

# CHAPTER 2

## A REVIEW ON ORGANIC LIGHT EMITTING DEVICE

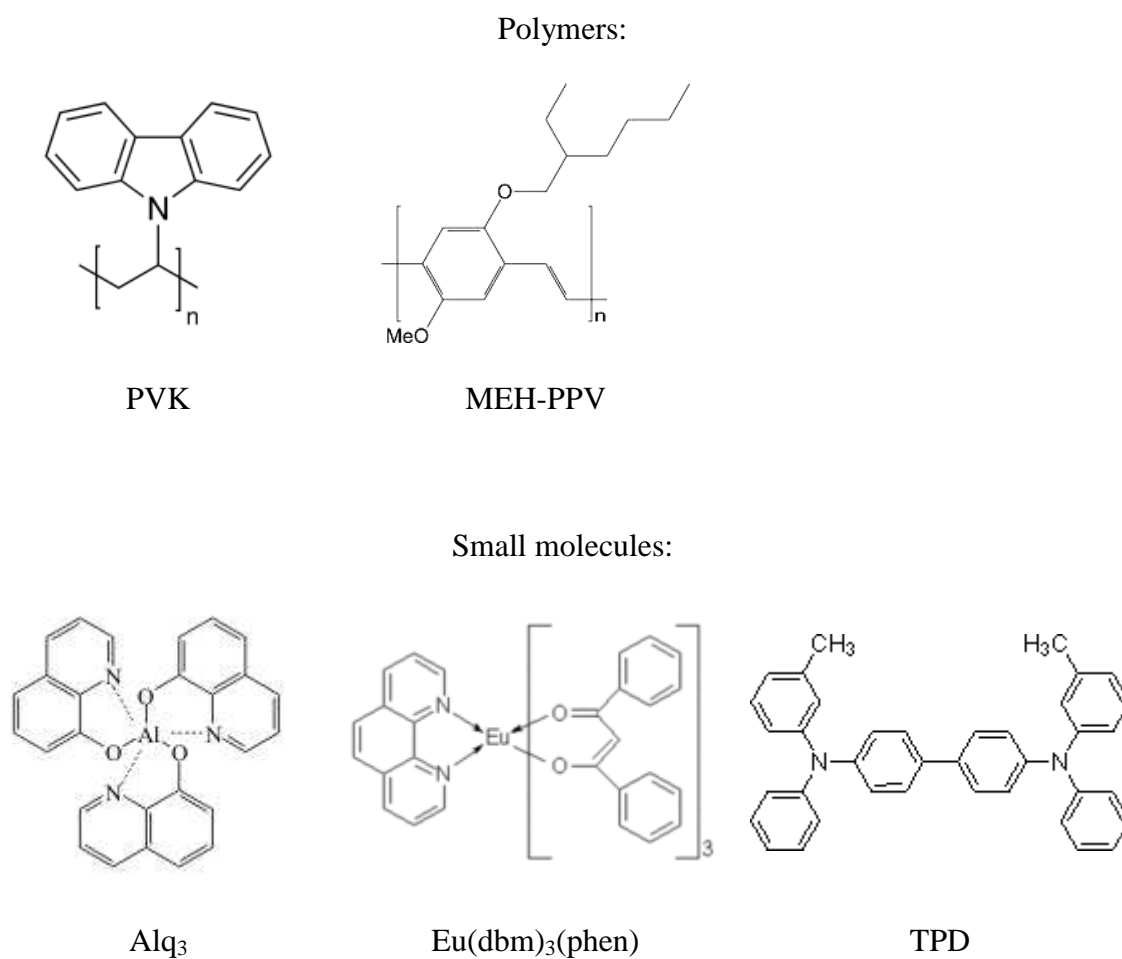
### 2.1 Organic Semiconductor

The general structure of inorganic semiconductor depends on the strong covalent or ionic bonding among atoms in the lattice point, thus creating strong interactions between atomic orbitals in a close packed structure. However, in organic semiconductor, the interaction among molecules is relatively much weaker. The overlap of molecular orbital is small, thus the molecular energy levels and other features of identical molecules are preserved in solids with minimal disturbances. Most of organic semiconductor compound contain conjugated bonding structure. These conjugated bonds are made of an alternation of single and double chemical bonds in the organic structure. The conjugated bonds structure can be seen in either polymer or small molecule. Both of them are organic compounds but can be distinguished by their identical structure. Polymer is an organic compound that consists of repeating monomer while small molecule doesn't have repeating monomer structure. Repeating set of monomer in polymer makes them larger in size as compared to small molecule compound, so that they are also known as macromolecules. Fig. 2.1 shows a few examples of polymer and small molecule compounds that are widely used in organic electronics. C.C. Yap et. al used Poly(*N*-vinylcarbazole) (PVK) polymer as a hole transporting material in a blend single layer OLED [Yap *et al.*, 2008]. Many

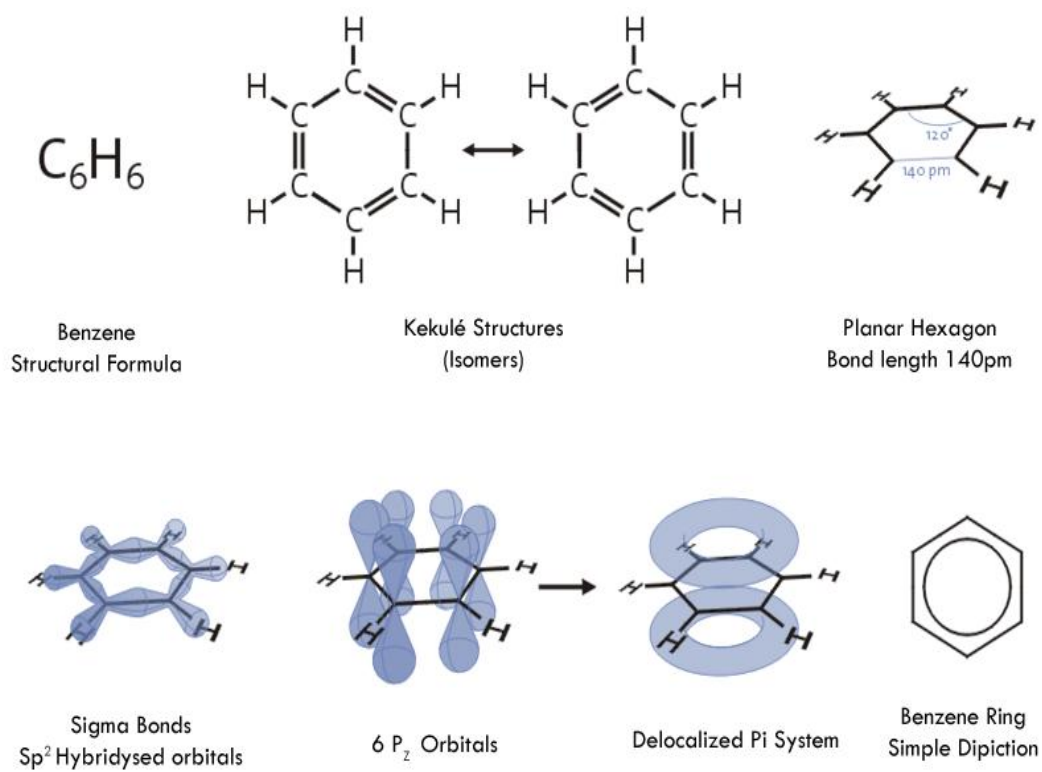
experiments have been performed on poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) polymer including doping effect [Cossiello *et al.*, 2008], and annealing effect [Ahn *et al.*, 2005] in the enhancement of the performance of polymer light emitting diodes. Common Alq<sub>3</sub> small molecule based OLED has been used as a reference device to investigate the general theoretical analysis on electrical and electroluminescence mechanisms of organic semiconductor device [Dong *et al.*, 2009].

