

Chapter 1. Introduction

1.1. Motivation and research overview

The organic semiconductor device has been studied for over five decades (Bergenti, Dediu, Prezioso, & Riminucci, 2011) and has progressed enormously since the first observation of the photoconductivity response of small molecules such as anthracene (Gutmann, 1967; Pasveer, 2004). Since then, the interest in the organic semiconductor devices has been impressive and has reached the point where several applications are routinely available for use while others are closed to be commercialized or in testing phase for novel application (Méndez, Thurzo, & Zahn, 2007). Boosted by the successful commercialization of organic photoconductors (OPC)(Borsenberger & Weiss, 1993, 1998; Dekker, 1993), the effort to bring optoelectronic devices based on organic materials such as organic light emitting diode (OLED), organic solar cell (OSC) and organic field effect transistor (OFET) into the market is now greater than ever. The tremendous interest in organic materials is especially caused by the simplicity in manufacturing (e.g solution processing or vacuum deposition), flexibility and lower cost (Dos Reis et al., 2011; Jurriaan, 2007; Kim et al.; Q.-D. Ling et al., 2008; Magdalena, 2010; Pivrikas, Neugebauer, & Sariciftci, 2011; Sokolov, Roberts, & Bao, 2009; Stathatos, Chen, & Dionysiou, 2008)

Organic semiconductor is now a rapidly evolving research field that has been conducted on a largely multidisciplinary level involving physics, chemistry, material science and device engineering. Although some organic semiconductor devices already meet the requirement for practical application, there is still necessity to design and discover new organic semiconductor materials for the development of the organic semiconductor technology. Therefore, further scientific effort devoted to the design of organic semiconductor with fascinating properties that are suitable for optoelectronic application has to be undertaken. Deep understanding on the materials properties is the

crucial prerequisite for the development and improvement in the performance of the optoelectronic devices. By providing a basic understanding of material properties, it is possible to facilitate a future materials design where a material is designed with specific properties for a certain application.

Research on molecular hybrid compound such as metal quinolate complexes has attracted scientific and commercial attention due to their promising applications in optoelectronic application such as organic light emitting devices (Du, Mei, & Lu, 2005). Aluminum tris(8-hydroxyquinoline) (Alq_3) is one of the metal quinolate complexes that has been successfully used in OLED since many years ago (Bergenti et al.; Li & Xu, 2008). This is because Alq_3 possesses a very good luminescence efficiency and high electron mobility (Luo et al., 2011; Shukla & Kumar, 2010). Therefore, a wide range of metal quinolate complexes has been investigated intensively in order to provide further development in the field of optoelectronic devices (Hernández, Gillin, & Somerton, 2009; Leung et al., 2009; Shukla & Kumar, 2010; Yu, Cho, & Perng, 2009). However, obtaining pure emission colour from the metal quinolate complexes has always been a problem because most of the materials exhibit broad emission spectra with a full width at half maximum (FWHM) around 50-200 nm (Q. D. Ling, Kang, Neoh, & Huang, 2003).

Rare earth metal ions can be used to solve this problem. This is due to the fact that the rare earth metals are unique elements, in which has fascinating optical properties that lead to an outstanding role in light conversion technologies (M. A. Katkova et al., 2009; Lv et al., 2010). Furthermore, the specific electronic structure of these metals provide a sharp emission bands due to the f-f transitions in the 4f orbitals that shielded from external fields by the closed 5s and 5p shells (Bünzli & Eliseeva, 2010; Quirino et al., 2006; Saleh, Kusrini, Mohd Sarjidan, & Abd. Majid, 2011). There have been numerous

published reports that were comprehensively studied regarding rare earth tris-8-hydroxyquinolines but most of them dealt with the rare earth metals which the emission occurs in the infrared region (M. Katkova, Vitukhnovsky, & Bochkarev, 2005). The most common rare earth tris-8-hydroxyquinolines complexes that have been intensively studied are neodymium tris-8-hydroxyquinolines (Ndq_3), erbium tris-8-hydroxyquinolines (Erq_3) and ytterbium tris-8-hydroxyquinolines (Ybq_3) which are actively used as efficient infrared electroluminescence materials (M. A. Katkova et al., 2011; Magennis et al., 2004; Sun et al., 2008). Less attention has been focused on the rare earth metals which the emission falls into the visible region. Rare earth metals complexes which exhibit emission in the visible region are potentially useful in the fabrication of organic light emitting diodes (OLEDs). Therefore this work will concentrate on investigating the characterization of such rare earth metals quinoline, Req_3 .

Europium is one of the rare earth metals in which the emission falls into the visible region. It is a well-known red emitter that is believed to be a promising candidate for pure red emission colour. It exhibits a sharp emission peak around 612 nm, which originates from the f-f-transition, resulting in almost monochromatic red emission with photoluminescence of nearly 95% (Quirino, et al., 2006; Santos et al., 2008; Teotonio et al., 2009). Another rare earth metal investigated in this work is Terbium. Terbium is also a green emitter which also exhibits a sharp emission peak corresponds to the 578 nm (Chen et al., 2009; Pereira et al., 2012). β -diketones are excellent chelating agents which can form stable complexes with the europium ions (Guan, Chen, Sun, Liang, & Zhang, 2005). It also can extend the conjugated system and thus increase the quantum efficiency of energy transfer in the luminescence materials due to the increase of absorptivity of the organic ligand (Guan, et al., 2005; Liu et al., 2003). Moreover, the

role of the secondary (neutral) ligand is not only to saturate the coordination number of the rare-earth metal ion (Re^{3+}) but also to improve the volatility and stability of the europium complex (Guan, et al., 2005). Inspired by this fact, molecular hybrid compounds based on four novel Re_3 quinoline ternary complexes namely Eu_3bpy_3 , Eu_3phen_3 , Tb_3bpy_3 and Tb_3phen_3 have been synthesized and investigated. As these compounds are newly synthesized material, the structural, thermal, optical and electrical properties are briefly discussed in this thesis. Even though a large variety of europium and terbium complex have been successfully synthesized and utilized in OLED application, but to our best knowledge no work has been reported on this novel material. The possibility of applying these materials as emitting and electron transport material in OLED is also evaluated.

As Re_3 ternary complexes are small molecules, a vacuum deposition technique is usually opted to deposit the thin film of the complexes. Although this technique has resulted in good device performance, it is still costly and requires a long time for deposition. For this reason, the spin coating technique was used to deposit the thin film since this technique is faster, easier to process and cheaper than the vacuum deposition (Fang, Chan Choy, Ma, & Ou, 2006). However, Re_3 ternary complexes are very insoluble complex, both only dissolved in DMSO. It is difficult to spin coat a solution if the solution has a high boiling point and viscosity. Therefore, the solvent was mixed with acetone in a ratio of 4:1 (acetone:DMSO) in order to achieve the essential viscosity and homogeneity of the solution for spin-coating.

