, 9].

In our recent study, we have used different cathodes for electron injection in Alq3 OLEDs and studied OMR, light output and efficiency changes upon application of the magnetic field [10]. We observed a very strong correlation between the electron injection, light emission and appearance of OMR for the first time in such devices. Light emission and OMR occurs at the same point on the J-V characteristics of the device at the point of electron injection (namely inflection point). The OMR is first seen at the same drive voltage as electron injection is occurring and the device is emitting
light. This leads us to conclude that OMR may be excitonic in nature [10], as described in section 1.7.3. Furthermore, we observed a sharp increase in the luminance and efficiency of devices at low magnetic fields, which saturates at high magnetic fields. This suggests that the singlet concentration is increasing in the magnetic field due to the hyperfine scale mixing of singlet-triplet, as already mentioned by many previous studies [1, 2]. A very similar characteristic is observed in device current upon application of the magnetic field further suggesting that the change in current (OMR) also shares the common origin. This means that the same hyperfine mixing of the singlet-triplet gives positive OMR. This is possible only when there is an interaction between a charge carrier and a triplet. On application of the magnetic field there may be a reduction of the triplet concentration as they are converted into singlets, which causes an increase in the mobility of the charge carrier, hence increasing current. Desai et al. conclude that the origin of OMR is due to the triplet interaction with charge carriers in the device [10].

Recently, spin dynamics was introduced in order to explore the underlying mechanism of OMR. Moreover, materials with different spin-orbit coupling were studied in order to tune OMR [11-13]. Many studies done on tris-(2-phenylpyridine) iridium (Ir(ppy)3) and platinum octaethylporphyrin (PtOEP) have shown an increase in the spin-orbit coupling brought from the presence of a heavy atom in the molecule, can reduce the magnitude of OMR significantly [6, 11, 12]. The reduction in OMR in these materials is consistent with our triplet-carrier interaction model [10]. This is because there could be a reduction of the diffusion of triplets due to short triplet life times brought about by the introduction of heavy atoms in the molecule. OMR measurements done on polyphenylene ethynelene (PPE) have also shown larger magnitude OMR than in platinum doped Pt-PPE [8]. Even though these experimental results have shown that OMR decreases due to presence of heavy atom, the study concluded that there is little effect of spin-orbit coupling on existing OMR. Clearly, the effect of the spin-orbit coupling on the OMR needs further investigation. In this context, we undertook OMR studies on a series of group III 8-hydroxyquinolates (Mq3), (where M=Al, Ga and In), as it has been shown that these materials exhibit comparable PL and EL efficiencies and transport properties [14]. It is therefore easy to investigate OMR in devices made from these materials and relate differences to the change of central atom. Further we will verify whether our proposed mechanisms are still applicable to these systems.

Desai et al. have extensively studied the thickness dependence of OMR in Alq3 based devices. Both positive and negative OMR were observed depending upon the
device thickness, applied magnetic field and operating voltage [15, 16]. This study suggested a cause of both the positive and negative magnetoresistance. The devices thicker than 150Å always exhibit positive OMR in the whole range of drive voltages. This is attributed to the interaction between carriers and triplets in the presence of a magnetic field. Once the device is operated in forward bias, there will be more triplets in the device than singlets. Upon the application of magnetic field, triplets change into singlets due to intersystem crossing possibly due to the hyperfine scale interaction as described in section 1.7. This decreases the triplet concentration so that the carrier-triplet interaction is reduced, increasing the mobility of charge carriers and resulting in positive OMR.

In contrast to the above, corresponding to the onset of electron injection and light emission of the device, a negative OMR is seen near to the turn-on of thin devices. This negative OMR is observed for the devices thinner than 150Å at low drive voltages and changes to positive on increasing the drive voltage. The occurrence of a negative OMR at low voltages for the thin devices cannot be explained by the carrier-triplet interaction model. This is because if carrier-triplet interaction is occurring in the device, there would be positive OMR upon application of magnetic field due to the increased carrier mobility caused by the reduced interaction of charge carriers with triplets. This strongly suggests that the triplets in the thin devices are playing a completely different role.

It is worth mentioning that the recombination life time of singlet and triplet in Alq3 is ~10-20ns and 25µs respectively [17, 18]. Due to their short life time of singlets they quickly undergo radiative recombination while the long lived triplets are able to diffuse through the device and be quenched at suitable interfaces such as electrodes. The negative OMR seen in the thin device could be due to the diffusion and dissociation of the triplets at the electrodes. Upon application of a magnetic field, if there is a decrease of the triplet concentration due to intersystem crossing, there will be lowering of the dissociation of the triplets at the electrodes and a decrease in the current flowing through the device and resulting in negative OMR. Further we believe that the process of dissociation is occurring at the Alq3/cathode interface. As there exists an energetic barrier between the LUMO of Alq3 and TPD, triplets are expected to be formed in the Alq3 and not to diffuse in to the TPD. In order to verify the hypothesis that negative OMR is due the dissociation and diffusion at the Alq3/cathode interface, we introduced 2,9,-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as a hole/exciton blocking layer.
between the emission layer and the cathode. The results of this study are presented below in section 5.3.1.

As a continuation of the thickness dependence studies in Alq$_3$ carried out in our research group, the results of the devices with BCP hole/exciton blocking layers are first presented. In sections 5.3.2 and 5.3.3, we study OMR of Gaq$_3$ and Inq$_3$ parametric in device thicknesses. OMR, light output and efficiency measurements are carried out with varying magnetic field and operating voltage. We demonstrate that OMR observed in Gaq$_3$ and Inq$_3$ is excitonic in nature as shown in Alq$_3$. Finally, we further compare the effect of the change in the ion on OMR of Mq$_3$ and explain the phenomenon in terms of the diffusion and dissociation of triplets and their life time changes due to heavy ions and the spin-orbit coupling introduced in the molecule.

5.2 Experimental

Devices with Alq$_3$ thickness varying from 150-900Å and with a 200Å BCP exciton blocking layer, interposed between the Alq$_3$ and the LiF/Al cathode were fabricated. In order to study the thickness dependent OMR, devices with various active layers of Gaq$_3$ and Inq$_3$ (ranging from 100-900Å) were fabricated. Diode structures where the active layer of Gaq$_3$ (500Å) was sandwiched between a plasma treated ITO anode and a 500Å TPD hole transporting layer using different electrodes such as Al, LiF/Al and Mg:Ag were also fabricated. The fabrication process was carried out as described in section 2.3. The measurements of OMR were carried out as explained in section 2.4.6.

5.3 Results and discussion

In this section, we first present the results of the thickness dependence OMR study in Alq$_3$ devices with a BCP hole/exciton blocking layer. This work forms a continuation of our OMR measurements in Alq$_3$. We also investigate OMR in Gaq$_3$ and Inq$_3$ with different thickness and compare them with the results obtained for Alq$_3$. These materials were chosen because once the Al is replaced by Ga and In, the ion mass increases which potentially introduces greater spin-orbit coupling. As their chemical structure remains identical to Alq$_3$, in which OMR is extensively studied by our research group, it will provide an opportunity to compare the mechanism of OMR in terms of the change in the central atom and spin-orbit coupling in the quinolate.
5.3.1 OMR of Alq₃ OLEDs with BCP Layer

Some of the important results of the thickness dependence studies of Alq₃ done in the group (Refs. [15, 16]) are presented first. Figure 5.1 summarises the thickness dependence of OMR (\(\Delta I/I\)) and efficiency (\(\Delta\eta/\eta\)) in a magnetic field for Alq₃ devices. It can clearly be seen that the efficiency change in the devices is always positive and comparable in magnitude for different thicknesses.

Figure 5.1: OMR (\(\Delta I/I\)) and efficiency (\(\Delta\eta/\eta\)) variation with magnetic field for Alq₃ devices with thickness ranging from 115 to 900Å (Refs. [15, 16]). The data corresponds to a current density of ~0.1Am⁻² for all devices.
A typical example of efficiency change for 900Å Alq₃ device at various drive voltages is shown in Figure 5.2. The sharp change in the efficiency at low fields is attributed to the mixing of the singlets and triplets in presence of the magnetic field. It is referred as hyperfine scale interaction as described in section 1.7.

In a device under electrical excitation, there are three triplets formed for every singlet. Intersystem crossing (i.e., conversion of singlets into triplets or vice versa) can occur and will be dependent upon temperature and the energy barrier between the singlet and triplet states. Previous studies show an increase in the mixing of singlets and triplets upon application of a magnetic field due to increase of the intersystem crossing rate [19, 20]. If there are more triplets in the system, such as in the case of electrical excitation, some will convert into singlets, which increases the singlet concentration. This produces more recombination resulting in an increase in the EL and efficiency of devices under magnetic field. The saturation of the efficiency plots for all devices with different thicknesses and at all drive voltages beyond low field process suggests that there is no additional process at high magnetic field.

Figure 5.2: Differential efficiency ($\Delta \eta / \eta$) of a 900Å Alq₃ device at various drive voltages.
The thickness dependence of OMR is quite interesting as both positive and negative OMR was observed depending on thickness and drive voltage. The devices thicker than 150Å always show positive OMR. In contrast to this, devices thinner than 150Å show negative OMR at low voltages. It is quite interesting to note that although the OMR changes from negative to positive, upon increase in the device thickness, the shape of OMR at low magnetic field remains same (see figure 5.1). We have observed a sharp change in OMR at low magnetic fields which is analogous to the change in efficiency at low magnetic fields as discussed above. This behaviour was observed for all devices and all thicknesses irrespective of the sign of the OMR. This suggests that same hyperfine scale conversion of triplets into singlets is responsible for the existing sharp change in OMR at low magnetic fields. The mechanism which is responsible for OMR however seems different for thick and thin devices.

Positive OMR for devices thicker than 150Å can be explained by the interaction of the triplet and free carrier in magnetic field as described in section 1.7.4. Ern et al. have studied the interaction of triplets with paramagnetic centres such as free charge carriers in a magnetic field [21]. They reported such interaction results in either the trapping of the free carriers or the quenching of triplets by forming an excited ground state. As there is a formation of an intermediate product by the combination of triplet and free carrier, the mobility of the free carrier is expected to decrease. The process can be denoted by the relation (1.10). If there is a reduction of the triplets in the presence of a magnetic field due to intersystem crossing, there will be smaller number of triplets available for the interaction with free carriers. This reduces the trapping of free carriers with triplets so that mobility of free charge carrier increases, giving the positive OMR.