Molecular energy level of such organic compound is controlled by their conjugated structure [Almeida *et al.*, 2002]. In order to understand this, a simple structure of benzene ring is taken as an example. Fig. 2.2 shows the molecular structure of benzene and its orbitals system. Carbon atom in benzene structure has trigonal Sp<sup>2</sup> hybrid orbital which forms  $\sigma$ -bond and  $\pi$ -bond. The  $\sigma$ -bond created from C-C and C-H single bonds which are strong covalent bonded. The electrons that occupy the  $\sigma$  bonds are known as  $\sigma$  electron and they are strongly localized. The term “localized” means that the  $\sigma$  electrons is not easily removed from its orbital and need high energy, e.g. thermal energy to removed it. On the other side, the  $\pi$ -bond is created from overlapping of 2p<sub>z</sub> orbital as a result of C=C covalent bonds. Thus, the electrons that occupy the  $\pi$ -bond are known as  $\pi$  electrons. These  $\pi$  electrons are delocalized and weakly bonded over the carbon atoms inside the conjugated structure. Here, “delocalized” means that the electrons can easily move over the neighbor’s atoms so that they display the semiconductor property of the compound. Larger conjugated structure will creates wider range of delocalized  $\pi$  electrons, thus more electrons can be hopping from one atom to another.

The delocalized  $\pi$  electron is an important feature in optical and electrical properties of organic semiconductor. The  $\pi$  molecular orbital is split into two energy



**Figure 2.1:** Typical molecular structure of polymers (top) and small molecules (bottom) used in organic electronic devices.

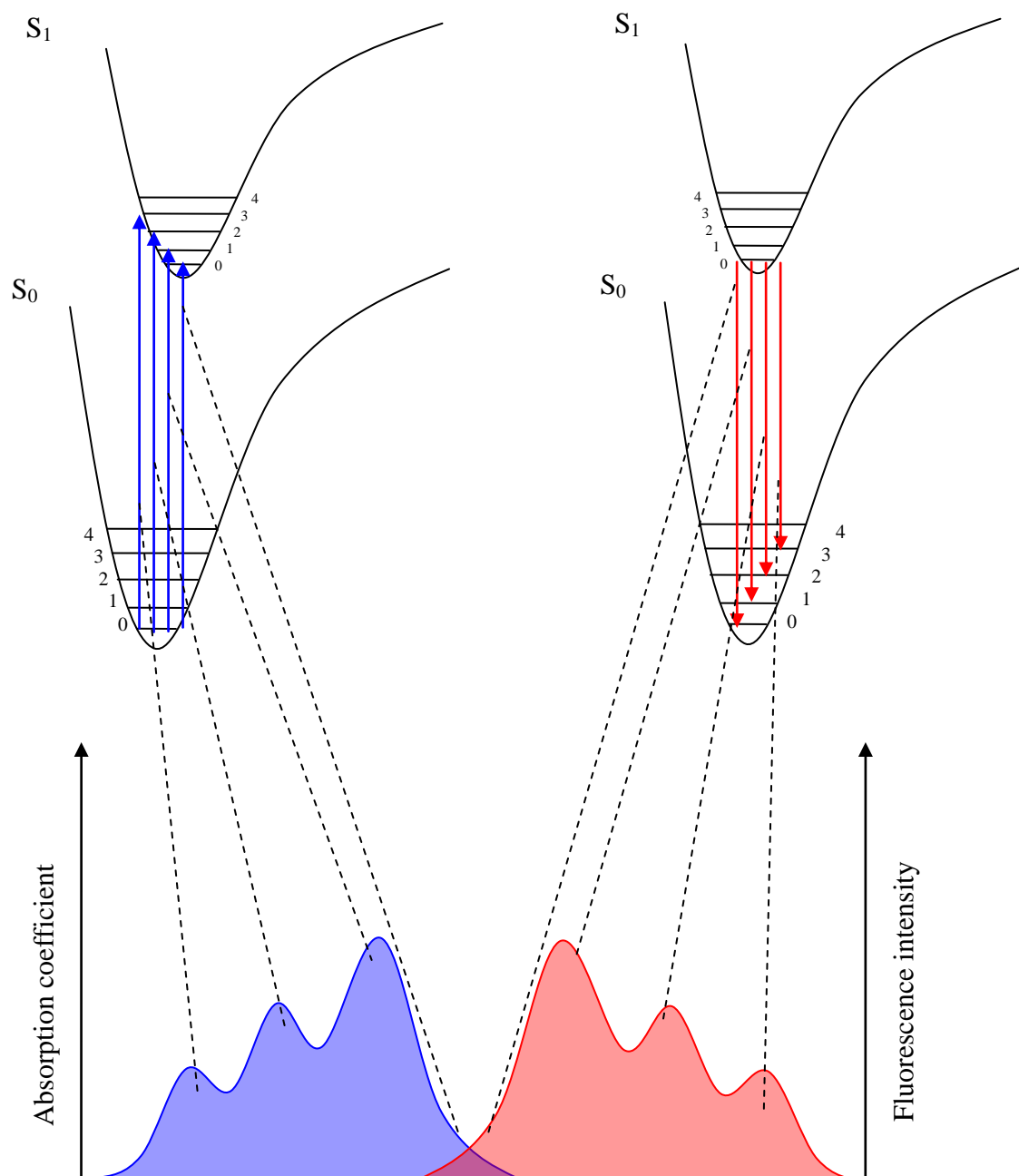


**Figure 2.2:** Molecular structure of benzene and its orbitals system

levels due to their electrons spin. Half of the molecular orbital are occupied and have energy levels lower than atomic orbital. These orbital are so called bonding molecular orbital ( $\pi$  orbital). The  $\pi$  orbital creates the highest occupied molecular orbital (HOMO) which refers to the distribution of energy band of weak tightly held electron in the molecule. On the other hand, another half of the molecular orbital is unoccupied and has larger energy levels than the atomic orbital. These orbital are so called antibonding molecular orbital ( $\pi^*$  orbital) and creates the lowest unoccupied molecular orbital (LUMO) which represent the easiest route to the excitation electrons from the lower levels. In inorganic semiconductor, HOMO and LUMO is referred as valance band (VB) and conduction band (CB), respectively. The gap between these two energy levels represents the energy gap of the compound and strongly depends on the size and configuration of the conjugated structure.