1.2. History on molecular hybrid compound

In the past decade, considerable effort have been made toward the development of molecular hybrid compound since the first report of organic light-emitting diodes

(OLEDs) fabricated from Alq₃ in 1987 (Tang & Vanslyke, 1987) due to its high thermal stability, adequate electron transport, and luminescent properties (Bergenti, et al.; Li & Xu, 2008; Luo, et al., 2011; Shukla & Kumar, 2010). Since then, tremendous scientific progress has been made resulting in numerous molecular hybrid compound based on metal chelate, Mq₃ suitable for application in OLEDs. In recent years, various Mq₃ with M= Al, Ga, In and Sc have been synthesized in which their emission properties have shown that the nature of the metallic ion does not affect significantly the position of the luminescence peak maximum indicating that the excited state is governed by the quinoline (8Hq) ligand (Hernández, et al., 2009; Leung, et al., 2009; Shukla & Kumar, 2010; Yu, et al., 2009). Other metals such as Zn, In and Ga have also been investigated (Hernández & Gillin, 2009; Muhammad & Sulaiman, 2011; Pimchan, Khaorapapong, & Ogawa, 2011; Sui & Yan, 2006). Recently, researchers have been investigating the potential strategies to tune Alq₃ emission by simple ligand modification (Irfan, Cui, & Zhang, 2009; Laxmikanth Rao & Bhanuprakash, 2011).

In recent years, the molecular hybrid compound based on transition metal ligand complexes has gained much attention among researcher since it has been proven to increase the efficiency of OLED enormously (Holder, Langeveld, & Schubert, 2005). Many metal complexes such as Os, Ru, Pt and Ir chelated with organic ligands demonstrate fascinating phosphorescence properties which will result in high electroluminescence quantum efficiency (Holder, et al., 2005). On the other hand, the rare earth metal-ligand complexes (rare earth complexes) have also attracted much attention owing to their fascinating optical properties that lead to an outstanding role in light conversion technologies (M. A. Katkova, et al., 2009; Lv, et al., 2010) due to the specific electronic structure of these metals that provide sharp emission bands due to the

f-f transitions in the 4f orbitals that shielded from external fields by the closed 5s and 5p shells (Bünzli & Eliseeva, 2010; Quirino, et al., 2006; Saleh, et al., 2011).

1.3. Research objectives

Aside from thorough investigation on improving the application and performance of the organic semiconductor, the synthesization and characterization of the newly synthesized material also plays an important role in the enormous progress in optoelectronic application. This thesis is primarily focuses on the investigating properties of the newly synthesized molecular hybrid compound based on the Req_3 ternary complexes (Req_3) chelated with 2,2-bipyridine (Bpy) and 1,10-phenanthroline (Phen) ligands. It is noteworthy to mention that the chelated ligand is known as a neutral or secondary ligand.

This research work aim to the study of the structural, thermal, optical and electrical properties of the Req_3 ternary compound. Knowledge on the properties is important in order to provide a step forward as potential materials, in organic optoelectronic devices application. The fundamental understanding of the material properties is the crucial prerequisite for further development of optoelectronic technology. Therefore, in this research, the investigation is concentrating on investigating the Req_3 ternary complexes properties rather than optimizing the device performance using this material. Overall, there are four main objectives to be achieved in this research work stated as follows:

- 1) To investigate the structural properties of the Req_3 ternary complexes thin film by observing the possible bonding and functional group that involve in the complexes as well as the phase of the thin films.
- 2) To investigate the thermal stability of Req_3 ternary compounds.

- 3) To investigate the optical properties by evaluating the electronic structure, optical band gap, emission characteristics and energy transfer mechanism of the Req_3 ternary complexes
- 4) To investigate the I-V characteristics of Req_3 ternary complexes apply as the active material in organic light emitting device (OLED) by evaluating the dominance transport mechanism in the devices and extracting the electronic parameters of devices containing the Req_3 ternary complexes

1.4. Organization and scope of the thesis

Basically each chapter is divided into several section and subsections with the main headings of introduction, theory and literature review, structural, thermal, optical and electrical analysis and conclusions. It should be noted that the result and discussion that involve the investigation on the structural, thermal, optical and electrical analysis were performed separately in two sequential sections beginning with the variations of secondary ligand but of the same rare earth metal.

In chapter 2, the theory and literatures related to this work are reviewed. The subtopics including the fundamental of organic semiconductor, basic concepts of luminescence of organic molecules, rare-earth metal complexes and application and electrical properties of organic semiconductor.

In chapter 3, the experimental details that were involved in this whole research work is discussed. The materials used in synthesizing all the Req_3 ternary complexes namely Euq_3bpy_3 , $\text{Euq}_3\text{phen}_3$, Tbq_3bpy_3 and $\text{Tbq}_3\text{phen}_3$ as well as the synthesis process are initially presented. The second part focuses on the thin films deposition and device fabrication method. The final part focuses on the measurement and characterization

technique which utilizes Profilometer, UV-VIS/NIR spectrometer, Photoluminescence Spectrometer (PL), Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analyzer and Differential Scanning Calorimeter (TGA & DSC) and Keithly 236 Source Measurement Unit (SMU). The theoretical aspects of some characterization tools are also discussed.

In chapter 4, the structural and thermal properties of Req_3 ternary complexes are discussed. Both spectroscopic and structural analyses were evaluated in thin films form. The spectroscopic study was performed by using Fourier transform infrared spectroscopy (FTIR). In this analysis, the bonding and the functional group involved in the coordination of the metal complexes were obtained. The structural study was evaluated by using X-ray diffractometer (XRD) in order to determine the phase of the resultant molecular hybrid compounds in thin film form. However the thermal behavior of the molecular hybrid compounds was performed in a powder form. The stability and decomposition pathway of the molecular hybrid compound were investigated by thermogravimetric (TGA) and differential thermogravimetric (DTG).

In chapter 5, the optical properties of the Req_3 ternary complexes are studied in a thin film form. The introduction of the Bpy and Phen ligand into the Euq_3 complex will give an insight into the study of possible influence of extended electronic delocalization on the photophysical properties. The significant differences in the optical analysis upon adduction of the neutral ligand to the same Req_3 metal as well as upon complexing different Req_3 metal to the same ligand are also highlighted. The films were characterized by using molecular spectroscopy of UV- Vis absorption and photoluminescence measurement. Both measurements are important in order to determine the mechanism of the photosensitization process between the rare earth metal and the ligand. The electronic structure of the molecular hybrid films were obtained

from the absorption spectra. The absorption measurement will provide a basic event which translates the electron density as the electron promoted from the ground state to the excited state. Other than that, the optical band gap and the transition (either direct or indirect) were also evaluated from the optical absorption spectra by applying the Tauc relations. The emission studied will provide the luminescence characteristics of the Req_3 ternary complexes which is the consequence of energy transfer process from the ligand to the metal.

In Chapter 6, the electrical properties related to the Req_3 ternary complexes are evaluated. Particularly, the investigation is focused on the electrical properties related to the current and voltage curves (I-V curves) of ITO/ Req_3 /Al. On the basis of its luminescence characteristics, Req_3 ternary complexes has been apply as the active material in organic light emitting device (OLED). For this purpose, indium tin oxide (ITO) is used as the transparent electrode. The luminosity is measured using Konica Minolta CS-200 chromameter which can measure as low as 0.01 cd/m^2 while programmable Keithley 2400 SMU (source measurement unit) is used to source the supply voltage and measure the resulting current of the device. The dominance of the transports mechanism is evaluated by power law conduction model and Richardson-Schottky thermionic emission model. Further analysis of the I-V characteristics, by utilizing the Shockley diode equation is applied to extract the electronic parameters of ITO/ Euq_3 ternary complexes/Al devices. Two different methods which are conventional In I-V and Cheung's functions are utilized in order to determine the electronic parameters of the diode such as the ideality factor, n , effective barrier height, Φ_b and saturation current, I_0 .