It is interesting to note that OMR for thin devices (Alq₃ thickness ≤ 150Å) is negative (see Figure 5.1) at low voltages, which goes to positive at high voltages. Negative OMR cannot be explained by a mechanism of the triplet-carrier interaction in the magnetic field as discussed above. This strongly suggests that triplets play a different role in thinner devices to give negative OMR. We attribute this to the diffusion and dissociation of triplets at interfaces. The life time of triplets is long enough that they remain in the device until they are quenched at an interface or by other quenching processes like TTA (relation 1.8) and triplet-carrier interaction (relation 1.10). In thin devices, however they can easily diffuse, dissociate and be quenched at the cathode interface. This is likely to occur at the cathode interface as most of the excitons are formed near to the TPD/Alq₃ interface and diffuse towards the Alq₃/cathode interfaces.
Upon applying the magnetic field, the triplet concentration and dissociation of triplets decrease due to intersystem crossing. As a result, the current in the device decreases, giving negative OMR.

To the best of our knowledge, the hypothesis of triplet dissociation and diffusion has not been studied to date. In order to test this hypothesis experimentally, we made a series of devices with various Alq3 thicknesses, including a 200Å BCP hole/exciton blocking layer between the Alq3 and the LiF/Al cathode.

![Graph showing OMR (ΔI/I) and efficiency (Δη/η) variation of Alq3 devices including a 200Å BCP hole/exciton blocking layer. The data corresponds to a current density of ~1Am⁻² for all devices.](image)

**Figure 5.3:** OMR (ΔI/I) and efficiency (Δη/η) variation of Alq3 devices including a 200Å BCP hole/exciton blocking layer. The data corresponds to a current density of ~1Am⁻² for all devices.
BCP is a wide energy gap material with HOMO and LUMO levels at 6.7 and 3.2eV respectively [22, 23]. Due to the higher value of the HOMO, it is regarded as an efficient hole/exciton blocking material. A detailed discussion of its hole/exciton blocking nature of BCP is carried out in section 6.3.1. Figure 5.3 presents a summary of OMR results for devices with BCP. As expected, we observed a positive efficiency change in all devices similar to Alq3 only devices (see Figure 5.1), which is attributed to a hyperfine scale interaction of singlets and triplets in the magnetic field. Further as in the case of Alq3 devices, the percentage change in efficiency decreases with increasing Alq3 thickness. OMR plots also show a positive OMR at all drive voltages for all devices, irrespective of the Alq3 thickness. This suggests that there is no more dissociation of triplets at the cathode interface for thin devices and all excitons are trapped and confined at Alq3 layer due to large energy barrier at Alq3/BCP. These results strongly suggest that negative OMR seen in the thin Alq3 devices is due to dissociation of triplet excitons at cathode.

**Figure 5.4:** A schematic diagram of the formation of the triplet excitons near to the TPD/Alq3 interface and their dissociation at Alq3/cathode interface in thin Alq3 devices. The dissociation of the excitons give holes, that entered at cathode and electrons are recycled back into the organic layer giving the device current.

The mechanism of negative OMR is schematically depicted in Figure 5.4. Due to the favourable condition of a small energetic barrier at the cathode, triplets formed at the TPD/Alq3 interface are able to diffuse to the Alq3/LiF/Al interface and will
dissociate. The holes belonging to the triplet excitons can enter the cathode releasing an electron back into the device. The released electron is recycled into the device, constituting part of the device current under forward bias. The carrier recycling is lowered in the presence of a magnetic field as the number of triplets is reduced due to intersystem crossing so that the device current decreases and giving negative OMR. Once BCP is inserted between the Alq3 and the LiF/Al cathode, the dissociation of triplets is stopped as BCP offers higher barrier for exciton dissociation as shown in Figure 5.5 and just positive OMR is observed, due to the carrier-triplet interaction as in thick devices.

**Figure 5.5:** A schematic energy level diagram for the device with BCP hole/exciton blocking layer. The triplet excitons could not dissociate at the cathode interface due to the higher barrier height offered by BCP.

### 5.3.2 OMR of Gaq3 OLEDs

A summary of percentage change in current and efficiency as a function of applied magnetic field for Gaq3 devices with thickness varying from 100-900Å is shown in Figure 5.6. Similar plots are also obtained at higher current densities for all devices. The efficiency variation with magnetic field is always positive and comparable in magnitude for all devices of different thickness. The magnitude of \( \Delta \eta / \eta \) decreases with increasing thickness, and these results are consistent to those obtained for Alq3 with and without BCP layers (shown in Figures 5.1 and 5.3 respectively). For all efficiency plots, a sharp
change in efficiency occurs at low magnetic fields, corresponding to hyperfine mixing of singlets and triplets. A plateau is obtained at high magnetic fields which indicate that there is no additional process.

![Graph showing the percentage change in current (ΔI/I) and efficiency (Δη/η) as a function of applied magnetic field for GaQ3 devices of different thickness.](image)

**Figure 5.6:** Percentage change in current (ΔI/I) and efficiency (Δη/η) as a function of applied magnetic field for GaQ3 devices of different thickness. (All measured at a current density of ~0.1 Am², near to the turn-on of each device.)

Figure 5.6 clearly shows that OMR of GaQ3 device can be positive, negative and a combination of both depending on thickness, magnetic field and drive voltage. As in the
case of thin Alq3 devices (section 5.3.1), we obtained negative OMR for thin Gaq3 devices with thickness $\leq 150\text{Å}$ and positive OMR for thickness $>150\text{Å}$ at low voltages. In the case of thin devices, a negative OMR was observed at low voltage, which goes to positive at high voltage (see Figure 5.8(a) and (b)). The magnitude of the negative OMR decreases with increasing Gaq3 thickness. For example, 100Å of Gaq3 shows maximum negative OMR $\sim$1%, at about turn-on voltage, while it is reduced to <0.5% for 145Å. Negative OMR of 200Å and 150Å Gaq3 devices was found to be smaller in magnitude than that of 100Å device. Negative OMR completely disappears for thicker devices (300-900Å). The reduction in the negative OMR with increased Gaq3 thickness is similar to that seen in Alq3 devices which are attributed to the dissociation of the triplet excitons at the cathode interface. This suggests that there is a dissociation of triplets at the Gaq3/cathode interface giving rise to negative OMR. Furthermore, we already demonstrated that the energetic barrier for Gaq3/LiF/Al interface is similar to that of Alq3/LiF/Al with barrier height for electron injection $\sim$0.40eV in chapter 3 (sections 3.3.2 and 3.3.3) which shows that the Gaq3/LiF/Al interface is as equally favourable for exciton dissociation as that of Alq3/LiF/Al interface. Hence it is obvious to conclude that negative OMR in Gaq3 device is also due to dissociation of triplets at the cathode interface. A reduction in negative OMR with increase in thickness of thin Gaq3 devices also agrees the theory of dissociation of triplets at the cathodes.

The percentage change in efficiency ($\Delta\eta/\eta$) of these devices at different driving voltages was also studied. Figure 5.7 shows a representative plot for a 900Å Gaq3 device. The shape of the plot remains same even though the maximum change in efficiency varies from $\sim$8% at low drive voltage (near to the turn-on voltage) to $\sim$2% at high voltage. A sharp change in efficiency at low magnetic fields, corresponding to the hyperfine scale mixing of singlets and triplets, is visible. This further suggests that there are no additional processes, such as TTA (relation 1.8) and/or triplet quenching (relation 1.10) by the free carriers occurring in the device at higher magnetic fields.
**Figure 5.7:** Percentage change in efficiency ($\Delta\eta/\eta$) as a function of applied magnetic field for a 900Å Gaq₃ device at different drive voltages. The solid lines are guidelines to the eye.

Figures 5.8(a) and 5.8(b) show OMR observed at various drive voltages for 100Å and 900Å Gaq₃ devices respectively. For the 100Å device, negative OMR is observed for all magnetic fields at low voltages, becoming positive at high drive voltages. A sharp change in OMR was seen only at very low voltages and low magnetic fields. The magnitude of negative OMR is found to be smaller than that in Alq₃ as seen in Figure 5.1. The sharpness of the low field negative OMR for thin devices is similar to that observed in the efficiency plots shown in Figure 5.7. Further at low drive voltages, there is complete saturation in OMR after a sharp change in low magnetic field. It indicates that the hyperfine scale conversion of triplets into singlets is responsible for the low field changes in efficiency and device current, just as in the case of Alq₃.
Figure 5.8: Magnetoresistance ($\Delta I/I$) as a function of applied magnetic field for (a) 100 Å and (b) 900Å Ga$q_3$ devices at various drive voltages. Inset of 5.8(b) shows the low voltage OMR data for a 900Å Ga$q_3$ device.

At high drive voltages, a small negative OMR of magnitude ~0.2% is observed which becomes positive at higher magnetic fields (see figure 5.8(a)). Upon increasing the drive voltage, the magnitude of the negative OMR decreases continuously and in
addition to the small negative OMR, another process starts to appear which gives rise to positive OMR (e.g. 2.3-2.5V). This is similar to the process noted for thick Alq₃ devices and tentatively attributed to the triplet-carrier interaction at high field. This process is proportional to magnetic field and also scales with the applied voltage. This clearly shows that for thin devices, at high current densities, a negative spike observed at low magnetic fields followed by positive OMR at high magnetic fields is the result of two processes namely triplet dissociation and triplet-carrier interaction. The linear rise of OMR with increasing magnetic field and drive voltage can be seen for all devices with different thickness, however, negative OMR completely disappears for the thicker devices (see inset of Figure 5.8(b)). There is only a single process visible for a 900Å Gaq₃ device, OMR remains ~0% at low fields and afterwards rises linearly. These results show that the magnetic field dependent triplet-carrier interaction is the only significant process for thick devices, whilst for thin devices, the triplet dissociation seems to be significant. It clearly shows that there are always two processes in OMR plots, however depending upon the device thickness, the magnetic field and the drive voltage, their significance in comparison to one another varies.

The excitonic nature of OMR in Gaq₃ devices were studied with three different cathodes namely Al, LiF/Al and Mg:Ag. A strong correlation between the inflection points in the I-V (i.e. electron injection), light emission and OMR were observed in all cases. A typical example of the I-V-L characteristics, OMR and the efficiency variation with the applied voltage at 125mT and 200mT is shown in Figure 5.9 for a 500Å Gaq₃ device with the LiF/Al cathode. Very similar plots were obtained for Al and Mg:Ag cathodes. No OMR was observed before the turn-on voltage of the device. This shows that OMR cannot be observed in the unipolar transport region. Furthermore, it strongly suggests that the bipolar transport and exciton formation are necessary for the origin of OMR. It is however in contradiction to previous studies where OMR was reported in the “hole-only” devices [7]. However, as stated in the introduction, these “hole only” devices showed a weak electroluminescence which indicates that they were not “hole only” and hence is compatible with our interpretation.
Figure 5.9: I-V-L and OMR characteristics for a 500Å Gaq₃ device with LiF/Al cathode. OMR and change in efficiency variation with drive voltages at 125mT (hollow circle) and 200 mT (solid circle) are shown. OMR is noted in the device at first, at the point of the inflection in the I-V characteristics which indicates that electron injection is started in the device. At the same voltage, the device is emitting light, showing that exciton formation and recombination is also occurring.
5.3.3 OMR of Inq₃ OLEDs

Figure 5.10 summarises OMR and efficiency changes due to a magnetic field for Inq₃ devices with different thickness varying from 100-900Å. The shape of $\Delta\eta/\eta$ for all devices with different thickness is similar to that of Alq₃ and Gaq₃, with only hyperfine scale mixing of singlets and triplets at low fields visible. The $\Delta\eta/\eta$ at different voltages is identical to that of 900Å Gaq₃ device presented in Figure 5.8.