## 2.2 Excited States and Emission Processes in Organic Semiconductor

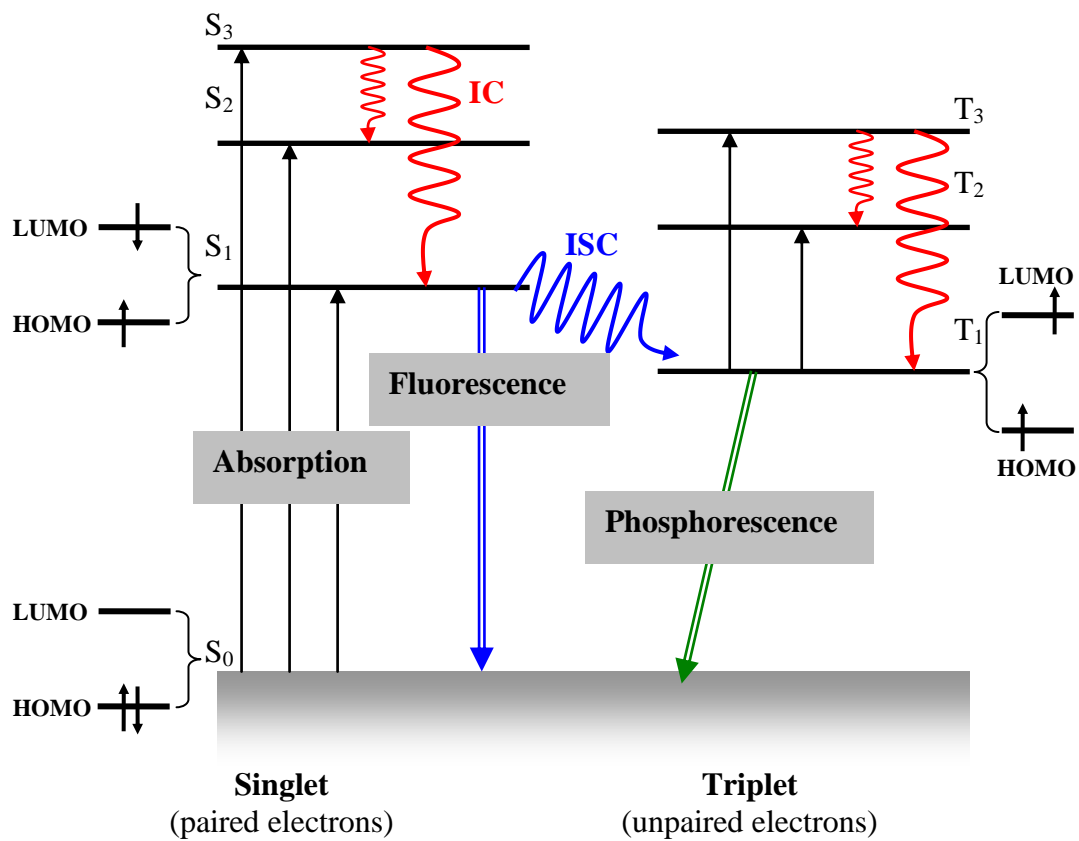
In room temperature, without excess energy induce to the organic semiconductor molecule, the electrons only fill the HOMO level and leave the LUMO empty. This condition is known as the ground state. Basically, the equilibrium position of the atomic nuclei is represented by a function of the configuration coordinated of the ground and excited states of the system. Each state has vibrational sublevels. When the molecule is excited by an external energy, e.g. light energy, electrons in HOMO level will absorb it and be excited to the LUMO level if the excitation photon energy is sufficient enough to overcome the energy gap between HOMO and LUMO level. The absorption of excitation energy will alter the electronic distribution on the molecule thus cause changes in the geometry of the molecule itself. Then, electronic transition may occur on a particular group of atoms in the molecule that is known as chromophore. This ground state to excited state transition is typically labeled to as  $\pi \rightarrow \pi^*$ .

**Figure 2.3:** Franck-Condon transitions

This transition is much faster than a nuclei motion, thus there is no change in the nuclear coordinates during an electronic state transition process. This is known as the Franck-Condon [A. D. McNaught, 1997] transitions where the electronic transitions are represented by vertical lines in Fig. 2.3. The probabilities of energy distribution corresponding to the electronic transition in excited state are also shown in Fig. 2.3.

The electrons in an excited state will undergo radiationless relaxation from the highest to the lowest vibrational state. This relaxation process occurs very fast as compared to the lifetime of the excited electronic state, where excited electrons loss their energy as vibrational energy. Subsequently, radiative relaxation (i.e. emission) occurs from the lowest vibrational state of the electronic excited state to various vibrational states of the electronic ground state. The differences between the absorption and emission energies is called the Franck-Condon shift and if the emission energy is less than absorption energy, the reduction of energy is called the Stokes shift [Albani, 2004].

In molecular organic solids, due to the strong interaction of atoms within a molecule the electronic excitation of an organic solid is therefore usually similar to that of an isolated atoms (i.e.  $\sigma$ -\* $\sigma$  bond). Under sufficient excitation energy, electron-hole pairs (i.e. excitons) are confined within or close to the molecule, i.e. Frenkel excitons [Frenkel, 1931], rather than free carriers where the electron and hole are far away separated. From Frenkel model, in the excited state, an electron is removed from HOMO and occupied LUMO, thus leaving a hole in the HOMO. If the electron in ground state and electron in excited state have antiparallel spins, the molecule is in the singlet excited state. Then if the electron in ground state and electron in excited state have parallel spins, it is in triplet excited state. Therefore, for each case,



**Figure 2.4:** Energy diagram for singlet (S) and triplet (T) excited state. IC and ISC are internal conversion and intersystem crossing, respectively.



the corresponding excitons are called singlet or triplet excitons. Fig. 2.4 shows a schematic energy diagram for the singlet and triplet excited state.

Under photoexcitation (i.e. absorption), the electron from the ground singlet state is excited to the singlet excited state. The ideal radiative relaxation from the excited state to the ground state produces photoluminescence. However, 100% of PL yield cannot occur due to other transition processes. Listed below are 5 important transition processes that occur in the real PL process.

- |   |                      |
|---|----------------------|
| 1) $S_2 \rightarrow S_1 + \text{heat};$ | Internal Conversion  |
| 2) $S_1 \rightarrow T_1 + \text{heat};$ | Intersystem Crossing |
| 3) $T_2 \rightarrow T_1 + \text{heat};$ | Internal Crossing    |
| 4) $T_1 \rightarrow S_0 + h\nu;$        | Phosphorescence      |
| 5) $S_1 \rightarrow S_0 + h\nu;$        | Fluorescence         |

Internal conversion is defined as a non-radiative transition between two states that have the same spin states. Intersystem crossing, also a non-radiative transition, is referred to as the transition between two states that have different spin states in the excited state. Therefore, it is also referred to as a radiationless transition between a singlet and a triplet excited state. Fluorescence and phosphorescence are radiative transitions to the ground state from singlet and triplet excited states, respectively. The lifetime of fluorescence is shorter ( $10^{-7}$  s) as compared to that of phosphorescence ( $10^{-5}$  s). These non-radiative transition processes, including internal conversion and intersystem crossing, may result in a reduction of PL yield [Harding *et al.*, 2008].

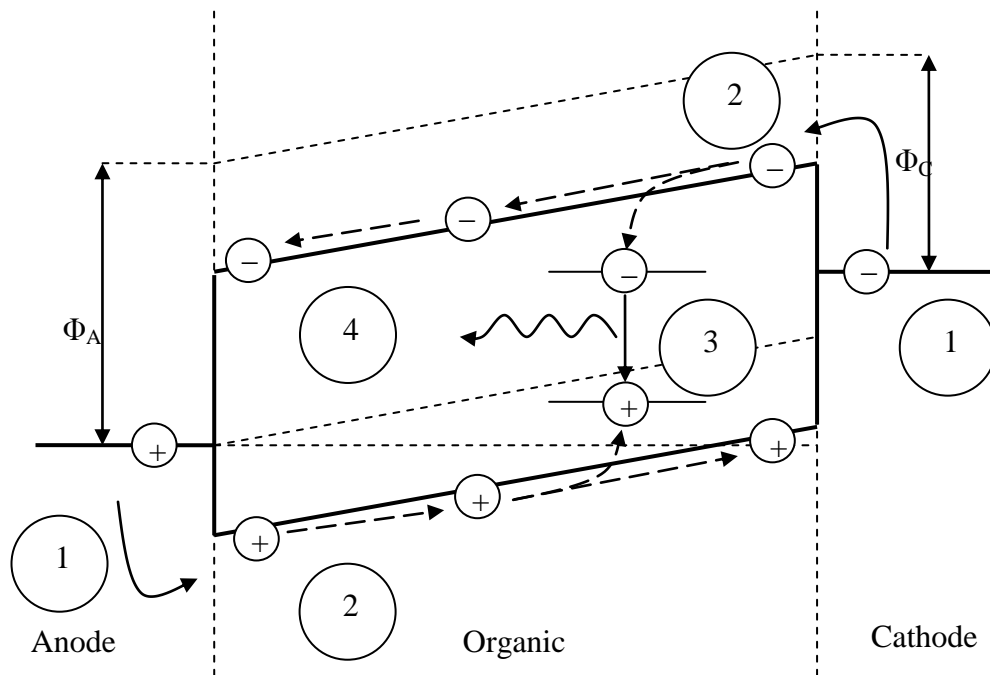
### 2.3 Organic Compound as Emitting Device

Basically, most electrical and luminescence concepts of organic semiconductor is originally derived from inorganic semiconductor physics. However, one should bear in mind of their specialties and differences. Most polymeric and small molecules materials used in OLEDs fabrication which have high molecular and low molecular weight, respectively, usually form disordered amorphous thin films without macroscopic crystal lattice [Brütting *et al.*, 2001], thus it is also difficult to simply adopt principles developed for inorganic molecule crystal. Due to the absence of extended delocalized states, charges are randomly transported by hopping between localized states. The stochastic behavior of charge transport which leads to low carriers mobility (typically less than  $1 \text{ cm}^2/\text{Vs}$ ) is different compared to that of a coherent motion in well-defined bands established for inorganic materials. Because of that, excitations are localized on certain identical molecules or in the short chain of polymer with large exciton binding energy. Additionally, most of organic semiconductor materials have large energy gap of 2-3eV [Jeong *et al.*, 2009] or even larger. By neglecting the concentration of thermally generated free carriers ( $<10^{10} \text{ cm}^{-3}$ ), the materials can be treated more as an insulator rather than semiconductor. Compared to inorganic semiconductor materials, impurities level are not only acting as sources of extrinsic mobile charge carrier, they also behaves as a carriers traps [Ramachandhran *et al.*, 2006]. Unlike in inorganic, the sources of traps in organic semiconductor can caused by two mechanisms; the residual impurities from the synthesized material [Klauk, 2006] and the structural traps of disorder conformation in molecules and polymeric chain [Nguyen, 2006].