Chapter 7 outlines a number of important conclusions and future works that can be drawn from this research. Summary of the research methodology that has been carried out in this work is shown in Figure 1.1.

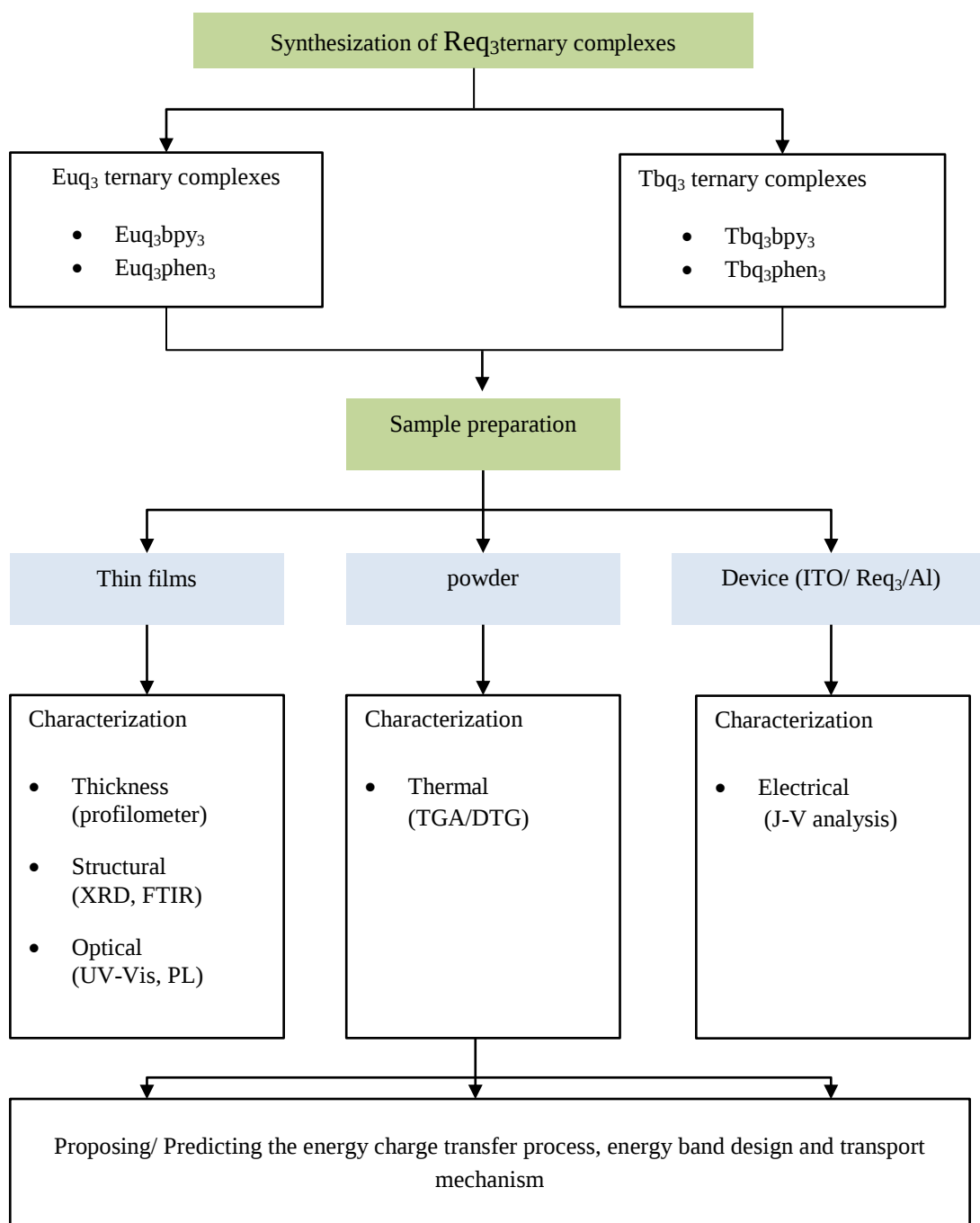


Figure 1.1 Research methodology design

Chapter 2. Theoretical background

2.1. Introduction

This chapter provides an overview of several topics. Initially, the fundamental of the organic semiconductor is explained. The basic concept of absorption and optical band gap of organic semiconductor is then described before describing the luminescence of organic molecules and the basic principles of the organic light emitting devices (OLED). The review on the carrier injection and transport in OLED is then discussed in detail. The general principle of the charge injection mechanism that involves Schottky thermionic injection and Fowler-Nordheim (FN) tunneling injection is described. Charge transport mechanism (transport limitation in the bulk) that present Ohmic transport regime, space charge limited current regime, trap charge limited current regime, trap filled space charge limited current regime and Poole-Frenkel (PF) emission are also explained. Finally, the properties of the rare-earth metal complexes are then reviewed. In this part the basics of Eu^{3+} luminescence, Tb^{3+} luminescence, energy transfer mechanism (sensitization) and ligand are discussed.

2.2. Organic semiconductor

An organic semiconductor is an organic material with the semiconducting behavior. The semiconductor behavior of organic materials is usually characterized from the presence of alternating single σ and double π carbon-carbon bond known as conjugated molecule. Basically, the existence of the single σ and double π carbon-carbon bond is originated from sp^2 hybridization as shown in Figure 2.1(a). A new molecular orbital, namely π -orbital is formed as a result of the interaction of the π -bonds in the molecule with each other. The π -electrons do not participate in any bonds and are delocalized over all the carbon atoms. These π -orbital may extend over the whole molecule as illustrated in

Figure 2.1(b) where the delocalized π -system of benzene molecule is shown. In the π -orbital, the highest occupied molecular orbital (HOMO) with lower energy corresponds to the π -bonding while the lowest unoccupied molecular orbital (LUMO) which is at the higher energy is related to the π^* -bonding. Normally, the intermolecular electron exchange will occur within HOMO or LUMO due to the π -orbital overlapping of neighboring molecules. However, the intermolecular interaction is very weak due the Van der Waals bonds that composed the molecules. As the result of the weak interactions, an extremely narrow band is obtained. Such narrow band limits the intermolecular charge transfer. Therefore the carrier mobility in organic semiconductor material is very low leading to the consideration for charge transport such as hopping and tunneling.

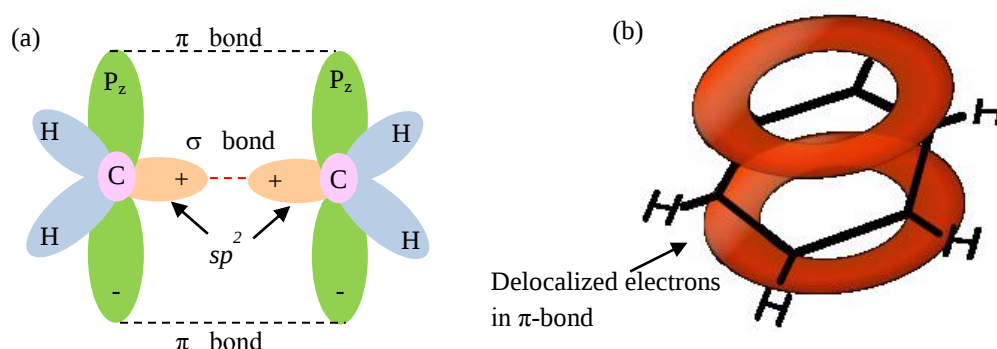


Figure 2.1 Schemes of (a) a double bond of two sp^2 -hybridised carbon atoms, which consists of σ and π bond, and (b) a delocalized π system of a benzene molecule.