**Figure 5.10**: OMR ($\Delta I/I$) and change in current efficiency ($\Delta\eta/\eta$) as a function of applied magnetic field for Inq₃ device with varying thickness from 100-900Å. The plots taken at a current density ~0.1A/m² which also correspond to the turn-on of each device.
OMR of Inq₃ devices is reduced dramatically in comparison to that of Alq₃ and Gaq₃. There is no sharp feature in OMR at low magnetic fields in contrast to the efficiency plots. Furthermore, OMR for Inq₃ shows more interesting properties with additional features appearing on the plots according to magnetic field. These additional features are also found to be dependent upon the thickness of Inq₃.

OMR of 100Å Inq₃ device at various operating voltages is presented in Figure 5.11(a) with low magnetic field data in the inset. At low fields, OMR goes to small negative values ~0.1% at about 6mT and then increases at higher fields. This characteristic is observed only for 100Å Inq₃ device at low magnetic fields. Small negative OMR at low field may be attributed to triplet diffusion and dissociation at the cathode as in the case of Alq₃ and Gaq₃. However, a clear negative OMR is not visible as in the case of thin Gaq₃ and Alq₃. This shows that the dissociation of triplets at the cathode interface is very weak in Inq₃ devices which may be due to the introduction of a heavy atom in the molecule. The heavy atom reduces the triplet life time and so diffusion and dissociation of triplets is decreased and less negative OMR is seen.

At high fields, OMR goes positive with a linear increase with magnetic field and scales with drive voltages. This nature is quite similar to Alq₃ OMR and attributed to the triplet-carrier interaction in the magnetic fields which is already described in section 5.3.1. A small negative spike was observed at very low magnetic field which is dissociation related whereas the positive OMR at high magnetic fields is due to the triplet-carrier interaction (see inset of Figure 5.11(a)). OMR data for the 100Å Inq₃ device shows a combination of two processes similar to that shown in Alq₃ and Gaq₃ devices.

OMR of a thick device (900Å of Inq₃) is shown in the Figure 5.10(b) along with low field data in the inset. OMR of Inq₃ at low magnetic field is totally different to that of Alq₃ and Gaq₃. An additional peak was seen in the thicker Inq₃ device which was not observed in 100Å device and other Alq₃ and Gaq₃ devices. The 900Å of Inq₃ device shows a small positive peak of magnitude ~0.05% in OMR at ~6mT. After this peak, the OMR goes to small negative value up to ~50mT and afterwards it increases to positive values with increasing magnetic field. The characteristic peak observed at low field was seen for all Inq₃ devices with thickness varying from 200Å to 900Å. At the moment, the cause of this peak is not clearly understood, as low field measurements were not carried out in detail and further investigation is needed. The positive OMR at high magnetic fields is similar to that observed in Alq₃ and Gaq₃.
Figure 5.11: Magnetoresistance ($\Delta I/I$) as a function of applied magnetic field for the devices (a) In$q_3$(100Å) and (b) In$q_3$(900Å) at various drive voltages. Insets show the low magnetic field data. Small negative OMR is observed at low magnetic field and goes to positive for 100Å In$q_3$. OMR for 900Å In$q_3$, a small positive peak (at ~6mT) is observed which is followed by a small negative OMR.
We examined the correlation of the electron injection, light emission and the OMR observation in Inq$_3$ devices with different thickness. Similar to Alq$_3$ and Gaq$_3$, we saw a strong correlation between these three processes (see Figure 5.12). It strongly confirms bipolar transport and exciton formation in the device is necessary for the existence of OMR.

![Image of Figure 5.12: I-V-L and OMR characteristics for a 500Å Inq$_3$ device with a LiF/Al cathode. The OMR (at 200mT) is noted in the device at first at 2.2V, at same point the device is emitting light. The voltage clearly corresponds to the electron injection point in the I-V characteristics.]

**Figure 5.12:** I-V-L and OMR characteristics for a 500Å Inq$_3$ device with a LiF/Al cathode. The OMR (at 200mT) is noted in the device at first at 2.2V, at same point the device is emitting light. The voltage clearly corresponds to the electron injection point in the I-V characteristics.
### 5.3.4 OMR Comparison in Group III Quinolates

A summary of comparison of OMR in Mq₃ is presented in this section.

**Figure 5.13:** OMR (ΔI/I) in 500Å Mq₃ devices at various drive voltages. The plots are taken at a constant magnetic field at 200mT.

In all Mq₃ devices studied, no OMR was observed below turn-on voltage (<2.0V). OMR increases to a maximum value with increasing drive voltage and then decays as shown in Figure 5.13. An abrupt increase in OMR (~2.5%) for the Alq₃ device, just after the device turn-on was observed, while Gaq₃ shows approximately 1.0% of OMR and Inq₃ has only 0.35% of OMR. This clearly indicates that the magnitude of the OMR diminishes very sharply due to presence of the heavy ion in the quinoline molecule. This observation is consistent to previous OMR studies done on small molecule organics containing heavy ions such as Ir(ppy)₃ [6, 8, 11] and PtOEP [8, 13]. A study on Alq₃ doped with Ir(ppy)₃ and PtOEP shows that OMR is reduced by a factor of 10 for Ir(ppy)₃ doped system while OMR completely disappears for the PtOEP doped system [8, 13]. The fact that reduction and disappearance of OMR is observed in those systems, due to introduction of a heavy ion with strong spin-orbit coupling in the molecules, is consistent with a reduction of the triplets-carrier interactions due to shorter triplet lifetime.

As stated in the introduction, Prigodin proposed the excitonic model stating that OMR is due to magnetic field modulation of the spin interconversion in the electron-
hole pair state of singlet and \( T_0 \) triplet state \([6]\). This will change the recombination and dissociation of electron-hole pairs in the device and thus the current. If this model is correct for our devices, then there should be a linear relation between \( \Delta I/I \) and \( \Delta \eta/\eta \). In order to examine whether this is the case, \( \Delta \eta/\eta \) is plotted against \( \Delta I/I \) for all Mq\( \_3 \) as shown in Figure 5.14. A linear relationship in between \( \Delta I/I \) and \( \Delta \eta/\eta \) was observed only for Alq\( \_3 \) for up to \( \Delta I/I=1.5\% \) which corresponds to a magnetic field of magnitude 25mT. A continuous rise in current was observed beyond 25mT while the efficiency remained constant. This shows that Prigodin’s model is applicable for Alq\( \_3 \), only at low magnetic fields (<25mT). It is interesting to note that no such linear relation has been observed for Gaq\( \_3 \) and Inq\( \_3 \). Figure 5.14 shows that there is a sharp rise in efficiency up to 2% and 4% for Gaq\( \_3 \) and Inq\( \_3 \) respectively, while the current change in the device is negligible (<0.1%). This clearly indicates that change in efficiency is not just the consequence of the change of dissociation current. Prigodin’s model does not satisfactorily explain the origin of OMR for all Mq\( \_3 \).

Figure 5.14: OMR (\( \Delta I/I \)) plotted against the efficiency change (\( \Delta \eta/\eta \)) for 500Å Mq\( \_3 \) devices at 2.8V. \( \Delta I/I \) show a linear rise with (\( \Delta \eta/\eta \)) up to a magnetic field ~25mT for Alq\( \_3 \) only. No linear relationship is observed in between \( \Delta I/I \) and \( \Delta \eta/\eta \) for Gaq\( \_3 \) and Inq\( \_3 \).

Figure 5.15 shows the \( \Delta \eta/\eta \) plot for 100Å Mq\( \_3 \) devices near to the turn-on. The plot shows that even though the magnitude \( \Delta \eta/\eta \) for Mq\( \_3 \) is comparable, the value of
maximum $\Delta \eta/\eta$ decreases as the ion mass increases. The value of maximum $\Delta \eta/\eta$ for Alq$_3$ is ~11%, for Gaq$_3$ is ~7.5% and for Inq$_3$ is ~6%. This indicates that introduction of heavy ion in the molecule with stronger spin-orbit coupling, there is some increase in the mixing of the singlet and triplet states beforehand as explained in section 1.7.1, chapter 1, so on applying the magnetic field, a lesser effect of mixing of triplets and singlets occurs so that a lower percentage change in the efficiency was observed. After 50 mT, the plot remains almost constant, showing the saturation in the change in efficiency for all Mq$_3$, indicating that there is no additional processes occurring at higher magnetic fields.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.15.png}
\caption{The percentage change in efficiency ($\Delta \eta/\eta$) at various magnetic fields for 100Å Mq$_3$ devices just after the device turn-on. The solid lines are guidelines to the eye.}
\end{figure}

Figure 5.16 shows a comparison of OMR for 900Å Mq$_3$ devices at a current density ~100Am$^{-2}$. OMR plot for Alq$_3$ is similar to the efficiency plot shown in Figure 5.15 with a sharp rise at low fields. OMR increases with the magnetic field afterwards almost linearly. There is no saturation in OMR plots at high fields, as in the case of efficiency within measurement range. OMR plots for Gaq$_3$ and Inq$_3$ are surprisingly different than that of Alq$_3$ and have no sharp rising component corresponding to efficiency plots at low fields. This indicates that the magnetic field effect of the triplet-singlet conversion at low field has no effect on the carrier mobility and the device
current for these materials. The OMR of Alq₃, however, suggests that the mobility of the carrier is highly affected by the presence of the triplets, which interact with the free carriers in order to lower the mobility. Since there is strong interaction between the free carriers and triplets in Alq₃ and the triplet concentration is magnetic field dependent, we observed similar magnetic field behaviour in efficiency and current. However in case of Gaq₃ and Inq₃, the interaction of the triplets and carriers is negligible at low magnetic field and a decrease in the triplet concentration does not appear to greatly affect the mobility and the device current. This further suggests that the free triplet-carrier interaction is less bound and there is a little energetic barrier for the trapped charge carrier at the triplet state for Gaq₃ and Inq₃.