## 2.4 Electroluminescence (EL) Mechanism in Organic Semiconductor

Several mechanisms were required in EL process starting with the injection, transport, exciton formation and radiative recombination of opposite charge carriers in molecular level of organic layer to produce visible emission due to appropriate HOMO-LUMO energy gap. Fig. 2.5 shows the schematic diagram of basic electroluminescence mechanism in organic solid. As mention before, the inorganic concepts can be implemented to simplify the explanation of EL mechanism in organic semiconductor by drawing the HOMO-LUMO molecular energy levels in a band-like approach. However, it has to remember that these organic semiconductors are disordered materials and do not have a well-defined band structure.

Alignment of energy levels for organic semiconductor EL system always affected by several interfacial effects including an interface dipole [*Yanagisawa & Morikawa, 2006*] and absence of impurity [*Pinato et al., 2010*]. The energy barrier of charge carriers are given by the offset energy different between the works functions of metals used as electrode and the energy levels of organic material. The works function of metal and the HOMO-LUMO energy levels of organic material usually obtained by photoelectron spectroscopy [*Park et al., 1996*] and cyclic voltammetry [*Tsutsui et al., 2005*], respectively. Problems always occur in the implementation of this height barrier alignment by oxidation of low work function metals due to the fabrication condition of OLEDs that is commonly not clean enough. Additionally, formation of interfacial layer due to chemical reactions between the metals and the organic layer can change the energetics properties at injection contact [*Kahn et al., 2003*]. Injection process is also affected by additional peculiarities due to disordered properties of organic materials [*Smertenko et al., 2005*].



**Figure 2.5:** Schematic diagram of electroluminescence mechanism in organic device where 1) injection, 2) transportation, 3) recombination, and 4) emission process.

When a sufficient electric field is applied, carriers are injected into the organic material and transported towards the opposite electrode. The transport mechanism of these carriers inside the organic materials is called hopping process because of the disordered nature of the materials. Charged carriers are hopping between sites with different energy and distance. Furthermore, as mentioned before, these carriers can be trapped in trapping level created from dopant impurities and disorder structural traps, which lead to low mobilities ( $10^{-3}$  to  $10^{-7}$  cm<sup>2</sup>/Vs) [Stallinga & Gomes, 2006]. Thus, these low mobilities may facilitate the injection of more carriers across metal-organic (MO) contact. Then, at a certain time, density of charge carriers becomes high enough to lead to the formation of space charges. This space charge creates an internal field that is against and reduces the applied electric field at MO contact which resists further charged carrier injection.

Generally, for EL to occur, electron and hole need to recombine and form an exciton, which is in meta-stable state and it is then decays radiatively. The recombination process of charged electron-hole is diffusion controlled due to low mobilities. This type of radiative decay is the Langevin type where electron-hole capture time,  $\tau_c$  is faster than carriers mobilities time,  $\tau_m$  ( $\tau_c \ll \tau_m$ ). The luminescent spectrum depends on the HOMO-LUMO energy levels of the organic materials. However, in real case, the excitons decay not only radiatively, but also irradiatively. Non-germinate pairs of charged carriers can recombine in triplet or singlet state that can lead to the generation of the total spin of excitons that have maximum internal quantum efficiency of 25% to convert the charged carriers into photon emission in singlet excitons [Baldo *et al.*, 1999]. Therefore, in order to fabricate very high efficient of organic electroluminescence device, organic materials that have high phosphorescence with short live time can be chosen, thus reduces the emission from triplet exciton.

## 2.5 Theoretical Concepts

### 2.5.1 Charge Carriers Injection

Electroluminescence of OLED devices is systematically through a several combination of various mechanisms and processes. One of the most important processes is charger carrier injection from metal electrode into organic semiconductor material through metal-organic contact.

Unlike inorganic semiconductor, the non-linear behavior of current-voltage characteristics of OLED always appeared due to their disordered nature [Shuttle *et al.*, 2010]. Charge injection process is defined by the mechanism of carriers enter through a surface boundary or interface contact. The amount of charge carrier injected depends on the charge injection barriers at metal-organic contact and the applied electric field. The injection barrier for electron is given by  $\Phi_e = W_c - A$ , and for holes by  $\Phi_h = I - W_a$ , where  $W_a$  and  $W_c$  are the work functions of anode and cathode, and  $I$  and  $A$  are ionization potential and electron affinity of the solid state. In an organic solid state,  $I$  and  $A$  are referred to HOMO and LUMO level of organic materials. The current density,  $J$  across this injection barrier can be denoted by general equation of Shockley diode [Sah, 1991]:

$$J = J_0 \left( \exp \left[ \frac{qV}{nkT} \right] - 1 \right) \quad (2.1)$$

where  $J_0$  is the saturation current density,  $q$  is the elementary charge,  $V$  is the applied voltage,  $n$  is the ideality factor,  $k$  is the Boltzmann constant, and  $T$  is the temperature. Additionally, due to thermionic emission and charge tunneling, charge carrier injection from metal electrode into organic semiconductor layer is usually referred as Richardson-Schottky (RS) [Dekker, 1957] and Fowler-Nordheim (FN) model [Lenzlinger & Snow, 1969], respectively. The general current density,  $J_{RS}$  relation with injection barrier,  $\Phi_B$  is given by:

$$J_{RS} = A^* T^2 \exp\left(-\frac{\Phi_B}{kT}\right), \quad (2.2)$$

where,

$A^*$  is the Richardson constant,  $A^* = 4\pi q m^* k^2 / h^3$  ( $=120 \text{A}/(\text{cm}^2 \text{K}^2)$  for  $m^* = m_0$ ) and  $\Phi_B$  is the injection barrier in eV. On the other hand, the FN model ignores Columbic effects and considers only charge tunneling, then the current density,  $J_{FN}$  as a function of field,  $F$  can be denoted as:

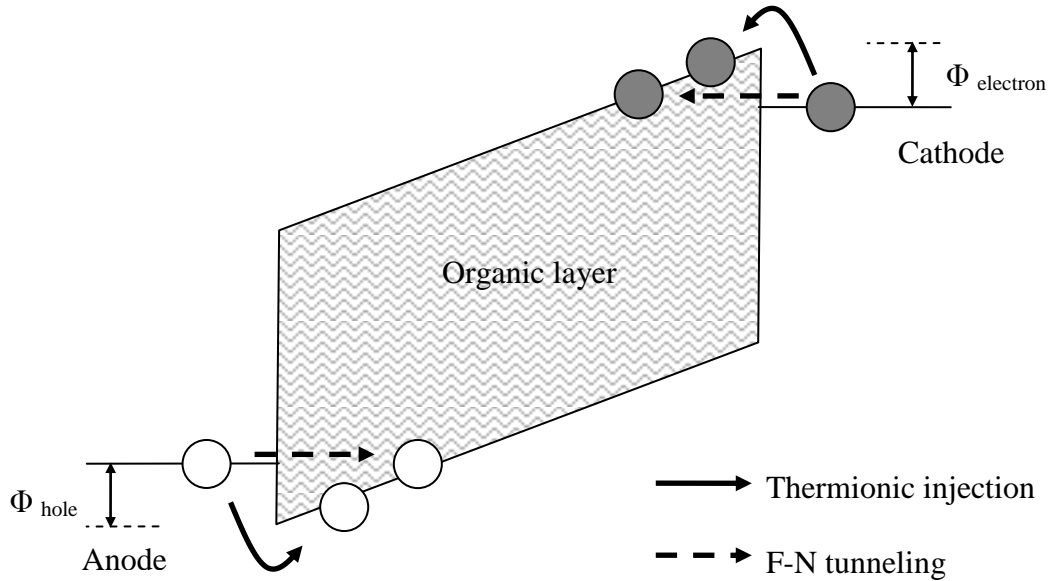
$$J_{FN} = \frac{A^* q^2 F^2}{\Phi_B \alpha^2 k^2} \exp\left(-\frac{2\alpha \Phi_B^{3/2}}{3qF}\right), \quad (2.3)$$

$$\text{with } \alpha = \frac{4\pi\sqrt{2m^*}}{h} \quad (2.4)$$

The FN tunneling injection of carriers can also be described mathematically by equation (2.5) and which is simplified to (2.6)

$$J_{FN} \propto F^2 \exp\left(\frac{-K}{F}\right), \text{ where } K = \frac{8\pi(2m^*)^{1/2} \phi^{3/2}}{3qh} \quad (2.5)$$

$$\ln\left(\frac{J_{FN}}{F^2}\right) \propto -K \cdot \frac{1}{F} \quad (2.6)$$



**Figure 2.6:** Comparison of thermionic injection and F-N tunneling mechanisms.  $\Phi_{\text{hole}}$  and  $\Phi_{\text{electron}}$  are the energy barrier for hole and electron injection, respectively.

Fig. 2.6 shows the schematic diagram of both injection mechanisms. These two modals are suitable in inorganic semiconductors with certain conditions where they have extended band state and larger mean free path. Unlike in inorganic, the models cannot be expected to be implemented in organic semiconductors due to a small average mean free path with the order of the molecular distances. Additionally, the presence of disorder nature in organic semiconductors can create intermolecular resistance related to random energy barriers that has to be overcome by the injected carriers. This results in an increase in the backflow of the injected carriers into the metal electrode [Davids *et al.*, 1997].

### 2.5.2 Charge Carriers Transport

The injected charge carriers are transported into an organic material and reach the opposite electrode in the direction of the applied field. The transportation of the carriers inside an organic semiconductor are referred as hopping process which is based on an electron-transfer mechanism as a result of movement of electrons among neighboring molecules. The movement of injected carriers inside the organic materials results in limitation in the current regimes, which strongly depends on the injection barrier.

For a low applied electric field, the charge transport in an organic semiconductor shows a linear increase of the current as given by the Ohmic drift current:

$$j_{ohmic} = n_o q \mu \frac{V}{d}, \quad (2.7)$$

where  $q$  is the elementary charge,  $n_o$  is the charge carrier density,  $\mu$  is the charge mobility,  $V$  is the applied voltage and  $d$  is the device thickness. However, due to low free-carriers density and also low mobility of carriers in the organic semiconductor, it is impossible to transport more injected carriers at a higher applied voltage. This then



leads to limitation of current where trapped carriers create an internal field that impede more carriers from injecting into the organic materials. The current is either space-charge limited current (SCLC) [Donovan & Wilson, 1981] or injection limited current (ILC), depending on the charge injection efficiency and charge carriers mobility.

The important condition for the occurrence of the SCLC requires that at least one of the metal-organic contacts has efficient injecting properties to trap more charge in carrier's reservoir. Mobility of the charge carriers is low and independent of the electric field, thus the organic material is treated as an insulator rather than a semiconductor. By assuming that the material is a perfect insulator without an intrinsic carrier, the SCLC can be explained by Mott-Gurney equation [Lampert & Mark, 1970]:

$$j_{SCLC} = \frac{9}{8} \varepsilon \varepsilon_0 \mu \frac{V^2}{d^3} \quad (2.8)$$

where  $\varepsilon$  is the dielectric constant and  $\varepsilon_0$  is the permittivity constant. This relation is derived for a trap-free SCLC where diffusion and boundary condition at injecting contact are neglected. This then result to an infinitely high carrier density at the metal-organic contact. However, in contrast, with the presence of traps the current is lower and then Eq. (2.8) has to be modified with a factor of  $\theta = n/(n+n_t)$  which is the ratio of free carriers to the total number of carriers (free and trapped). Then Eq. (2.8) becomes,

$$j_{SCLC} = \frac{9}{8} \theta \varepsilon \varepsilon_0 \mu \frac{V^2}{d^3} \quad (2.9)$$

If the traps are distributed in energy, they will be drastically filled when the electric field is increased, on the other hands,  $\theta$  depends on the applied electric field. The current will increase faster until all traps are filled. The general solution for the so-called trap-charge limited current (TCLC) is usually approximated by Mark and Helfrich [Mark & Helfrich, 1962]:

$$j_{TCLC} = N_c \mu q \left( \frac{\epsilon_0 l}{N_t q (l+1)} \right)^l \left( \frac{2l+1}{l+1} \right)^{l+1} \frac{V^{l+1}}{d^{2l+1}} \quad (2.10)$$

where  $l = E_t / kT$  (typically  $1.5 < l < 20$ ) in room temperature),  $N_c$  and  $N_t$  are the effective and traps carrier concentration, respectively. The electric field dependence of carriers mobility is the current feature observed in organic amorphous molecular materials and in most conjugated and doped polymer. This behavior is so-called Poole-Frenkel (PF) field dependence of the mobility [Mizutani & Ieda, 1979],

$$\mu(F) = \mu_0 \exp(\beta \sqrt{F}), \quad (2.11)$$

where  $\mu_0$  is the zero-field mobility and  $\beta$  is field-dependence of the mobility. Then, by multiplied this PF mobility relation with the trap-free SCLC,

$$j_{SCLC} = \frac{9}{8} \epsilon_0 \mu_0 \frac{V^2}{d^3} \exp(0.89 \beta \sqrt{V/d}) \quad (2.12)$$

Injection-limited current (ILC) occurs when the injection barrier is too large thus lead to insufficient injecting carrier from the metal electrode into the organic materials. Carriers require very high voltage to overcome this injection barrier. However, at a very high electric field, Ohmic contact properties occur causing a strong injection due to tunneling or other mechanisms related with the electric field. Thus the injecting contacts do not act as a carrier reservoir anymore and the current injected is saturated at a sufficiently high voltage.

### 2.5.3 Charge Carriers Recombination

One of the crucial mechanisms in the electroluminescence process is the recombination of electron and hole which leads to formation of exciton and decaying of the radiative photon energy. The recombination occurs when one element which is moving with a thermal energy,  $kT$ , is trapped in the Columbic potential of the other

element which is stationary at a distance less than Coulombic distance,  $r_c$  from each other. At this distance, the coulomb attractive potential energy is equal to the thermal energy:

$$\frac{e^2}{4\pi\epsilon_0\epsilon r_c} = kT \quad (2.13)$$

The term  $r_c$  can be determined as:

$$r_c = \frac{e^2}{4\pi\epsilon_0\epsilon kT} \quad (2.14)$$

In classical physics, the process of carrier recombination is related with two types of recombination processes which are a Langvenin [*Langevin, 1903*] and Thomson [*Thomson, 1924*]. These two mechanisms are related to their recombination times. The recombination time,  $\tau_{rec}$  is defined as a combination of the carrier motion time,  $\tau_m$  and the electron-hole capture time,  $\tau_c$  for the overall recombination event and can be expressed as:

$$\tau_{rec}^{-1} = \tau_m^{-1} + \tau_c^{-1} \quad (2.15)$$

Then, Langvenin and Thomson recombination can be described as  $\tau_c \ll \tau_m$  and  $\tau_c \gg \tau_m$ , respectively. In solid state physics, these two mechanisms can be distinguished by comparing the relation of the mean free path of optical photon emission,  $\lambda$ , with the average distance across a sphere of critical radius,  $r_c$ . The Langvenin recombination has  $\lambda \ll r_c$  and the Thomson recombination occurs when  $\lambda \gg r_c$ .