There are three major classes of organic semiconductor materials which are small molecules, short chain (oligomers) and polymers. Example of semiconducting small molecules includes pentacene, anthracene, rubrene and aluminum tris(8-hydroxyquinoline) Alq_3 , while example for semiconducting polymers are poly(3-hexylthiophene) P3HT, poly(p-phenylene vinylene) PPV as well as polyacetylene (Figure 2.2).

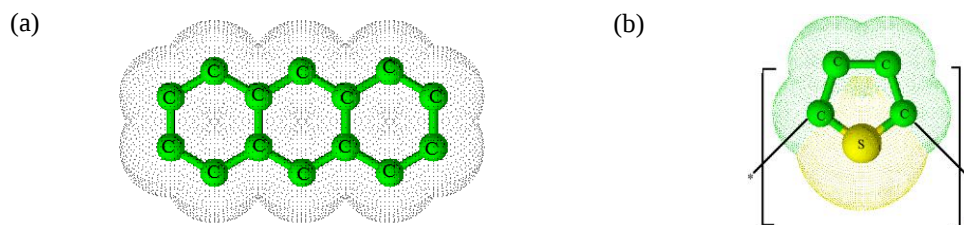


Figure 2.2 Molecular structure of (a) anthracene (small molecule) and (b) the monomer repeat unit of substituted polythiophene (polymer)

In particular, the organic semiconductor materials are lighter in weight and tunable in structural optical and electrical properties compare to that of inorganic semiconductor (Dong, Zhu, Meng, Gong, & Hu, 2012). Therefore the variety of the chemical and physical properties such as thermal stability, luminescence and charge carrier transport is expected to depend on their molecular structure as it can be modified (Cicoira & Santato, 2007). Moreover, the high flexibility in the organic synthesis allows the possibility to combine several interesting properties such as ease of processing on a wide range of substrates, photoluminescence, electroluminescence and excellent charge carrier transport. These properties make the organic semiconductors ideal for variety of applications, for instance organic photovoltaic cells (OPVCs), organic field effect transistors (OFETs) and organic light emitting diodes (OLEDs) (Malliaras & Friend, 2005).

2.3. Absorption and optical band gap in organic semiconductor

The detailed study of the interaction of light with molecules can provide useful information about the molecule's structure, energetics and electronic configuration. When sample molecules are exposed to the light, some of the light energy will be absorbed and cause the electron from the highest occupied molecular orbital (HOMO) to move to the lowest unoccupied molecular orbital (LUMO). The process of moving electrons from HOMO to LUMO is known as electronic excitation. There are three types

of electrons involved in the transition. The electron in single bond is known as σ -bond whereas the electrons in double and triple bonding are known as π -bond. It is worth to note that the electrons in this bond can be excited easily. One of the examples of compounds with π -bond is aromatic compound. The third type of electron is known as n-electrons. It does not involve in bonding between atoms. Generally, the excitation of an electron in HOMO to LUMO is usually involved in promoting electrons from bonding to anti-bonding orbitals such as π - π^* and σ - σ^* transitions.

Basically, the optical band gap of an organic semiconductor is defined as the energy difference between the HOMO and LUMO state. The HOMO state of organic semiconductor is known as valence band in inorganic semiconductor whereas the LUMO state is referred as the conduction band in inorganic semiconductor devices. In organic semiconductor, the conduction mechanism may arise from the presence of hole and electrons conduction layer separated by the band gap. Therefore, the determination of the optical band gap of the organic semiconductor is considerably importance in order to provide foundations in the understanding of the optical as well as the electrical process occurring within the organic materials. Due to that reason, the optical band gap has become one of the most important parameter in the organic semiconductor physics. There are many established methods has been discovered to calculate the band gap. One of the methods is the Tauc model in which is derived from the absorption coefficient, α which is associated with the optical absorption of amorphous semiconductor materials (Ferlauto et al., 2002). Assuming that the absorption edge has a parabolic variation with photon energy, the absorption coefficient, α can be derived by the relation (Dridi et al., 2009):

$$\alpha h\nu = \alpha_o(h\nu - E_g)^n \quad (2.1)$$

where α_0 is the energy independent constant, E_g and n is the exponential value that will determine the type of the absorption transition either is direct ($n=1/2$) or indirect ($n=1$). The value of n can be obtained mathematically from the logarithm and derivation of equation (2.1) given by (Muhammad, Abdul Hapip, & Sulaiman, 2010):

$$\frac{d\ln(\alpha h\nu)}{dh\nu} = \frac{n}{h\nu - E_g} \quad (2.2)$$

Referring to Equation (2.2), a plot of $d\ln(\alpha h\nu)/dh\nu$ vs. $h\nu$ for both compound gives a maximum when $h\nu = E_g$. It can be clearly deduced that the maximum point of the graph yields the approximation values of E_g . These initial values are the estimated value used to plot a graph of $\ln(\alpha h\nu)$ vs $\ln(h\nu - E_g)$ in relation from equation (2.1) to obtain the value of n (Muhammad, et al., 2010). By applying equation (2.1), the optical band gap of both compounds is evaluated from a plot of $(\alpha h\nu)^{1/n}$ against $h\nu$. From the plot, the band gap can be extrapolated by fitting a straight line to $h\nu = 0$. Since a specific model for organic semiconductor has not yet been developed, it is reasonable to calculate the optical band gap using this model as qualitative indicator. Many researchers have also applied this method to calculate the optical band gap of organic semiconductor.

2.4. Luminescence of organic semiconductor

Luminescence is defined as the generation or emission of light by a molecule or an atom. It arises when an electron in atoms or molecules excited from the ground state, S_0 to the higher excited state, S_1 and then decays to the lower energy of the S_0 state. Fluorescence, phosphorescence, photoluminescence and electroluminescence are four fundamental processes that constitute luminescence of organic molecules. Basically photoluminescence is a process where photons are absorbed and emitted by molecules while electroluminescence defines a process where an applied electric field generates an

excited species which upon relaxation emits photons. The concept of the fluorescence and phosphorescence process of organic molecules is illustrated from the Jablonski diagram (Mikhnenko, 2012) as shown in Figure 2.3. In order to understand the concepts of fluorescence and phosphorescence, a brief explanation on the electronic state of organic molecules is essential.

The electronic state of organic molecules can be distinguished based on two broad categories which are singlet state, S_1 and triplet state, T_1 . In S_1 state, the two electrons have their spins paired while in a T_1 state, the set of their electrons spins are unpaired (Figure 2.4). When a molecule absorbs a photon of sufficient energy, one of its valence electrons (HOMO) from vibrational level of the ground state, S_0 will be promoted to a higher excited state, S_1 (LUMO). Electrons present at the S_1 will either undergo one of the three possible processes which are internal or external conversion to ground state, S_0 , emission of a photon to give fluorescence or intersystem crossing.