![Graph](image)

*Figure 5.16: OMR (ΔI/I) variation with magnetic field for 900Å Mq₃ devices at a current density of ~100Am⁻².*

The linear increase in OMR for all three Mq₃ at high magnetic fields is similar and is due to the triplet-carrier interaction. As explained in section 1.7.2, in relation (1.10), since the triplet is involved in the triplet-carrier interaction, the process is expected to be spin and, hence magnetic field dependent. A linear increase of OMR with magnetic field seen in Figure 5.16 may be due to such magnetic field dependence of the triplet-carrier interaction.
A comparison of negative OMR for thin Mq₃ devices is presented in Figure 5.17. For Alq₃, the negative OMR obtained in the thin devices at low voltages is visible clearly for 150Å (and thinner) and no negative OMR is seen for devices thicker than 200Å. For Gaq₃, the negative OMR is just visible for 145Å and it is significant only when the thickness is decreased to 100Å (or less). In contrast to this, a complete negative OMR is not observed for 100Å Inq₃ device even at low voltages. The big differences in magnitude of the negative OMR show that dissociation of triplets is different in Mq₃ and decreases with increasing the central ion in the quinolate molecules. This may be due to a decrease in the diffusion length of the triplets due to the shorter life time, as a result of strong spin-orbit coupling, introduced by the heavy atom.

![Graph showing comparison of OMR for different Mq₃ devices](image)

**Figure 5.17:** Comparison of the OMR ($\Delta I/I$) for thin devices with different Mq₃ with varying magnetic field at about the turn-on voltage. The clear dissociation related negative OMR is seen for the 150Å Alq₃ device and 100Å Gaq₃ device. For Inq₃, the process is not significant even at 100Å. The solid line is guidelines to the eye.

It is worth noting that even though the OMR of thin devices for all Mq₃ at low operating voltages is similar. Once the voltage increases, a linear process corresponding to the carrier-triplet interaction process dominates in the case of Gaq₃ and Inq₃. This shows that for Gaq₃ and Inq₃, the magnetic field dependent triplet-carrier interaction is the dominant process while for Alq₃, the dissociation of the triplets is equally significant.
5.4 Conclusions

Magnetoresistance measurements in Gaq3 and Inq3 OLEDs were made using different thickness devices. All devices have shown a correlation between the electron injection, light emission and OMR, which suggests that, as in the case of Alq3, the excitonic nature of OMR is still applicable. Al, Mg:Ag and LiF/Al cathodes were used with Gaq3 devices, to further verify the excitonic nature. Despite having different electron injection capacities, all these cathodes showed no OMR in the unipolar transport region. OMR only appears once the electron injection started, which strongly suggests that OMR is excitonic nature.

OMR in thin Gaq3 devices was found to be essentially similar to that of thin Alq3 devices with both negative and positive OMR. The negative OMR for the thin device is due to the diffusion and the dissociation of the triplet excitons at the cathodes. OMR at high voltage, however, shows a linear dependence to the applied field. While the linear increase of the positive OMR at high voltage and at high magnetic field is due to the field dependent interaction between the free carriers and triplets. OMR for thick Gaq3 devices always shows positive OMR that varies linearly with the magnetic field and scales with the drive voltage.

OMR variations with the magnetic field are studied with varying the thickness of Inq3. For the thin Inq3 devices, there is a very small negative OMR corresponding to the dissociation of the triplets to the cathode. There is no sharp change in OMR at low magnetic field as in the case of Alq3 devices. However, the positive OMR seen at high fields is similar to Alq3. In addition to the normal low field negative OMR, there is a feature peaking at very low magnetic field for 200-900Å Inq3 devices. The mechanism responsible for this process needs more investigation.

The magnetic field effect on the efficiency and light output of Gaq3 and Inq3 devices show a sharp increases at very low magnetic field which is attributed to the hyperfine scale mixing of the triplets and singlet resulting in an increase of the singlet excitons in the device which then recombine to give increased light output and efficiency. Further, as in the case of Alq3, the saturation in the plots after a low field process shows that there is no additional process at high magnetic fields.

The $\Delta \eta/\eta$ with applied field for all Mq3 is comparable, however, the maximum value of $\Delta \eta/\eta$ decreases in the series from Alq3 to Inq3. This indicates that due to the heavy ion substitution in Mq3, due to a prior mixing of singlets and triplets, there is a
lower degree of conversion of triplets into singlets in the applied magnetic field, resulting lower magnitude of efficiency changes.

The comparison of OMR in thin Mq₃ devices has shown that negative OMR decreases when one goes from Al to Ga and In. This indicates that there is less dissociation of triplets at the cathode for higher atomic size samples. It is probably due to the decrease in the life time of the triplet. Once a heavy ion is inserted in the materials, the spin-orbit coupling is introduced which lowers a triplet life time. As a result, the diffusion length of the triplets becomes shorter and fewer of triplets arrive at the cathode. OMR for Mq₃ is found to be quite different for thick devices. The magnitude of positive OMR decreases from Alq₃ to Inq₃ significantly. OMR data for Alq₃ shows that there is a strong interaction between the triplet and the free carrier. The linear increase of OMR with the applied magnetic field for Gaq₃ and Inq₃ show that there is weak interaction between the triplet and carrier in these materials at low magnetic fields.

5.5 References

Chapter 6

Performance and Magnetoresistance measurements of Triphenyl-diamine Derivative (TPD) Blue Organic Light Emitting Diodes

6.1 Introduction

There has been growing interest in the effects of a magnetic field on the device current, light output and the efficiency of OLED devices since the first reports by Kalinowski et al. in Alq3 OLEDs [1, 2]. Since then a number of researches were carried out to study this effect on “hole-transport” polymers such as, Poly(9,9-dioctyfluorenyl-2,7-diy) (PFO) and poly(3,4-ethylenedioxythiophene)poly-(styrenesulfonate)(PEDOT). OMR studies dedicated to PFO have shown some interesting results; in two studies, OMR is studied extensively with different cathode and anode materials in order to make bipolar and “hole only” devices [3, 4]. Upon using Au and ITO as the anode material, Francis et al. found that OMR is the same in magnitude, whilst switching to a PEDOT anode, they found a significant decrease in the onset voltage and an increase in OMR. From this result, they concluded that there is lowering of hole injection barrier, that decreases the onset of voltage and the interface series resistance, which eventually increases OMR. Further, upon changing cathode materials in the device, they did not see any change in OMR. They also observed OMR in “hole only” devices, with a Au cathode. With these observations, they concluded that OMR in their device is due to hole transport. They only observed OMR in these devices at very high driving voltages >40V, where they also noted a very weak electroluminescence from the devices. This strongly suggests that there was electron injection and recombination in PFO and the device is no longer “hole only” device, as stated, due to electron injection occurring from gold cathode. Despite this observation, in the study, they ascribed OMR to holes, without any certain mechanism [4]. In the another study, however by observing a very similar shape of the magnetic field effect on the current and the electroluminescence of the PFO devices, they acknowledged the fact that there must be a common origin for the increase of both OMR and light output [3].
PEDOT devices with different cathodes such as Al, Au and Ca have been studied by Nguyen et al. and they reported that OMR can only be seen with a Ca cathode (not with Au and Al cathodes) [5]. The devices with Au and Al cathodes show linear current-voltage characteristics (ohmic contact) and no OMR was observed. For Ca cathode, the observed current-voltage characteristics suggested that there is non-ohmic contact, which could be due to low work function of Ca and there is possibility of a large barrier for electrons at the cathode. Despite this, OMR is observed at low voltage ~0.2V, which was very unusual, as the carrier concentration (current) for this cathode is much lower than that of Au and Al cathodes. Further OMR is seen in both forward and reverse bias, which indicates that there was unipolar transport. The authors suggested it could be due to the charge provided by the dopant of the polymer instead of the injected charge carriers. As OMR is not observed with other cathodes, they related OMR to the interface resistance and mention that they could not provide any mechanism for it.

Looking at the data presented in Ref. [5], due to the ohmic contact, the current using Al and Au cathodes seems higher when compared to the Ca cathode. It is possible that the devices with Au and Al cathodes are “hole only” devices. Due to the high work function of these cathodes, the work functions are closer to the HOMO of PEDOT instead of the LUMO, thus supporting hole transport rather than electron injection. Further PEDOT is a hole transporting material and once a hole is injected from the ITO anode, it is easily transferred to the Al or Au cathode giving only hole current. Linear IV characteristics for Au and Al strongly suggest this. If this is what is happening in those Au and Al devices, no OMR is expected in accordance to our previous results presented in Ref. [6] and those in chapter 5. In the study, however it is not stated whether the devices were “hole only”, clearly more work must be done in order to understand OMR in hole transport materials.

TPD is a well known hole transport material, usually used in bilayer OLED devices incorporating small molecule organic materials. It is usually inserted between the plasma treated ITO and the emissive layer, which is usually an electron transport layer. Our results on the bilayer Alq₃ OLED devices with TPD as a hole transport layer have shown that it dramatically enhances the hole injection and lowers the operating voltage and improves the device efficiency. This is due to the reduction of the hole barrier at ITO/TPD interface which increases the $V_{bi}$ of the devices (Section 4.3.8.2). Further it isolates the surface abnormalities of ITO and improves device life time and uniformity. Even though TPD is extensively studied as an important constituent as a
hole injector/transporter in bilayer structure, its device performance as OLED and OMR has not yet been studied to our knowledge. Hence it is worth examining whether TPD on its own can be used as an OLED material and study its OMR. This chapter is dedicated to this investigation.

In this chapter, we first study the performance of TPD OLED devices with different cathode material such as Al, Au and LiF/Al. Furthermore, we attempt to fabricate an efficient blue OLED by using TPD as an emission layer incorporating with BCP as a hole blocking layer, between the cathode and the emission layer. Moreover, we demonstrate from the measurement of EL spectra that TPD is not only a conventional hole injection or transport material but it is also a good electron transporter, which has a potential application as a blue emitter. It is already explained that OMR of Alq3 devices is excitonic in nature in chapter 5. This is further tested in TPD devices with different cathodes. OMR measurements of TPD devices are investigated with different TPD thickness and with a BCP layer. We study the magnetic field effect on the device current, luminance and the efficiency as a function of drive voltage and current density. Further we demonstrate that the OMR effect is also observable in TPD but only where the carrier transport is bipolar.

6.2 Experimental

A typical diode structures where the active layer was sandwiched between the anode and cathode were fabricated to study the magnetoresistance in TPD. We used ITO as the anode and Al (1000Å) and Au (500Å) as the cathode. The details of device fabrication can be found in section 2.3. In order to assess the thickness dependent OMR, devices with various active layer thicknesses, ranging from 200 to 2000Å, were fabricated. Furthermore, devices incorporating a BCP hole blocking/electron injection layer (~200Å) were also fabricated and studied. Device J-V-L performance and magnetoresistance measurements were carried out immediately after the device fabrication. In addition, the EL spectra of each device and the PL spectra of purified TPD and BCP were also collected.