However, due to the low mobility carrier in the organic semiconductor ( $\mu \ll 1 \text{cm}^2/\text{Vs}$ ) and the mean free path for elastic scattering of  $\lambda = 10 \text{\AA}$  which is much lower than  $r_c \approx 200 \text{\AA}$  with  $\epsilon \approx 3$ , it can be strongly suggested that the Langvenin recombination model is the most appropriate model to explain the recombination process of organic materials. On the other words, the recombination process in organic

semiconductor can be simplified as a drift of opposite elements towards each other due to Coulombic field. The recombination of electron and hole then results in a charge-neutral excited state of molecule. In this stage, the electron and hole presence in LUMO and HOMO level, respectively. The Langvin recombination rate is given by:

$$\dot{n}_+ = \dot{n}_- = -n_+n_e(\mu_e + \mu_h) / \varepsilon \varepsilon_o \quad (2.16)$$

where  $\dot{n}_+$  and  $\dot{n}_-$  is the density of hole and electron, respectively,  $\mu_e$  and  $\mu_h$  is the mobility of electron and hole, respectively and  $\varepsilon$  and  $\varepsilon_o$  is the permittivity and dielectric constant, respectively.

#### 2.5.4 Light Emission

The main propose of the electroluminescence processes are to convert the electrical energy into emissive light and the emission spectra of OLED must covered all visible spectral range from infrared to ultraviolet especially for display panel and other optoelectronic devices. Those emission spectra can give various shapes and characteristics due to their molecular properties. For an instant, the broad spectrum emission maxima can be obtained from the disordered emitter molecules which involves the excited state of two-molecules [Baldo & Forrest, 2001], while the narrow line emissions are reflected from the excitation of metal ions in organic complexes material [G. Li, 2011] or coming from the lasing and microcavity effect in OLED structure [Melpignano et al., 2010].

In organic semiconductor, the large Stokes shift (distance from absorption to emission of molecule) is observed due to structural distortion of molecule that facilitates the deep localization of the first excited singlet. Additionally, the disordered structure of organic material leads to larger width and extended long-wavelength tail of emission reflecting from a high density of defects for inhomogeneities structural. The emission

color of EL from OLED devices can be selected by modifying the chemical structure [Ali *et al.*, 2009]. The EL color also can be tuned by doping process [W. X. Li *et al.*, 2007] where the host polymer has a wider energy gap while the dopant molecule has a small energy gap.

## 2.6 Impedance Model for OLED

Impedance spectroscopy is one of the powerful approaches that can be used to investigate the charge transport and relaxation processes in solid state devices [Rhee *et al.*, 2000]. In electroluminescence of OLED, this technique can discover precisely the difference processes that occur on different time scales. From that, information of the carrier and field distributions inside the device are fully described. Depending on energy band alignment in OLEDs, there are divided into two types; single-carrier (hole or electron) and double-carrier (hole and electron) device. Additionally, single-carrier (SC) device are divided into two part; hole-only (HO) and electron-only (EO) device.

The OLED device operation is obtained by three major processes: injection, transportation and recombination processes. Those processed have been discussed earlier in chapter. By taking consideration of single injection model, where only one type of carrier (electron or hole) is injected into a semiconductor, the transportation properties of organic semiconductors can be investigated via space-charge-limited-current (SCLC) theory. The basic equations describing transportation and carrier distribution in a single-carrier model are the current-flow equation and Poisson's equation [K.C. Kao, 1981], [Malliaras & Scott, 1999]:

$$J_o = qn(x,t)\mu E(x,t) + \varepsilon \frac{\partial E(x,t)}{\partial t}, \quad (2.17)$$

$$\frac{\partial E(x,t)}{\partial x} = \frac{qn(x,t)}{\varepsilon}, \quad (2.18)$$

where  $n(x,t)$  is the time-dependent local carrier density,  $\mu$  is the charge-carrier mobility,  $\epsilon$  is the dielectric constant of a semiconductor and  $q$  is the charge. Two assumptions are considered; 1) the injection barrier and localized states are neglected, and 2) carrier mobility is field and time independent under a small ac perturbation signal. The boundary condition for the semiconducting thin film with thickness of  $d$  is  $E(0,d)=0$  followed by an ideal Ohmic injection contact, where at the anode ( $x=0$ ) and cathode ( $x=d$ ). Since the diffusion of charge carriers is neglected, thus the injected charge carriers are accumulated in semiconducting thin film which creates an internal field of space-charge limited current (SCLC). The solution of Eq (2.17) and (2.18) with particular boundary condition is given by the Mott-Gurney square-law equation also known as Child's equation:

$$J_o = \frac{9}{8} \epsilon \mu \frac{V^2}{d^3} \quad (2.19)$$

where  $V$  is the voltage applied across the thin film.

The impedance measurement corresponds to a small sinusoidal perturbation over a steady state. For the analysis of the admittance of the SCLC, steady state and modulated contributions of small-signal conditions are considered [Okachi *et al.*, 2008]:

$$E(x,t) = E_0(x) + E_1(x,t) \quad (2.20)$$

$$V(x,t) = V_0(x) + V_1(x,t) \quad (2.21)$$

$$n(x,t) = n_0(x) + n_1(x,t) \quad (2.22)$$

$$J(t) = J_0 + J_1(t) \quad (2.23)$$

Then the AC current density  $J_1(t)$  can be written in the form

$$J_1(t) = q\mu n E_1(x,t) + \epsilon \mu E \frac{\partial E_1(x,t)}{\partial x} + \epsilon \frac{\partial E_1(x,t)}{\partial t} \quad (2.24)$$

The first term in Eq. (2.24) refers to the dc charge carrier density in the device, while the second term describes the current of additional time-dependent and the third term comes from dielectric displacement.

Due to the small-signal ac perturbation, the complex impedance of the device is given as

$$Z(\omega) = \frac{6}{g_0(i\omega\tau)^3} \left[ 1 - i\omega\tau + \frac{1}{2}(i\omega\tau)^2 - e^{-i\omega\tau} \right] \quad (2.25)$$

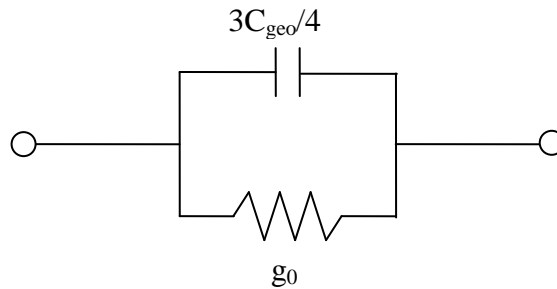
By expanding the exponential terms of complex admittance,  $Y_1 = C_1 + iB_1 = G_1 + i\omega C_1 = J_1/V_1$ , and solving the low frequency limit for the admittance, the next complex admittance expression for the low frequency limit can be obtained as:

$$Y = g_0 + i\omega \frac{g_0\tau}{4} \quad (2.26)$$

where

$$g_0 = \frac{9}{4} \epsilon\mu \frac{V_0}{d^3} = 3 \frac{C_{geo}}{\tau} \quad (2.27)$$

where  $C_{geo}$  and  $\tau$  are the geometric capacitance (which is equal to  $\epsilon/d$  per unit area) and carrier transit time, respectively. This admittance represents a parallel circuit of capacitance and resistance as shown in Fig. 2.7:



**Figure 2.7:** Equivalent circuit of impedance in space-charge-limited-current condition in organic semiconductor.

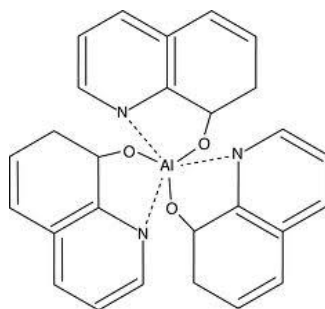
## 2.7 Chromophores-Small Molecule

There are many organic compounds that can be used in fabrication of organic light emitting diode (OLED). These organic semiconductor material should have well optical or/and electrical properties in order to enhance the efficiency of OLED performance. The organic semiconductor compounds can be divided into two major groups which are conjugated polymer and small molecule. Small molecule can be simply referred as an organic compound that have low atomic molecular weight which can not be categorized as polymer. Depending on their derivatives and molecular structures, small molecules can be used as an electron transporting material, a hole transporting material and even better as an emissive material. In this work, three small molecule compounds (refer Fig. 2.7) have been used and will be briefly described.