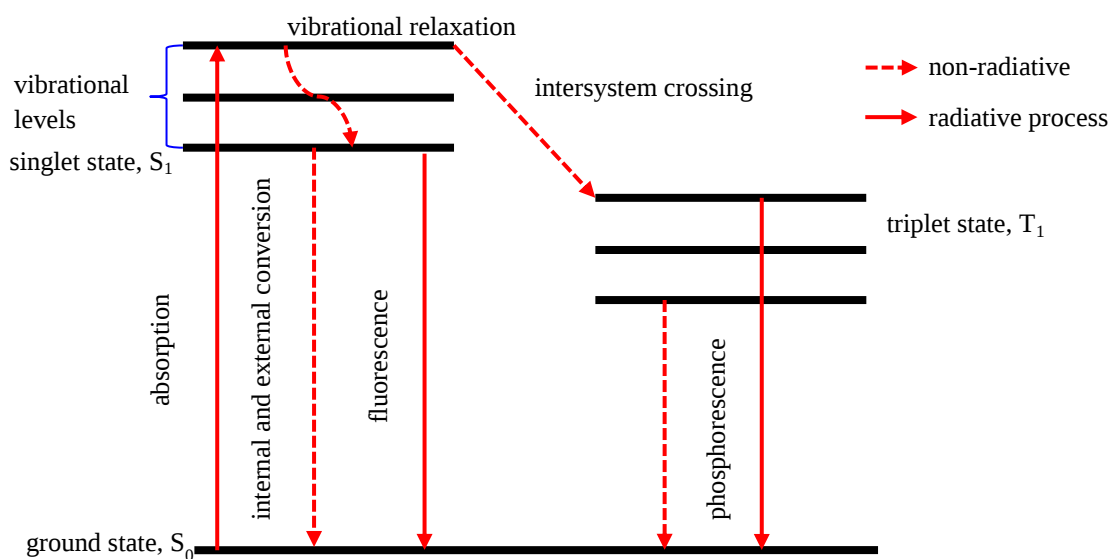


Figure 2.3 Jablonski diagram illustrated absorption, internal and external conversion, fluorescence, intersystem crossing and phosphorescence process.

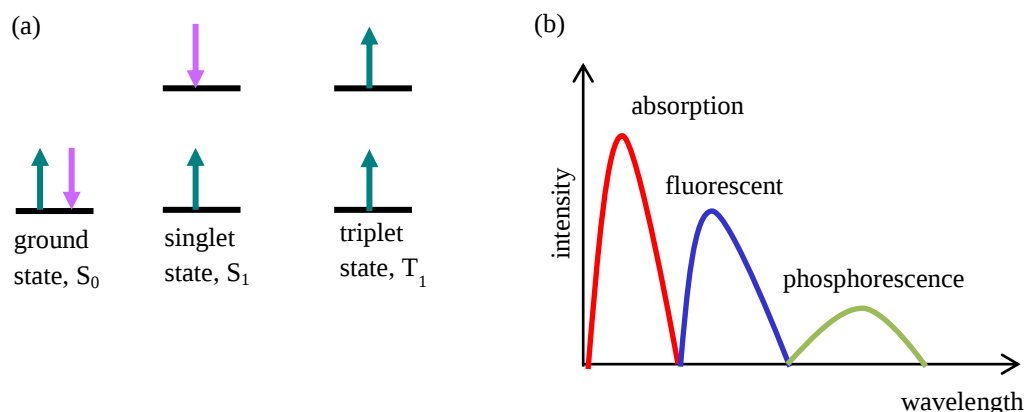


Figure 2.4 Schematic diagram showing (a) spin pair and unpaired in S_1 and T_1 respectively and (b) absorption, fluorescence and phosphorescence spectra.

Internal conversion is a non-radiative process where excited molecules lose their energy and decay to the ground state, S_0 without emitting a photon. One of the possible reasons that might contribute to this process is that all the excitation energy is converted to heat (Köhler, Wilson, & Friend, 2002). The other possible reasons maybe arise due the collisions of the excited molecules with other molecules which will cause the excited molecules to lose their energy and return back to the ground state, S_0 . The excited energy might also be lost as it can be transferred to the solvent or other unexcited molecules (Köhler, et al., 2002; Schulman, 1985). Fluorescence is a radiative process where the excited electrons lose their energy to the ground state as a photon (Schulman, 1985). Principally the lifetime of the fluorescence process which is in the range from 10^{-7} to 10^{-9} s is much greater than the absorption time. The probability of the fluorescence process will be decreased as the lifetime in the excited state is increased and cause non-radiative processes to take place (Schulman, 1985). However, not all excited molecules that lose their energy to the ground state, S_0 exhibit fluorescence. Most of the energy is usually dissipated as heat. In other cases, the excitation energy might be lose upon colliding with other molecules or solvent as have been described previously (Schulman, 1985).

The intersystem crossing is also a non-radiative process that is related to the energy transfer of the electrons from S_1 state to a T_1 state (Schulman, 1985). An excited electron in T_1 state can lose their excess energy through several processes. The possible process includes transition to the singlet state, S_1 , relaxation to the ground state, S_0 by internal (heat) or/and external conversion (quenching) and emitted the energy as a photon known as phosphorescence (Schulman, 1985). The average lifetime of the phosphorescence process is much longer compare to that of fluorescence (10^{-4} s to up to few s (Schulman, 1985). Due to this reason, the possibility of having non-radiative process is very high as the fact that probability of the phosphorescence to occur is low. Therefore, it can be observed that the intensity of the phosphorescence spectrum is decreased compare to the fluorescent and absorption spectrum (Figure 2.4) (Schulman, 1985).

Based on the luminescence process, an organic luminescence material can be divided into two main categories which are fluorescence and phosphorescence material. Fluorescent and phosphorescent materials continue to attract commercial and scientific interest since they can be used to fabricate OLED (Köhler, et al., 2002). In recent years, the ability to understand, control and tailor luminescent materials have improved dramatically (Köhler, et al., 2002). The highly efficient OLED based on fluorescence and phosphorescence material that can now be produced (Adachi, Baldo, Thompson, & Forrest, 2001; Baldo et al., 1998; Baldo, Thompson, & Forrest, 2000; Segal et al., 2007) are now becoming an attractive alternative to those based on conventional inorganic material (Friend et al., 1999). Basically, there are two categories of fluorescent materials which are small molecules and polymer fluorescent materials. Various fluorescent small molecules materials such as Alq₃, rubrene, coumarine and some metal chelates (zinc, beryllium, copper and barium chelates) have been widely used as

an emitter in OLED (Junhong, 2009; Shinar & Shinar, 2008). On the other hand, fluorescent polymer materials have also been investigated for their role in OLED. Polymers such as poly (phenylenevinylene) (PPV), polythiophene (PT), poly (*para*-phenylene) (PPP) and polyfluorene (PF) and derivatives have been intensively studied and green, blue, and red emissions have been achieved (Guha et al., 2003; Junhong, 2009). The molecular structure of the small molecules and polymer fluorescent materials are shown in Figure 2.5. It should be noted that the alteration and modification of the chemical structure of fluorescent materials have a crucial effect on the materials properties. Therefore, fluorescent materials offer the possibility of tuning their properties towards particular needs.