6.3 Results and discussion

In this section, we first present a study of TPD as a blue light emitting diode. EL spectra were measured in TPD devices with and without BCP layer and LiF/Al cathodes. The saturated photoconductivity measurements were performed on the TPD
with BCP layer devices in order to monitor the built-in potential of the devices. With the help of the measured value of the built-in potential, we show that the electron injection barrier is lowered at the TPD/cathode interface.

We present the magnetoresistance studies of the TPD devices with BCP layer with different TPD thickness and different cathodes Au and Al. From the results, we demonstrate the excitonic nature of OMR in TPD. We also show that the OMR of the TPD device is highly dependent on drive voltage, magnetic field and the thickness.

6.3.1 Performance Measurement

Figure 6.1 shows the J-V characteristics for single layer TPD devices with Al, LiF/Al and Au cathodes and a 100Å and 200Å BCP hole blocking/electron injection layer with LiF/Al cathode. Devices with Al and Au have higher leakage currents at low voltages compared to the device with a LiF/Al cathode. This is attributed to unipolar transport (hole only) providing the current in the device at low voltage. Moreover the reduced hole current at low voltage in LiF/Al devices shows that the LiF layer is acting as an insulating layer for hole extraction. The leakage current is almost reduced to the background level once BCP is inserted in between the TPD and the LiF/Al cathode. In contrast to this, the J-V characteristics of the device with a Au cathode show a very high leakage current as the hole injection and conduction become easier in the device due to the high work function of Au.

At ~1.4V, there is an inflection point in the J-V characteristics for the devices with Al and LiF/Al cathodes, indicating that there is electron injection occurring. Furthermore the voltage at which electron injection occurs for the devices increases with the insertion of the BCP layer (eg. from ~2V at 100Å thick BCP to ~2.4V at 200Å as shown in Figure 6.1). This indicates there is a limitation either on the electron injection due to the higher barrier at the TPD/BCP/LiF/Al interface, or to the electron transport in the BCP layer.

Literature values of the LUMO and HOMO of BCP are 3.2 and 6.7eV respectively as shown in references [7-9]. Based on these values, a higher electron injection barrier is not possible as the LUMO of BCP serves as a bridge in between the LUMO of TPD (2.4eV) and the work function of the LiF/Al cathode. This implies that there is not any restriction imposed by the BCP layer for electron injection. Moreover, we have measured the $V_{bi}$ in the TPD devices with and without BCP layer and demonstrated that the barrier height for electron injection at TPD/BCP/LiF/Al is smaller than that of
TPD/LiF/Al (see chapter 3.3.1). This indicates that BCP layer favours the electron injection in the TPD and this will be discussed in detail in the forthcoming section 6.3.3.

Figure 6.1: Current-voltage (J-V) characteristics for ITO/TPD(1000Å)/cathode devices. The different cathode materials used are Al, LiF/Al and Au. The characteristic of the devices with 100Å and 200Å BCP as a hole blocking/electron injection layer are also shown.

The shift of operating voltage for electron injection by ~0.4V when the thickness of BCP is increased by 100Å is equivalent to a voltage drop (~4×10^{-3}V Å^{-1}) across the BCP layer. This is noticeable in the J-V characteristics of the 200Å BCP device which has a current density an order of magnitude less at all the drive voltages, compared to the 100Å device. This is attributed to the low electron mobility in the BCP layer which is further responsible in increasing the operating voltage. Our results are also compatible with other published works [8-10] which show that the shift of operating voltage to higher values is due to a very low electron mobility (~6×10^{-7}cm²V⁻¹s⁻¹ at an applied field of 7×10^{4}Vm⁻¹) in the BCP [9, 10]. As there is no electron mobility value reported yet in literature for TPD, it is hard to give a quantitative account in the context of the overall device.
Figure 6.2: Luminance-voltage (L-V) characteristics for ITO/TPD(1000Å)/cathode devices with and without BCP hole blocking layer. There is dramatic increase in the light output due to the presence of a BCP layer in the device.

Figure 6.2 shows the electroluminescent output of the TPD devices with drive voltage. The L-V characteristics for samples with different cathodes are significantly different from each other. The turn-on voltage $V_{on}$, the voltage at which first light output is detected by the measurement unit, is $\sim$2.6V and $\sim$3.5V for LiF/Al and Al cathode devices respectively. It is worth mentioning here that although there is electron injection at $\sim$1.4V for both cathodes (as seen Figure 6.1), the light output is appeared only at these points due to very weak EL output. However, the light output of the devices is dramatically increased upon insertion of the BCP layer and is visible very close to the electron injection points. For example, for the 100Å BCP device, the light output is observed at $\sim$2.5V while the electron injection occurs at $\sim$2V for this device, similarly for the 200Å BCP, the device turns on at $\sim$2.6V with electron injection at $\sim$2.4V. This indicates that BCP is very efficient at blocking holes from reaching to the cathode and is responsible for the dramatic increase in light output of the devices. In contrast, a device with Au cathode has a very weak electroluminescence output which is seen at voltages $>$12V (see Figure 6.12). This is because the electron injection is very poor due to the large barrier height at cathode and the device is dominated with the hole current.
Figure 6.3 shows the EL output variation of various devices with current density. The slope of the linear curves of L-J gives the injection efficiency of the devices. The injection efficiency is \(9.11 \times 10^{-8}\) W/A for the Al cathode and \(2.076 \times 10^{-6}\) W/A for the LiF/Al cathode. While the injection efficiency increases to \(3.27 \times 10^{-4}\) W/A and \(1.56 \times 10^{-3}\) W/A for the 100Å and 200Å BCP layer devices respectively. The introduction of the 100Å and 200Å BCP layers, hence can improve the injection efficiency by \(3.59 \times 10^3\) and \(1.71 \times 10^4\) times that of the Al cathode device, and \(1.58 \times 10^2\) and \(7.51 \times 10^2\) times that of LiF/Al. Similarly light output obtained for the devices with Al and LiF/Al cathode at current density, \(J=100\text{A/m}^2\) is \(4.155 \times 10^{-6}\) and \(1.707 \times 10^{-4}\) W/m² respectively which is increased to \(2.56 \times 10^{-2}\) and \(1.66 \times 10^{-1}\) W/m² for the 100 and 200Å BCP devices. This shows that the 200Å BCP device has \(6.5\) times more light output than that of the 100Å BCP device. This observation leads to the fact that the 100Å BCP is only able to block some fraction of the holes from reaching the cathode. Therefore, for the complete blocking of holes and exciton confinement in the TPD layer, the BCP layer should be thicker than 100Å.

**Figure 6.3:** Electroluminance output variation with current density for TPD devices with different cathodes. The characteristics for the devices with a 100Å and 200Å BCP layer are also shown. The inset shows the characteristics for Al, Au and LiF/Al cathodes at low current density.
The power efficiency variation with the current density is shown in Figure 6.4. The Al and LiF/Al cathode devices show power efficiencies of $\sim 1.5 \times 10^{-6}\%$ and $3.75 \times 10^{-5}\%$ respectively. The 100Å BCP device has a power efficiency ranging from $\sim 10^{-4}\%$ at low voltages to the peak value up to $10^{-2}\%$ at high voltages. For the 200Å BCP device, the power efficiency approaches $10^{-1}\%$. Furthermore, the devices with a BCP layer are found to be more efficient at lower current densities compared to those without. For example, the 100Å and 200Å BCP devices have shown light output at very low current densities $\sim 10^{-1}$ and $\sim 10^{-3}\text{Am}^{-2}$ respectively, while for the devices without BCP emit light only above a current density $\sim 1\text{Am}^{-2}$. The reason of the improved performance of BCP devices at low current density is due to the carrier confinement in the TPD increasing the carrier concentration and recombination rate inside the emission layer. The TPD device with Au cathode is very inefficient, with the power efficiency of only $10^{-11}\%$ at 15V which is due to the very low concentration of electrons in the device.
### 6.3.2 Electroluminescent (EL) Spectra

Figure 6.5 shows the EL spectra of the TPD devices with and without a BCP layer with a LiF/Al cathode. The PL spectra of purified TPD and BCP are also shown for comparison. The PL spectra were obtained in the purified materials from powder for both materials, with an excitation wavelength of 355nm. Both of these materials were purified in the evaporator as described in section 2.2.2.2. TPD has a characteristic PL peak at 422nm, which is similar to that of the other published literature values [11-15]. BCP has a characteristic PL peak at ~475nm and it is consistent with the literature values [16, 17].

![Electroluminescence Spectra (EL) of TPD devices with and without a BCP layer with a LiF/Al cathode. The photoluminance (PL) spectra of purified TPD and BCP are also shown.](image)

The EL spectra obtained for all TPD devices have shown the characteristic peak at ~422nm with an additional peak appearing at ~400nm. This spectrum is similar to that obtained in literature [12, 13, 18]. Furthermore, a considerable amount of the
electroluminescence was also observed from the other vibrational states. For devices with BCP layers, there is no evidence of BCP emission at the wavelength 390nm, from where the photoluminescence of BCP starts to be visible. This shows that the recombination is occurring only in the TPD layer and BCP is purely acting as an efficient hole blocking layer. Moreover, the recombination and the electroluminescent output from the TPD layer indicates that TPD is not only a good hole transporter but equally good in electron transport. Due to very poor performance of the devices with Au and Al cathodes, we could not measure the spectra of the emitted light.

6.3.3 $V_{bi}$ Measurement

![Figure 6.6: Photocurrent variation with bias voltage in semi log plot for the devices with structure ITO/TPD(1000Å)/BCP(100Å or 200Å)/LiF/Al.](image)

Figure 6.6 shows the semi logarithmic plot of photocurrent variation with bias voltage in the devices with 100Å and 200Å BCP layer. The average value of $V_{bi}$ for a number of devices of both BCP thicknesses is $(2.21\pm0.04)V$. This value of $V_{bi}$ is greater than the $V_{bi}$ of the TPD single layer devices with Al and LiF/Al only cathodes by $1.29V$ and $0.25V$ respectively (see section 3.3.1.2). The effective work function of a composite cathode BCP/LiF/Al is $2.59eV$ which is calculated from the difference of the work function of plasma treated ITO ($4.8eV$) and the measured value of $V_{bi}$. The effective work function of BCP/LiF/Al cathode is lowered by $1.71eV$ from the
literature value of work function of bare Al cathode (4.3eV). This indicates a dipole of magnitude 1.71eV is formed at the interface which shifts the vacuum level downward. Therefore, the barrier height for the electron injection from composite cathode to TPD becomes 0.19eV \(\{\text{i.e. \(W_{\text{cathode}} - E_{\text{LUMO}}\} = (2.59-2.4)eV\}\). The electron injection barrier calculated for the TPD from Al and LiF/Al cathode is 1.5eV and 0.44eV respectively (see section 3.3.1.3). These calculated values of barrier height show that devices with BCP layers have a better electron injection than that of the Al and LiF/Al cathode as the barrier is significantly lowered due to the presence of BCP at the cathode interface. Moreover, we have shown above a dramatic increase in the light output and efficiency of the TPD devices with a BCP hole blocking layer. We believe that this is not only due to the increase in the concentration and confinement of holes in the TPD layer but also due to the increase in the electron density. Furthermore, we observed a shift of the operating voltage to higher values in the J-V characteristics due to the insertion of the BCP layer (see section 6.3.1). The observation of smaller barrier height due to BCP shows that the shift in the operating voltage is not due to the limitation imposed by the BCP layer on electron injection and is solely due to low electron mobility in the BCP layer. This also shows that BCP is a good electron injection layer to use as interface material in cooperation with LiF/Al cathode.