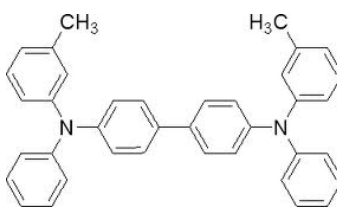
### 2.7.1 Alq<sub>3</sub> : Organo-metallic Chelate

The small molecule compound that have been synthesized for fabrication of OLED is aluminum triquinolate (Alq<sub>3</sub>), which was successfully reported by C.W Tang and S.A Van Slyke from Kodak Corp [*Tang & VanSlyke, 1987*]. This was the most highlighted achievement in OLED fabrication in recent years. Since then, many group of researchers perform several experiments for other type of small molecule compound. In terms of molecular structure, Alq<sub>3</sub> has three 8-quinolate ligands that distorted octahedrally and attached to the aluminum metal, which avoid the photoluminescence (PL) quenching in solid state. It has a  $T_g$  of 172°C [*Higginson et al., 1998*] and can be easily deposited using thermal evaporation technique to form good amorphous thin film. From the time-of-flight (TOF) measurement [*Kepler et al., 1995*], the electron mobility of Alq<sub>3</sub> is  $1.4 \times 10^{-6} \text{ cm}^2/(\text{Vs})$ , which is much higher then its hole mobility of  $2.0 \times 10^{-8} \text{ cm}^2/(\text{Vs})$ . This organo-metalic chelate shows both good electron transport properties and reasonably efficient emission as a result of HOMO and LUMO energy level of

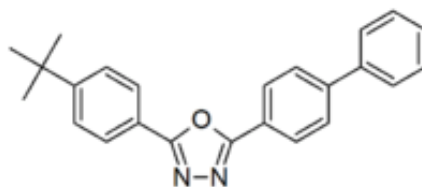




Alq<sub>3</sub>: Guest emissive molecule



TPD: Host HTM



PBD: Host ETM

**Figure 2.7:** Molecular structure of organic materials used in this work

-5.95eV and -3.00eV [Anderson *et al.*, 1998], respectively. The mobility of electron in Alq<sub>3</sub> can be improved by doping method such as co-hosting the hydroxyquinoline with the phenanthroline derivatives [Choy *et al.*, 2006]. In a multilayer structure, the lifetime of OLED can be improved by depositing the co-evaporated materials which are inactive chemically and optically [T. S. Kim & *et al.*, 2004].

### 2.7.2 PBD: Oxadiazole Derivative

Another small molecule compound that is widely studied for an electron transporting material in OLED fabrication is oxadiazole derivative material. The common example of the derivative is 5(4-biphenyl)-2-(4-tert-butyl-phenyl)-1,3,4-oxadiazole (PBD). PBD has great thermal stability and excellent electronic behavior. The low  $T_g$  around 60°C makes PBD easily thermally deposited. It also tends to change the phase from amorphous to crystalline structure during device operation due to Joule heating [Adachi *et al.*, 1990]. PBD also has a significant high LUMO level of -2.16eV and a low HOMO level of 6.06eV [Pommerehne *et al.*, 1995] as compared to that of Alq<sub>3</sub>, thus PBD has a larger energy gap.

### 2.7.3 TPD: Triarylamines Derivative

A hole transporting material is referred to the materials that have higher HOMO energy level, such that it can conduct the positive charge carrier (holes) and avoid the hole-traps. A hole transporting material can also act as an electron blocking material which prevents the back-flow of electron to anode. In this case, the LUMO level should be very low. The N,N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) is one of the most commonly studied as a hole transporting material. This triarylamine family has demonstrated a high value of hole mobility,  $1.1 \times 10^{-2} \text{ cm}^2/(\text{V s})$  as reported in [Kageyama *et al.*, 2010]. However, TPD has a very low glass transition,  $T_g$ , of 65°C.

Therefore it can be easily crystallized or expanded during a device operation at a high voltage.

## **2.8 Summary**

It is noted that the electroluminescence process in OLED device are related to the chemical and physical properties of the organic material and also the respective electrode. Suitable alignment of energy level among the organic and the electrodes could be a major key for high efficient device. Balance charge accumulation on the emission region of organic layer may increase the possibility of exciton formation and recombination process. Base on this theory, this work are focus on finding a suitable organic dopant and host with a good alignment of energy level, fabricated via solution processing method.

## References

- A. D. McNaught, A. W. (Ed.). (1997). *IUPAC Compendium of Chemical Terminology* (2nd ed.).
- Adachi, C., Tsutsui, T., & Saito, S. (1990). Confinement of Charge Carriers and Molecular Excitons within 5-nm-Thick Emitter Layer in Organic Electroluminescent Devices with a Double Heterostructure. *Applied Physics Letters*, 57, 531-533.
- Ahn, J. H., Wang, C., Widdowson, N. E., Pearson, C., Bryce, M. R., & Petty, M. C. (2005). Thermal Annealing of Blended-Layer Organic Light-Emitting Diodes. *Journal of Applied Physics*, 98, 054508-054507.
- Albani, J. R. (2004). *Structure and Dynamics of Macromolecules: Absorption and Fluorescence Studies* (pp. 58): Elsevier.
- Ali, B., Jabar, S., Salih, W., Al Tamimi, R. K., Al Attar, H., & Monkman, A. P. (2009). Synthesis and Spectroscopic Characterization Studies of Low Molecular Weight Light Emitting PPV Segmented Copolymers. *Optical Materials*, 32, 350-357.
- Almeida, A. M., Ramos, M. M. D., & Cadilhe, A. M. (2002). Quantum Molecular Dynamics Simulations of Conjugated Polymers. *Computational Materials Science*, 24, 54-57.
- Anderson, J. D., McDonald, E. M., Lee, P. A., Anderson, M. L., Ritchie, E. L., Hall, H. K., et al. (1998). Electrochemistry and Electrogenerated Chemiluminescence Processes of the Components of Aluminum Quinolate/Triarylamine, and Related Organic Light-Emitting Diodes. *Journal of the American Chemical Society*, 120, 9646-9655.
- Baldo, M. A., & Forrest, S. R. (2001). Interface-Limited Injection in Amorphous Organic Semiconductors. *Physical Review B*, 64, 085201.
- Baldo, M. A., O'Brien, D. F., Thompson, M. E., & Forrest, S. R. (1999). Excitonic Singlet-Triplet Ratio in a Semiconducting Organic Thin Film. *Physical Review B*, 60, 14422.
- Brütting, W., Berleb, S., & Mückl, A. G. (2001). Device Physics of Organic Light-Emitting Diodes Based on Molecular Materials. *Organic Electronics*, 2, 1-36.
- Cossiello, R. F., Cirpan, A., Karasz, F. E., Akcelrud, L., & Atvars, T. D. Z. (2008). Electroluminescence of (Styrene-Co-Acrylic Acid) Ionomer/Conjugated MEH-PPV Blends. *Synthetic Metals*, 158, 219-225.