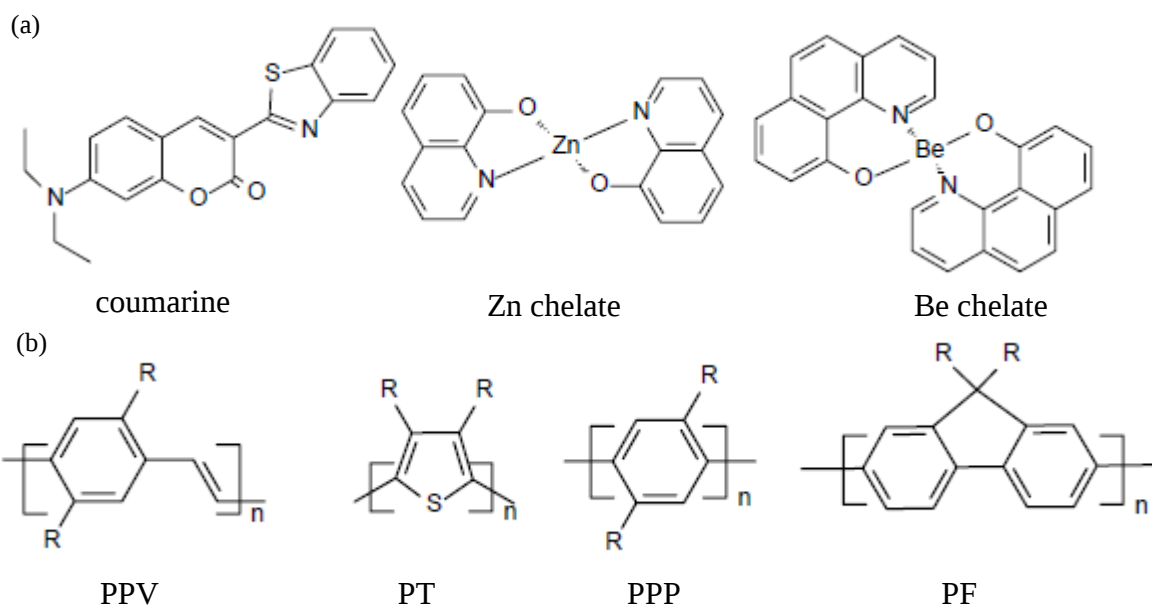


Figure 2.5 Molecular structure of (a) small molecules and (b) polymer fluorescent materials (JUNHONG, 2009)

Different from fluorescent materials, phosphorescence materials can generate emission from both singlet and triplet excitons. In the last decade, tremendous scientific effort devoted to the phosphorescence materials in OLED has been impressive (Binnemans, 2005; Chou & Chi, 2006; Kappaun, Slugovc, & List, 2008; Kavitha et al., 2005). The

interest in the phosphorescence material is especially caused by the higher external quantum efficiency (EQE) exhibits by this material is exceeding the EQE for fluorescent materials (Seo et al., 2008)

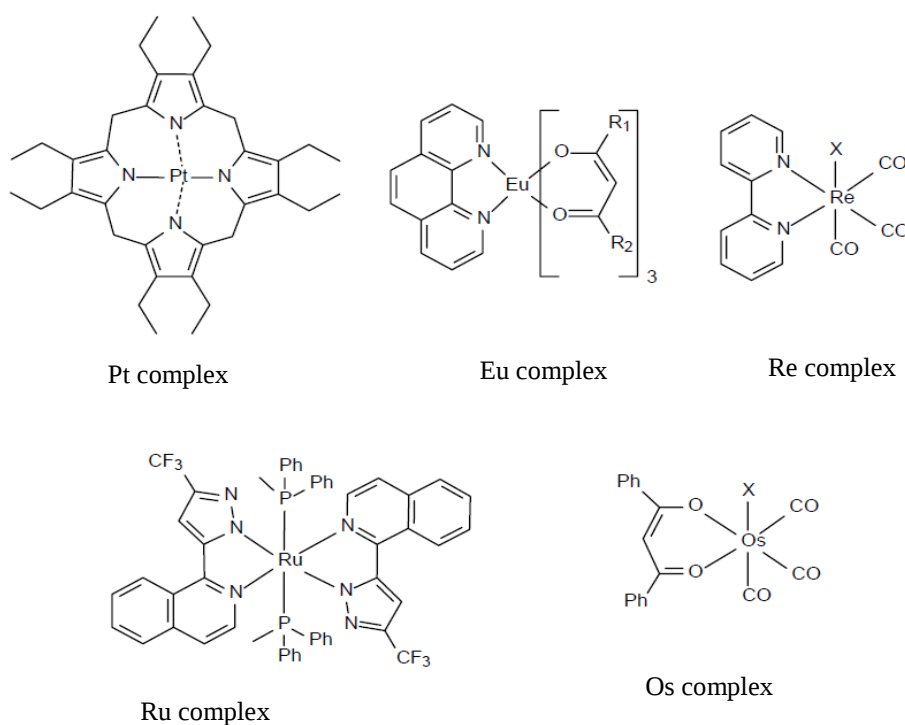


Figure 2.6 Molecular structures of transition heavy metal complexes that have been widely used as emitter in OLED (JUNHONG, 2009).

Many transition heavy metal such as Platinum (Pt), Ruthenium (Ru), Iridium (Ir), Rhenium (Re) and Osmium (Os) complexes and rare-earth metal complexes, for instance europium (Eu) and terbium (Tb) with appropriate ligands have recognized to exhibit highly efficient phosphorescence at room temperature (Binnemans, 2005; Chou & Chi, 2006; Kappaun, et al., 2008; Kavitha, et al., 2005) . Their luminescent properties result from the metal to ligand charge transfer (MLCT). MLCT is referred as a metal-to-ligand transfer in which arises from transition of an electron located in a metal-based d-orbital to the ligands. In contrast to the metal complexes discussed above, the optical emission from the rare earth metals is based on the ligand to metal charge transfer

(LMCT). The molecular structures of some of the phosphorescent material are shown in Figure 2.6.

2.5. Organic light emitting devices (OLED)

A typical OLED structure consists of thin organic layer sandwiched between the transparent anode and a metallic cathode as shown in Figure 2.7 (a). The light generating mechanism of OLED can be explained as follow. When a forward bias is applied between the cathode and the anode, electrons and holes are injected from the cathode and the anode into the LUMO and HOMO respectively in the organic layer. Once electrons and holes have been injected, they drift in the presence of the externally applied electric field by means of so called “charge hopping mechanism” through the organic material. The chargers meet within the organic layer and recombine to form a neutral “exciton” and depending upon the nature of the emission material and according to the appropriate selection rules, a bound excited state that is decayed by emitting singlet fluorescence or triplet phosphorescence (Kondakova et al., 2010).