### 6.3.4 Magnetoresistance (OMR) Measurement

In this section, we describe the OMR study on TPD devices with various thicknesses (~200 to 2000Å) of TPD with fixed thickness of BCP (~200Å) layer and LiF/Al cathode. We show that OMR of TPD devices strongly depends upon the magnetic field, device current and device thickness. Furthermore, we also examine the proposed mechanisms such as dissociations of triplets at low magnetic fields and carrier-triplet interaction at higher magnetic fields. OMR of TPD devices is investigated with two different cathodes, Al and Au. We show that the observed OMR in these devices supports our previous observations and follows the excitonic model.

#### 6.3.4.1 OMR Variation With TPD Thickness

Figure 6.7 shows a percentage change in efficiency for the device with 500Å TPD and 200Å BCP with a LiF/Al cathode at various drive voltages. A sharp increase in efficiency (within a magnetic field of 50mT) was observed at low magnetic fields indicating that there is more radiative recombination in the device. The shape of the
efficiency change at low field is similar to Mq₃ devices (see section 5.3.2) and in Alq₃ [6, 19, 20]. This is characteristic of the hyperfine scale process of mixing of triplets and singlets in the magnetic field. Under the forward biased condition, electrons and holes entering from the corresponding electrodes form triplets and singlets in a ratio of 3:1. Upon application of the magnetic field, triplets are converted into singlets (see section 1.7.1 and Refs. [21, 22]). An increase in singlet concentration leads to increased EL output and efficiency of the device. A complete saturation is observed after the low field process showing that there is no additional process at higher magnetic fields. Moreover, the shape of the efficiency with different drive voltage is also identical. This shows that there is no evidence of another process such as TTA (relation 1.8) at high magnetic fields and at high current density despite an increase of the triplet concentration in the device.

![Figure 6.7](image.png)

**Figure 6.7:** The percentage change of efficiency ($\Delta\eta/\eta$) as a function of applied magnetic field for the device ITO/TPD(500Å)/BCP(200Å)/LiF/Al at different drive voltages. The solid lines are guidelines to the eyes.
OMR (percentage change of current) in the same device at different driving voltages from 3.2V to 4.2V is presented in Figure 6.8. A negative OMR is observed in the whole range of drive voltage (2.5 to 6V). However the magnitude of negative OMR decreases with increasing drive voltage. A change in the current at low magnetic field has a similar shape to that of the efficiency increase shown in Figure 6.7. This shows that the effect of the magnetic field on the current and efficiency at low fields has a common origin. It is clear that an increase in singlet concentration and a decrease in triplet concentration can give rise to negative OMR in the device. The negative OMR observed here is similar to the thin devices of Alq3 and attributed to the diffusion and dissociation of triplets at cathode interfaces [19]. In the magnetic field, if the triplet concentration is reduced due to the hyperfine scale mixing process, there will be less diffusion of triplets and will decrease the current, giving negative OMR (see section 5.3.1). The negative OMR in the TPD device may be due to the diffusion and dissociation of triplets at anode interface. This is because using BCP at the cathode interface, blocks the triplet dissociation. We have already demonstrated the diffusion and dissociation of triplet at cathode for Alq3 devices and the exciton blocking nature of BCP in chapter 5.

OMR plots in Figure 6.8 have shown a single process at low magnetic fields and saturation after ~50mT. There is no evidence of another process except hyperfine scale interaction affecting the diffusion and dissociation of triplets at the anode. This is in contrast to what we have observed in case of Alq3. In Alq3, after the low field process, another linear process starts, which is attributed to the magnetic field dependent triplet-carrier interaction expressed by relation (1.10). Due to the magnetic field dependent triplet-carrier interaction, OMR increases as magnetic field and/or drive voltage increases. In some of thin Alq3 devices, due to the strong magnetic field dependent triplet-carrier interaction, the negative OMR changes into positive OMR at high magnetic fields and high voltages [19]. No such kind of interaction was observed in 500 Å TPD devices. This indicates that a field dependent linear process occurring at high magnetic fields is weaker in thin TPD devices than that of Alq3 devices. This suggests that either there is less carrier/triplet concentration available for an interaction or the magnetic field effect on the carrier-triplet interaction at high fields is less significant in TPD devices. More investigations are needed in this direction in order to confirm it.
Figure 6.8: OMR ($\Delta I/I$) as a function of applied magnetic field for a device ITO/TPD(500Å)/BCP(200Å)LiF//Al at different drive voltages. The solid lines are guidelines to the eyes.

A very similar result was obtained for a 200Å TPD device with 200Å of BCP layer, the OMR data however, becomes very noisy. The magnitude of negative OMR observed is larger (~0.7%) than that of 500Å (~0.15%) near to the device turn-on, which confirms that more diffusion and dissociation of the triplets is occurring in the device which may be the result of the thinner device structure. This observation is consistent with the results of thin Mq$_3$ devices where the magnitude of negative OMR increases with decreasing Alq$_3$ thickness [19]. The change in efficiency (~1.7%) is similar to that of the 500Å TPD device with a visible hyperfine scale interaction of mixing of singlets and triplets in the magnetic field.

Figure 6.9 shows the change in efficiency ($\Delta \eta/\eta$) for a 1000Å TPD and 200Å BCP device with applied magnetic field. A very similar characteristic is seen for the change in light output.
Figure 6.9: The percentage change of efficiency ($\Delta \eta/\eta$) as a function of applied magnetic field for a ITO/TPD(1000Å)/BCP(200Å)/LiF/Al device at different drive voltages.

At low magnetic field, the hyperfine scale process is clearly visible as in the case of thin devices. The shape of the plots of the efficiency remains same even if the drive voltage is increased from 2.8 to 6V which shows that there is no other process going on with increasing in operating voltage. Furthermore, it is worth noting that the slope of the plots at high fields is different than that of 200 and 500Å devices and is not totally flat as observed in Figure 6.7. The slopes at high fields are $\approx 2.2 \times 10^{-3}\%/\text{mT}$ for the 1000Å TPD devices while that for thin TPD devices (200-500Å) is $\approx 1.3 \times 10^{-4}\%/\text{mT}$. This indicates that at high magnetic fields, for thick TPD devices, there is an additional process which is responsible for linear increase in light output and efficiency with increasing magnetic field. As the light output and efficiency is increasing linearly, it strongly suggests that the singlet population must be increasing. It is possible that this
may be due to the magnetic field dependent carrier-triplet interaction with the quenching of triplets into singlet (relation 1.10) or TTA (relation 1.8). In the presence of the magnetic field, a pair of triplets can interact to give a singlet exciton which then decays with EL output (relation 1.8). Moreover, a decrease in the triplets and generation of singlet leads to the positive OMR followed by increase in EL and efficiency (see Figures 6.9 and 6.10).

*Figure 6.10:* OMR ($\Delta I/I$) as a function of applied magnetic field for a ITO/TPD(1000Å)/BCP(200Å)/LiF/Al device at different drive voltages.

OMR for a device with 1000Å of TPD and 200Å of BCP with LiF/Al cathode at different drive voltages is shown in Figure 6.10. A maximum negative OMR is observed at a 2.4V drive voltage, near to turn-on voltage (2.5V) of the device. OMR in
the device with BCP layer can either be positive or negative or both depending upon the drive voltage and applied magnetic field.

At low drive voltages, OMR has a characteristic hyperfine scale interaction shape at low magnetic fields, which then remains negative and nearly constant with increasing magnetic field. At high drive voltages, however, the OMR becomes less negative. At 4V, OMR is almost zero for low fields and becomes positive for high fields. Above 4V, OMR initially goes negative at low field up to ~-0.1% and goes to positive at high fields, depending upon the drive voltage. For example, at a drive voltage 5V, a hyperfine scale process at low field gives OMR up to ~-0.1% and at high field OMR increases up to ~+0.2%. OMR becomes positive only at high drive voltages and high magnetic fields. Such kind of positive OMR is seen in devices with thicker TPD (1000Å) and is not observed with thinner ones (200Å and 500Å). This indicates that the thick device OMR is the sum of two processes, namely a low field process, dissociation of the triplets and a high field process, triplet-carrier interaction. The mechanism of the carrier-triplet interaction in the device was by the proposed by Ern and Merrifield [24]. According to them, the triplets can interact to the paramagnetic centre such as free charge carriers in the device that can result either quenching of the triplet states or trapping of the free carriers. Both of these processes cause a decrease in the mobility. Hence due to the magnetic field if there is decrease in the triplet concentration, then there is increase in the mobility of the free charge carrier and this gives positive OMR. As the positive OMR is not observed in thin devices, this suggests that magnetic field dependent triplet-carrier interaction becomes significant only for thicker TPD devices. It is quite interesting to note that there is zero percentage change in the current in the device at 4V in OMR characteristics (see Figure 6.10) while at the same time, ~3% change in the efficiency is observed (see Figure 6.9). This shows that the change in the efficiency of the device is not due to the change in the device current introduced due to the magnetic field.

OMR, light output and efficiency variation with magnetic field and the drive voltage for 2000Å TPD is essentially identical to that of 1000Å TPD and 200Å BCP device. However, the negative OMR seen in 2000Å TPD/200Å BCP device near to the turn-on of the device (~0.2%) is smaller than that of 1000Å TPD/200Å BCP device (~0.8%). A summary of the OMR and the efficiency with varying thickness of 200-2000Å TPD devices with 200Å BCP layer at a current density ~1Am² is shown in Figure 6.11. As OMR data for 200Å TPD/200 Å BCP was very noisy and this data is not presented
in the figure, however we had a well functioning device with good IV and IL characteristics and ~0.7% of negative OMR near to the turn-on. There is a continuous decrease in negative OMR with increasing device thickness. These results are consistent with the results obtained for the different thickness of Mq₁ (Chapter 5).