- Davids, P. S., Campbell, I. H., & Smith, D. L. (1997). Device Model for Single Carrier Organic Diodes. *Journal of Applied Physics*, 82, 6319-6325.
- Dekker, A. J. (1957). *Solid State Physics* Englewood Cliffs, New Jersey: Prentice-Hall, Inc.
- Dong, S., Wang, W., Yin, S., Li, C., & Lu, J. (2009). Theoretical Studies on Charge Transport Character and Optional Properties of Alq<sub>3</sub> and its Difluorinated Derivatives. *Synthetic Metals*, 159, 385-390.
- Donovan, K. J., & Wilson, E. G. (1981). (Vol. 44).
- Frenkel, J. (1931). On the Transformation of Light into Heat in Solids. II. *Physical Review*, 37, 1276.
- Harding, R. E., Lo, S.-C., Burn, P. L., & Samuel, I. D. W. (2008). Non-Radiative Decay Mechanisms in Blue Phosphorescent Iridium(III) Complexes. *Organic Electronics*, 9, 377-384.
- Higginson, K. A., Zhang, X.-M., & Papadimitrakopoulos, F. (1998). Thermal and Morphological Effects on the Hydrolytic Stability of Aluminum Tris(8-hydroxyquinoline) (Alq<sub>3</sub>). *Chemistry of Materials*, 10, 1017-1020.
- Jeong, W. I., Kim, S. Y., Kim, J. J., & Kang, J. W. (2009). Thickness Dependence of PL Efficiency of Organic Thin Films. *Chemical Physics*, 355, 25-30.
- K.C. Kao, W. H. (1981). *Electrical Transport in Solids*: Oxford.
- Kageyama, H., Ohishi, H., Tanaka, M., Ohmori, Y., & Shirota, Y. (2010). Organic Photovoltaic Devices Using an Amorphous Molecular Material With High Hole Drift Mobility, Tris[4-(2-thienyl)phenyl]amine. *Selected Topics in Quantum Electronics*, IEEE Journal of, 16, 1528-1536.
- Kahn, A., Koch, N., & Gao, W. (2003). Electronic Structure and Electrical Properties of Interfaces Between Metals and  $\pi$ -Conjugated Molecular Films. *Journal of Polymer Science Part B: Polymer Physics*, 41, 2529-2548.
- Kepler, R. G., Beeson, P. M., Jacobs, S. J., Anderson, R. A., Sinclair, M. B., Valencia, V. S., et al. (1995). Electron and Hole Mobility in Tris(8-Hydroxyquinolinolato-N1,O8) Aluminum. *Applied Physics Letters*, 66, 3618-3620.
- Klauk, H. (Ed.). (2006). *Organic electronics: materials, manufacturing and applications*: WILEY-VCH.
- Lampert, M. A., & Mark, P. (1970). *Current Injection in Solids* New York.
- Langevin, P. (1903). Recombinaison et mobilités des ions dans les gaz. *Annales de Chimie et de Physique*, 28, 433.
- Lenzlinger, M., & Snow, E. H. (1969). Fowler-Nordheim Tunneling into Thermally Grown SiO<sub>2</sub>. *Journal of Applied Physics*, 40, 278-283.

- Li, G. (2011). A Novel Deep-Red-Emitting Iridium Complex with Single-Peaked Narrow Emission Band: Synthesis, Photophysical Properties, and Electroluminescence Performances. *Journal of Luminescence*, 131, 184-189.
- Li, W. X., Hagen, J., Jones, R., Heikenfeld, J., & Steckl, A. J. (2007). Color Tunable Organic Light Emitting Diodes Using Eu Complex Doping. *Solid-State Electronics*, 51, 500-504.
- Malliaras, G. G., & Scott, J. C. (1999). Numerical Simulations of the Electrical Characteristics and the Efficiencies of Single-Layer Organic Light Emitting Diodes. *Journal of Applied Physics*, 85, 7426-7432.
- Mark, P., & Helfrich, W. (1962). Space-Charge-Limited Currents in Organic Crystals. *Journal of Applied Physics*, 33, 205-215.
- Melpignano, P., Cioarec, C., Clergereaux, R., Gherardi, N., Villeneuve, C., & Datas, L. (2010). E-Beam Deposited Ultra-Smooth Silver Thin Film on Glass with Different Nucleation Layers: An Optimization Study for OLED Micro-Cavity Application. *Organic Electronics*, 11, 1111-1119.
- Mizutani, T., & Ieda, M. (1979). Carrier Transport In High-Density Polyethylene. *Journal of Physics D: Applied Physics*, 12, 291.
- Nguyen, T. P. (2006). Defect Analysis In Organic Semiconductors. *Materials Science in Semiconductor Processing*, 9, 198-203.
- Okachi, T., Nagase, T., Kobayashi, T., & Naito, H. (2008). Influence of Injection Barrier on the Determination of Charge-Carrier Mobility in Organic Light-Emitting Diodes by Impedance Spectroscopy. *Thin Solid Films*, 517, 1331-1334.
- Park, Y., Choong, V., Gao, Y., Hsieh, B. R., & Tang, C. W. (1996). Work Function of Indium Tin Oxide Transparent Conductor Measured by Photoelectron Spectroscopy. *Applied Physics Letters*, 68, 2699-2701.
- Pinato, A., Cester, A., Meneghini, M., Wrachien, N., Tazzoli, A., Xia, S., et al. (2010). Impact of Trapped Charge and Interface Defects on the Degradation of the Optical and Electrical Characteristics in NPD/Alq<sub>3</sub> OLEDs. *Electron Devices, IEEE Transactions on*, 57, 178-187.
- Pommerehne, J., Vestweber, H., Guss, W., Mahrt, R. F., Bässler, H., Porsch, M., et al. (1995). Efficient Two Layer Leds On A Polymer Blend Basis. *Advanced Materials*, 7, 551-554.
- Ramachandhran, B., Huizing, H. G. A., & Coehoorn, R. (2006). Charge Transport In Metal/Semiconductor/Metal Devices Based On Organic Semiconductors With An Exponential Density Of States. *Physical Review B*, 73, 233306.
- Rhee, H.-W., Sik Chin, K., Young Oh, S., & Choi, J.-W. (2000). Application Of Impedance Technique To OELD. *Thin Solid Films*, 363, 236-239.

- Sah, C.-T. (1991). P/N and Other Junction Diodes *Fundamentals of solid-state electronics* (pp. 432): World Scientific Publishing Co. Pte. Ltd.
- Shuttle, C. G., Hamilton, R., O'Regan, B. C., Nelson, J., & Durrant, J. R. (2010). Charge-Density-Based Analysis Of The Current-Voltage Response Of Polythiophene/Fullerene Photovoltaic Devices. *Proceedings of the National Academy of Sciences*, 107, 16448-16452.
- Smertenko, P., Fenenko, L., Brehmer, L., & Schrader, S. (2005). Differential Approach To The Study Of Integral Characteristics In Polymer Films. *Advances In Colloid And Interface Science*, 116, 255-261.
- Stallinga, P., & Gomes, H. L. (2006). Modeling Electrical Characteristics Of Thin-Film Field-Effect Transistors: II: Effects Of Traps And Impurities. *Synthetic Metals*, 156, 1316-1326.
- Tang, C. W., & VanSlyke, S. A. (1987). Organic Electroluminescent Diodes. *Applied Physics Letters*, 51, 913-915.
- Thomson, J. J. (1924). Recombination of Gaseous Ions. *Philosophical Magazine S6*, 47, 337-378.
- Tsutsui, S., Sakamoto, K., Yoshida, H., & Kunai, A. (2005). Cyclic Voltammetry And Theoretical Calculations Of Silyl-Substituted 1,4-Benzoquinones. *Journal of Organometallic Chemistry*, 690, 1324-1331.
- Yanagisawa, S., & Morikawa, Y. (2006). Important Role Of Molecular Permanent Dipoles Of The Alq3/Al Interface Studied From First-Principles. *Chemical Physics Letters*, 420, 523-528.
- Yap, C. C., Yahaya, M., & Salleh, M. M. (2008). Influence of Thickness Of Functional Layer On Performance Of Organic Salt-Doped OLED With ITO/PVK:PBD:TBAPF6/Al Structure. *Current Applied Physics*, 8, 637-644.