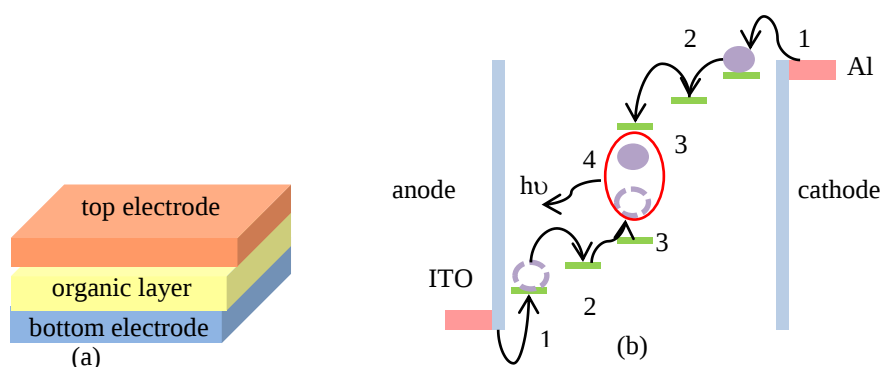


Figure 2.7 (a) Schematic of the structure of an OLED, (b) mechanism in OLED (1) Charge injection (2) Charge transport (3) Exciton formation (4) Light emission.

Schematic of the basic operation of OLED is shown in Figure 2.7 (b) and the step by step mechanism of generation of light in a typical OLED structure is shown in Figure 2.8.

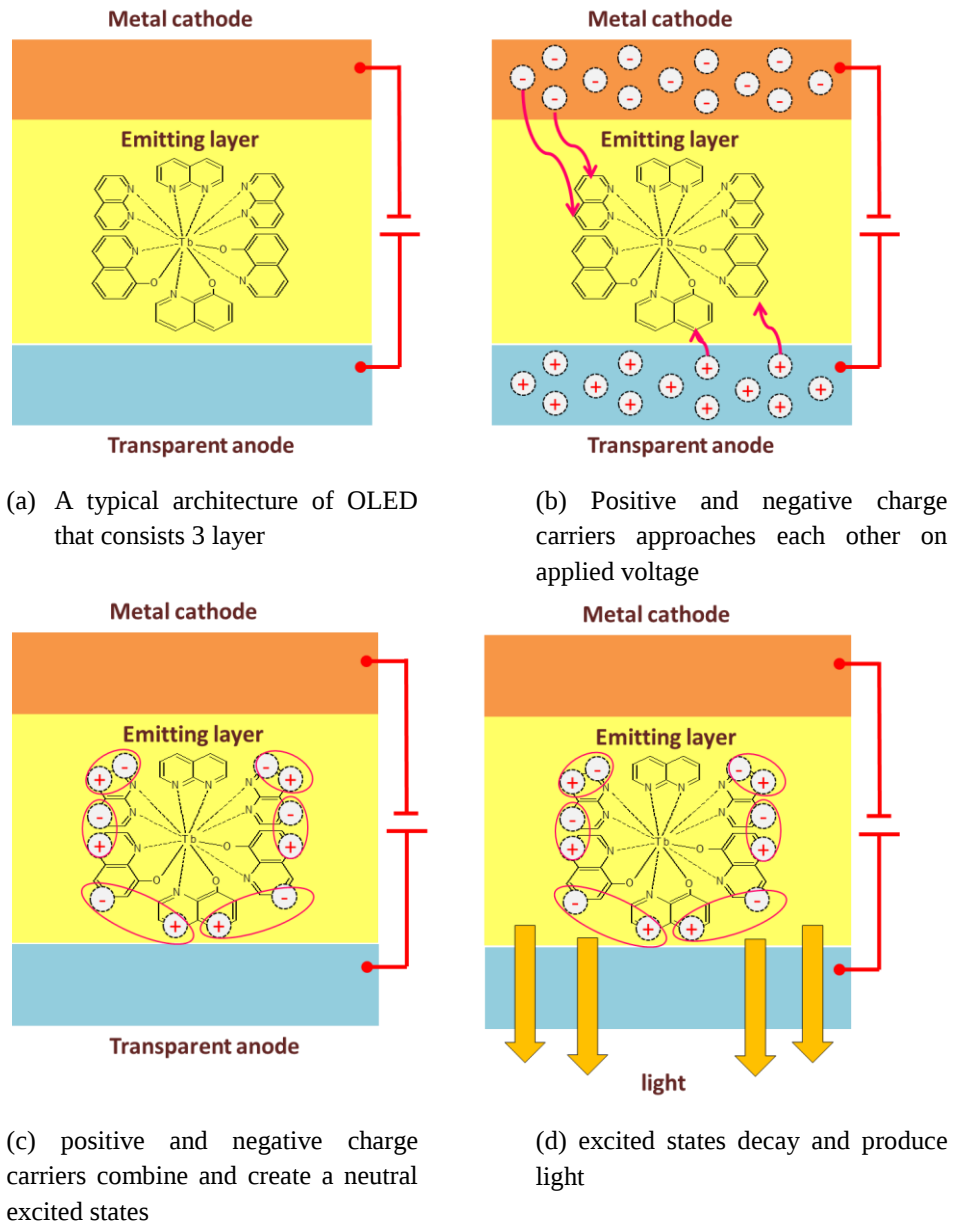


Figure 2.8 Step by step mechanism of generation of light in a typical OLED structure.

2.6. Operating principle in OLED

According to (Y. Kim & Ha, 2008), a six step mechanisms is considered for the organic semiconductor during the actual device operation. These six steps mechanism is summarized by the following process and is illustrated in Figure 2.9.

i. Before connecting the electrodes of the device

At this step, the organic semiconductor layer exhibits their energy state with respect to the vacuum level. The energy band remain flat in which the build in voltage, V_B can be theoretically estimated.

ii. Upon connecting the electrodes with no external voltage applied (short circuit condition)

During this step, the work function of the anode and cathode demonstrate the same energy level which cause the Fermi level to be aligned and thereby causes the energy band of the organic semiconductor to bend. As a result of this band bending, the charge carriers will flow to the corresponding electrodes and generate dark current internally without external injection as illustrated in Figure 2.9 (b) where $b1$ and $b2$ denote dark current flows of electrons and holes. Figure 2.9 (c) described the energy band before the current flow. At this time

iii. The build in voltage is equal to the applied voltage.

Figure 2.9 (c) described the energy band before the current flow. At this time the built in voltage is equal to the applied voltage.

iv. The external voltage is slightly higher than the build in voltage but lower than turn on voltage

At this step, the charge injection from the electrodes is permitted. However, the applied voltage is insufficient to produce enough charge transport in an organic semiconductor layer to ensure hole-electron recombination. Therefore, no light emission was observed. In this case, the charge injection from the electrodes to the organic semiconductor layer is governed by Schottky thermionic emission. The schematic energy band diagram during this step is illustrated in Figure 2.9 (d) where $d1$ and $d2$ is refer to as holes and electrons injection, while $d3$ and $d4$ represent the dark current flows of holes and electrons which are generated internally without external injection.

v. Applied voltage higher than turn on voltage

When the applied voltage is higher than the turn on voltage, the injected holes and electrons is sufficiently enough to be transported towards the organic semiconductor layer and recombine to produce light. At this point, the charge injection could occur via Schottky thermionic emission and Fowler-Nordheim tunneling. The schematic energy band diagram during this step is illustrated in Figure 2.9 (e) where $e1$ and $e2$ represent holes and electrons injection by Schottky thermionic emission, $e3$ and $e4$ represent holes and electrons injection by Fowler-Nordheim tunneling as well as $e5$ and $e6$ which represent holes and electrons transport. It should be noted that the dark current flow is omitted because of its relatively low magnitude when compared with the externally injected current.

vi. Higher applied voltage

Further biasing the device with much higher voltage will result in high luminance. However, a considerably higher leakage current is also expected due to ballistic charge transport through the organic semiconductor layer. The schematic energy band diagram at this point is illustrated in Figure 2.9 (f) where $f1$ and $f2$ represent holes and electrons injection by Schottky thermionic emission, $f3$ and $f4$ represent holes and electrons injection by Fowler-Nordheim tunneling, $f5$ and $f6$ represent holes and electrons transport and $f7$ and $f8$ represent the holes and electrons leakage current.