Figure 6.11: The plots of $\Delta \eta/\eta$ and $\Delta I/I$ at low current density (~1Am$^{-2}$) for various TPD thickness devices as a function of magnetic field. The solid lines in the plots are a guide to the eyes.
Voltages corresponding to electron injection ($V_{\text{injection}}$), the device turn-on ($V_{\text{on}}$) and onset of OMR ($V_{\text{OMR}}$) are summarised for these devices in Table 6.1. There is good correlation of the onset of OMR with electron injection and the light output showing that OMR is consequence of exciton formation in the devices. However, in these cases we observed OMR slightly before the observation of the light output.

Table 6.1: Voltages corresponding to electron injection ($V_{\text{injection}}$), the device turn-on ($V_{\text{on}}$) and onset of OMR ($V_{\text{OMR}}$) for devices with TPD thickness varying from 500 to 2000Å with 200Å of BCP as exciton blocking layer and the LiF/Al cathode.

<table>
<thead>
<tr>
<th>Thickness (Å)</th>
<th>$V_{\text{injection}}$ (V)</th>
<th>$V_{\text{on}}$ (V)</th>
<th>$V_{\text{OMR}}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>2.4</td>
<td>2.7</td>
<td>2.5</td>
</tr>
<tr>
<td>1000</td>
<td>2.2</td>
<td>2.5</td>
<td>2.4</td>
</tr>
<tr>
<td>2000</td>
<td>2.4</td>
<td>2.7</td>
<td>2.4</td>
</tr>
</tbody>
</table>

6.3.4.2 OMR Variation with Cathode Material

We have already demonstrated that there is a correlation between the turn-on voltage of the device with the observation of OMR for TPD devices of different thicknesses, incorporating BCP as an exciton blocking layer. No OMR was observed below the electron injection voltage. This observation agrees with the proposed excitonic nature of the OMR. In this section, two different cathode materials, Al and Au, are used to examine the excitonic nature of OMR in TPD devices.

The J-V characteristics for Al and Au devices are already shown in Figures 6.1 and 6.2 (Section 6.3.1). For Al cathode, a kink is observed in the J-V characteristic at 1.4V, suggesting that the electron injection is occurring at this point (see Figures 6.1 and 6.12). However the light output is observed only at 3.5V (see Figure 6.2). Although electron injection is occurring at 1.4V, we were unable to detect the light output from the device until 3.5V, it indicates that below this point, light output is very small and is not measurable due to sensitivity of the collection system. We have also measured the built-in voltage and calculated the energetic barrier for electrons at a TPD/Al interface to be very large ~1.5eV (section 3.3.1.3). Due to this huge barrier, it is possible that the device has unequal charge densities with a large hole and low electron density, which may result in very poor recombination and light output. It is only when the number of
electrons and holes is more balanced and a significant amount of light is emitted (at ~3.5V), that the system is able to measure the light output. The OMR variation with drive voltage at magnetic field ~200mT and I-V characteristics of the device with Al cathode is shown in Figure 6.12. The evidence of electron injection at 1.4V from J-V shows that there is exciton formation in the device near to 1.4V and once the magnetic field is applied, it modulates the concentration of the excitons and the effect is seen as OMR at this voltage.

![Figure 6.12: I-V and OMR (ΔI/I) at 200mT as a function of applied voltage for TPD device with Al cathode. The dotted line indicates the coincidence of the electron injection and OMR observation at 1.4V.](image)

Weak OMR is also observed for the TPD device with Au cathode as shown in Figure 6.13. The device has a high current density which is about 5 times higher at low voltages than the device with other cathodes and BCP layer (see Figure 6.1). The device shows very weak light output after 12V (see inset Figure 6.13). Despite having high current density, no OMR is seen at low voltages. The OMR is first observed at 7V. This suggests that the device is hole only device until 7V, after which the injection of electrons occur in the device. Due to a weak light output, however, it is detected only after 12V. This concludes that OMR is observable only in the bipolar transport region and an exciton formation is essential. This finding is similar to the study of Gärditz et
al., where no OMR was observed for electron-only Al/Alq3/Ca/Al devices [23]. Furthermore, the excitonic nature of OMR for TPD devices is consistent with our previous observations of Alq3 devices [6, 19, 20] and Mq3 (see chapter 5), however it contradicts a few previous OMR studies [3-5].

OMR for the device with Au cathode is always negative for all drive voltages from 7 to 15V. It indicates that the diffusion and the dissociation of the triplets at the electrode are the contributing factors to OMR. As the device current increases, the negative OMR decreases. The OMR observed is similar to that in the thin (200-500Å) TPD (with BCP) devices where we always observed negative OMR (see section 6.3.4.1).

Figure 6.13: OMR ($\Delta I/I$) as a function of applied magnetic field for a ITO/TPD(1000Å)/Au device at different drive voltages. The inset shows the L-V characteristic of the device at high operating voltages.
The nature of the decrease in negative OMR with the increase in the drive voltage seen in a TPD device with the Au cathode is similar to that in the 1000Å TPD/200Å BCP device. At high voltages, in the 1000Å TPD/200Å BCP devices, OMR shows a combination of two processes i.e diffusion related process giving negative OMR and carrier-triplet interaction related process giving positive OMR. The decrease in the negative OMR in TPD device with the Au cathode is attributed to same carrier-triplet interaction process causing a continuous decrease in negative OMR upon increase in drive voltage. However, in the device, OMR is less sensitive with increasing drive voltage than for TPD/BCP/LiF/Al devices and the carrier-triplet interaction process seems to be less significant. It could be due to smaller carrier/triplet concentration in the device. As a result, the dissociation of triplets is the dominant process for all drive voltages. We strongly believe that upon increase in the drive voltage beyond 15V, OMR will go positive and follow same trend as that of thick TPD/BCP/LiF/Al device as we observed in Figure 6.10. In the present experiment, however it was not possible to perform the measurements at high voltages due to device breakdown above 15V.

### 6.4 Conclusion

We successfully demonstrated a conventional hole injection/transport material, TPD, as a potential blue emitter as well as an electron transporter. It was also demonstrated that a BCP layer can be used as a hole blocking material in these TPD devices in combination with LiF/Al cathode in order to achieve an efficient TPD device. Furthermore, it was also shown that 100Å of BCP can improve the injection and power efficiencies of the device compared to that of Al and LiF/Al cathodes.

Insertion of the BCP layer increases the $V_{bi}$ of the devices, showing that it decreases the energetic barrier height at the cathode. The observation of improved efficiency due to the BCP layer is attributed to the higher carrier density in the TPD layer by hole confinement, as well as good electron injection due to lowering of the electron injection barrier. However there is an increase in the operating voltage of the device which is tentatively attributed to the low electron mobility in the bulk BCP layer. The electroluminescent spectra measured for the TPD devices shows a typical PL peak of TPD which suggests that the major recombination is occurring within the TPD layer. It further leads to the discovery that a conventional hole injection/transport material such as TPD is also electron transporting.
All TPD devices with a BCP hole blocking layer show an excellent correlation between the electron injection, light emission and OMR, indicating that OMR is due to the presence of both type of charge carriers and hence the exciton formation in the device. However, the correlation in the TPD device with Al and Au cathodes is poor due to the poor device performance and measurement limitations. Even though there is higher current density in the device with Au cathode, OMR is not observed when the device is “hole only” as expected. Furthermore, it indicates that the current density alone is not responsible for OMR but the presence of excitons is essential.

We observed OMR of TPD OLEDs with and without BCP layer and found that it is strongly dependent on the magnetic field, device thickness and drive voltage. Both positive and negative magnetoresistance can be observed. For the thin TPD (200-500 Å), the OMR always remains negative even at high voltages and high magnetic fields, which indicates that dissociation of the exciton is a dominant process. We have already discussed in section 5.3.1 that the negative OMR in Alq3 thin devices is attributed to dissociation of triplet excitons at the cathode. When a hole blocking layer BCP was inserted in between cathode and Alq3, OMR was found to be always positive for all Alq3 thicknesses. This is due to the fact that the BCP layer is blocking the excitons from dissociating at the cathode. In very similar way, in TPD, it seems that same hyperfine scale interaction process of the triplet-singlet conversion and the triplet dissociation at the electrode is occurring, which results in a negative OMR. Even using the BCP layer, the negative OMR, however, does not change to positive OMR in thin TPD devices which could be due to dissociation of excitons at the anode interface. This interface appears an energetically favourable arrangement for triplets dissociation due to small hole barrier. Therefore, very thin TPD (200-500Å) devices with BCP always show negative OMR irrespective of drive voltage and the magnetic field and due to the thin device structure, the dissociation of the excitons at interface is a dominant process.

OMR for the thick devices shows different characteristics to the thin devices. For thick devices, OMR characteristics show combination of low field hyperfine interaction process and high field triplet-carrier interaction process. For the thick devices, OMR is always negative at low voltage and which becomes positive once the drive voltage is increased. This indicates that the dissociation of the triplets at low voltages is the dominant process and that triplet-carrier interaction becomes significant at high voltages. These two processes have different magnetic field dependences and the
resultant OMR at any point is sum of these two processes. This observation is consistent to the observation of thickness dependent OMR observed in Alq3.

Positive OMR appears for the TPD devices at high magnetic fields and current densities as a result of interaction of free carriers with triplets depending on magnetic field. However, the interaction of the triplet-carrier in the magnetic field is not as effective in TPD as in the Alq3. Due to the less effective triplet-carrier interaction in thin TPD devices, only negative OMR was observed, which did not go to positive even at high voltages as in the case of thin Alq3 devices. Further investigations are needed to confirm whether this is due to a smaller number of carriers/triplets available in the device or whether the interaction has weak magnetic field dependence.

The shape of the change in the EL and efficiency with magnetic field for the thicker device has also shown different characteristics to the thin devices. The complete saturation in these plots for the thin devices indicates that only a hyperfine scale mixing of triplets and singlets is responsible for increasing light output and efficiency of the device in magnetic field. It is also worth noting that the carrier-triplet interaction is not significant for thin devices, where OMR and efficiency remain saturated after a low field process. It does not mean that the carrier-triplet interaction is not occurring in the thin devices but that it is less significant in contributing observable changes in OMR and efficiency. However, in thick devices, there is a linear increase in EL and efficiency with increase in the magnetic field suggests the presence of additional processes. Further, it is quite interesting to note that the percentage change in the device current is always less than the percentage change in efficiency. This indicates that the change in device current due to the magnetic field alone is not responsible for the change in the carrier density which brings the increase in magnitude of light output and efficiency. This may be due to TTA occurring in the device in addition to the magnetic field dependent free carrier-triplet interaction. As there is a decrease in triplets and generation of singlets in the process, there would be increase in OMR, EL and efficiency as experimentally observed.

The transport of the charge carriers in TPD is heavily affected by the presence of the triplets in the device as the triplet shows strong interaction with the free carriers especially at high voltages and lowers the mobility of the carrier. This lowering of the mobility may be responsible for making J-V characteristics identical at high voltages even different cathodes are used. A closer inspection of the J-V plots shows a very similar nature at high voltages, despite using different cathodes and J-V plots turn-over.
with roughly same slope in these plots indicates there is impedance in all devices. This suggests that the charge transport in this J-V region is limited by the presence of the triplet which may act as trap.

### 6.5 Reference

Chapter 7

Conclusions and Future Work

This chapter is divided into three major parts in accordance to the content of this thesis.

*Band offset measurement at organic/metal interfaces*

The study of the energy barrier at the organic/metal interface is an important issue in device engineering as it influences a carrier injection in the device. It is now obvious that knowledge of the work function of metals used as electrodes and the HOMO and LUMO of the organics is not enough to get an insight into such interfaces and energy barriers. In the present study, by measuring the built-in voltage of the complete single and double layer devices, the energetic barrier at the interface of different organic material and cathodes was calculated. It is demonstrated that there is a vacuum level shift at all interfaces, lowering the vacuum level and HOMO-LUMO of the organic materials. This work has shown that a model of the band diagram obtained just by adding isolated energy levels together for different metals and organics does not give a true picture of such interfaces, as there is a vacuum level shift, $\Delta \sim 1.0\text{eV}$, at the interfaces. The shift of the vacuum level may be due to different causes such as dipole formations, chemical modifications and charge rearrangement. The deep understanding of such interfacial properties is very advantageous in order to obtain optimised devices with low driving voltage and high efficiency.

Even though the different metal cathodes such as Al, LiF/Al and Mg:Ag and the organic interfaces are studied here, it does not cover whole range of metals available for cathodes such as Ba, Ca, Li, Mg, Ag, Au etc. An extended study of such interfaces could be advantageous in order to understand the correlation between the vacuum level shift, dipole formation and the work function of the metal for the given organic material. The magnitude of dipole can be measured by using UPS measurements, however, it is not performed in the study. Such a kind of comparative study could be performed in order to add the validity of $V_{bi}$ measurement technique that is used in the study.

Furthermore, the previous studies done by UPS have shown that the magnitude of the dipole at the interface is found to be strongly dependent on the thickness of material...
evaporated on the metal. Knowledge of thickness varying dipole formation is needed in order to predict the barrier heights at the interface. This process becomes very important in the case of thin injection layers such as the Mqs used in this study, where the device performances strongly degrade beyond an optimised thickness of injection layer.

In principle, the existence of a dipole at the interfaces has shown that there may be one or many interfacial activities such as charge rearrangement, electron transfer from metal to organic and vice versa, chemical reaction, permanent dipole of material, image charge formation etc. occurring on at metal/organic interfaces. However, a careful study must be done in order to investigate which is responsible for origin of the dipole in the case of the organic materials and metals presented here.

**Interface modification using thin Mq electron injection layer**

Studies of the performance of Alq3 devices with a thin alkali metal quinolates (Mqs) as electron injection layer has shown that these materials are able to lower the drive voltage and improve the efficiency significantly. The improvement in the device drive voltage is attributed to improvement of the electron injection. Furthermore, the amount of improvement of electron injection observed in the study depends upon the thickness of injection layer and ~10Å of Mq (M stands Li, Na, K, Rd and Cs) is sufficient enough to lower the operating voltage of the device in comparison to the Al only cathode. The device performance is comparable to the conventional LiF/Al cathode. This is not just due to improved matching of the energy levels at the interfaces, because the HOMO-LUMO of these Mq and Alq3 are not very different in magnitude. The study of the $V_{bi}$ measurement has shown that there is a lowering of the barrier due to presence of a thin layer of Mq in between the Alq3 and the Al cathode. Further there is a vacuum level shift of ~1.0eV at the interface. This indicates that the interfacial activity is responsible for lowering the barrier height for electrons. Furthermore, in the study, it is observed that the magnitude of electron injection is a function of the thickness of Mqs. 5Å Mq interfacial layer device is not efficient as that of 10-30Å devices in lowering the drive voltage. This strongly suggests that the improvement of the electron injection (barrier height lowering) may be attributed to the formation of the dipole, is further dependent on the interfacial layer thickness. This fact needs more investigation in order to confirm whether the dipole formation and lowering of the barrier height for electron injection depend on the thickness.
There are many mechanisms proposed for the improved electron injection. One of them is liberation of low work function metals such as Li from LiF on thermal evaporation of Al. However, it seems that this mechanism may not be responsible in case of Mqs. It is not very easy for the evaporated high work function Al cathode to react and liberate the low work function metals such as Li from stable Mqs as in the case of LiF thin injection layer devices. However, the hygroscopic nature of the material which introduces a strong dipole at interfaces, lowering the vacuum level of the organic material, can be the possible mechanism. As the alkaline metal quinolates are highly hygroscopic in nature, this kind of strong dipole formation is not very unusual. More work could be done in this direction in order to confirm this.

Moreover, the injection efficiency of the thin Mqs is found to improve if one goes from Li i.e. low atomic mass to Cs, larger atomic mass. The measurement of the $V_{bs}$ has shown that the magnitude of the dipole formed at Csq/Al interface is slightly bigger than that of Liq/Al. This suggests that the magnitude of the dipole formed increase in the series from Li to Cs and this fact needs more extensive study with varying thickness of Mqs. Furthermore, it is found that as the thickness of Mqs increases, the device operating voltage shifts towards higher values, which may be attributed to low electron mobility in bulk Mqs. An extensive study of the electron mobility of Mqs could be done to explain the transport of the charge carriers and the injection efficiency of the device.

*Magnetoresistance (OMR) in Alq3, Gaq3, Inq3 and TPD*

(a) Alq3, Gaq3, Inq3

An extensive study of OMR in Alq3, Gaq3, Inq3 has shown that OMR is excitonic in origin for all devices with different cathodes and different thicknesses. The appearance of OMR in all Mq3 devices only at the point where the electron injection begins and light emission occurs, gives evidence that of presence of excitons and their concentration modulation in a magnetic field are essential for OMR.

The percentage change in efficiency in magnetic field decreases with increasing the atomic mass in the series, indicating that there is less additional recombination with applied field. This indicates that if one goes from low atomic mass to higher atomic mass, there is lower degree of mixing of singlets and triplets in the magnetic field. This is thought to be due to the increased spin-orbit coupling, there is mixing of the triplet and singlet states before applying magnetic field. The plots however have all shown a
similar shape in the change in efficiency with magnetic field, with only a low-field hyperfine process of mixing of singlets and triplets visible.

One of the factors that change OMR is the size of the atom attached to the ligand and it is demonstrated in many previous studies that an increase in the size of atom decreases OMR. We demonstrated this in the metal quinolates devices with substitution of central atom. Both negative and positive OMR are observed depending upon thickness. The negative OMR of thin devices, which is due to the diffusion and dissociation of the triplets at the cathode interface, is heavily reduced from Alq₃ to Inq₃. This is consistent with the decrease in diffusion of the triplets, due to decrease in the triplet life time brought by the strong spin-orbit coupling introduced by attachment of the heavy atom in the material. In the study, the measurement of the diffusion of the triplets with varying the atomic size is performed in a complete device structure, however, the values are not verified by any other methods. The measurement of the delayed fluorescence of Mq₃ could add more information on the life time of triplets and whether it is affected by a magnetic field.

In the case of thick Alq₃ devices, it is found that, OMR shows combination of two processes i.e. the low field process that resembles to the hyperfine interaction of triplets and singlets and the high field process of the triplet-carrier interaction. This shows that for Alq₃, there is a magnetic field dependent triplet-carrier interaction occurring in the device changing the mobility of the carriers. However, OMR of Gaq₃ and Inq₃ are quite different to this, as there is no low field process and the OMR shows an approximately linear increase at high fields. This suggests that there is a weak interaction between the triplet and carrier at null field showing a little energetic barrier for the trapped carrier in the triplet state at low fields and changing the triplet concentration does not change the mobility of the carrier and OMR. However, at high field, the triplet-carrier interaction is visible and similar to Alq₃. It is interesting to note that there exists a sharp, small positive peak in the case of Inq₃ at about 6 mT. This peak needs further investigation.

(b) TPD

Studies of the performance of TPD as a blue OLED has shown that TPD is an excellent bipolar transport material for OLED application in cooperation with suitable electrodes such as ITO anode and LiF/Al cathode. More importantly, the performance of the device can be improved by adding 100Å BCP as hole blocking layer and ~160 times higher injection efficiency is observed in comparison to the control device. This
clearly shows that BCP layer blocks the holes effectively at TPD layer, confining the recombination of excitons in the emission layer. The \( V_{bi} \) measurement of the devices has shown that the BCP also lowers the electron injection barrier at LiF/Al cathode. This further suggests that addition of BCP in between TPD and LiF/Al cathode, there is also higher electron concentration in the device. In contrast to this, however, upon addition of BCP, the operating voltage of the device increases, which is tentatively attributed to low electron mobility of BCP. The hole transporting character of TPD is well demonstrated from many years of use in bilayer OLED devices. Our study shows that it also supports electron transport because the electroluminescent spectra of TPD OLED devices show that there is recombination occurring in the TPD layer. In the present study, the electron mobility of TPD is not measured and can be a future work.

OMR in TPD devices with different cathode materials has shown that the origin of OMR is excitonic in nature. OMR can be positive and negative depending upon the device structure, magnetic field and operating voltage. For the thin TPD devices, OMR is always negative showing that the diffusion and dissociation of the triplet exciton is occurring at the interface. While for the thick devices, OMR is negative at low fields and positive at high fields. This strongly suggests that even at low magnetic fields, the diffusion and dissociation is occurring at the interfaces, upon increase in the magnetic field, the triplet-carrier interaction becomes important. A field dependent triplet-carrier interaction is responsible for positive OMR at high magnetic fields.

The percentage change in efficiency in magnetic field has shown two processes. One of them is a characteristics hyperfine scale interaction of singlets and triplets at low magnetic fields. There is no saturation after the hyperfine interaction process in thick TPD devices, which suggests there is another process. This process shows linear dependence with magnetic field and also scales with the applied voltage. This indicates that additional processes such as TTA and/or the quenching of the triplets by the free carriers are occurring. As a linear process is especially visible at high voltages or current densities, TTA may be occurring significantly. An increase in the EL output with high drive voltage suggests that it may be due to TTA, where two triplets are combined with the formation of an excited singlet. Furthermore a linear process shows that there may be magnetic field dependent triplet-carrier interaction occurring, in which a pair state can either dissociate to the triplet and free carrier or triplet can quenched with formation of free carrier and excited ground state. However a detailed study is needed in order to explain the mechanism properly.