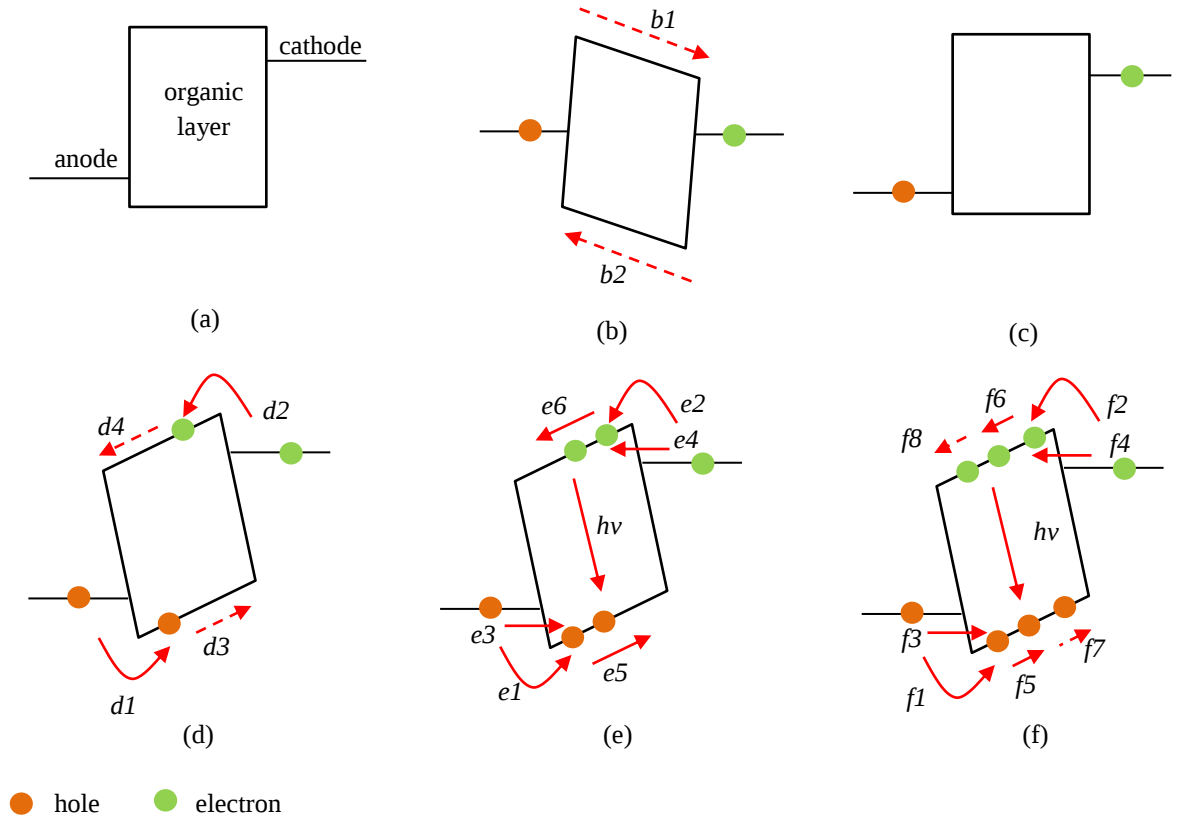


Figure 2.9 Schematic energy band diagrams for charge carrier injection, transport, recombination and leakage as a function of applied voltage (Y. Kim & Ha, 2008).

Basically, there are two important features of an OLED which are the charge injection from the electrodes to the organic semiconductor layer and charge transport through the organic semiconductor layer. Both mechanisms can be distinguished theoretically by considering the injected limited and transport limited conditions. Injected limited is sometimes referred by researchers as injection limitation at the contacts while transport limited is referred as transport limitation in the bulk (Méndez Pinzón, 2006).

2.6.1. Charge injection mechanism (injection limitation at the contact)

Two representative theories namely Schottky thermionic injection and Fowler-Nordheim tunneling have been considered reasonable for describing charge injection from the electrode to the organic semiconductor layer.

i. Schottky thermionic injection

Schottky thermionic emission or sometimes known as Richardson-Schottky (RS) thermionic emission is usually more significant at high temperatures where the carriers have sufficient thermal energy to overcome the potential barrier. Therefore, the device operating temperature is importance in this thermionic emission. The Schottky thermionic injection is described by (Lim, Lee, Park, Park, & Yeom, 2008; Yang & Yang, 2008):

$$J = A^* T^2 \exp\left(-\frac{q\Phi}{kT}\right) \exp\left(\frac{qV}{kT}\right) \quad (2.3)$$

Where A^* ($A^* = 4\pi q m^* k^2/h^2$), T , q , k , Φ and V are the Richardson constant, the effective electron mass, Planck constant absolute temperature (in Kelvin), elementary charge, energy barrier height and applied voltage. The presence of the Schottky thermionic emission can be identified from the linear independence of $\ln J \sim V^{1/2}$ (Meškinis et al.).

ii. Fowler-Nordheim (FN) tunneling injection

As proposed by Parker, the FN tunneling injection mechanism is based upon tunneling injections of holes and electrons into the organic semiconducting layer through the triangular barrier created by bending due to the high electric field (Parker, 1994). Assuming that the injected charge tunnels through a triangular barrier at the interface (Lim, et al., 2008; Yang & Yang, 2008) the current characteristic J_{FN} can be predicted by using the FN model,:

$$J_{FN} = AF^2 \exp\left(-\frac{B}{F}\right) \quad (2.4)$$

where $A = q^3/8\pi\hbar\phi$ and $B = 8\pi(2m^*)^{1/2}\phi^{3/2}/3\hbar q$, here q is the electron charge, $\hbar$ is the constant, m^* is the effective mass of the carrier, F is the applied electric field, and ϕ is the barrier height at the electrode contacts. It is generally considered that the FN tunneling current is insensitive to temperature. Presence of the FN injection can be identified from the linear relationship of $\ln(J/V^2)$ as a function of $1/V$ (Meškinis, et al.).

2.6.2. Charge transport mechanism (transport limitation in the bulk)

A charge transport limitation condition involves the dependent of actual current upon the charge transport across the organic semiconductor layer (Y. Kim & Ha, 2008). The charge transport through the organic semiconductor layer can be divided into four different regime (Figure 2.10), by assuming that the trap energy, E_t within the organic semiconductor layer is distributed exponentially between the HOMO and LUMO (Y. Kim & Ha, 2008). According to the power law model, the four regimes is distinguished with distinctively different slope, m of the $\log J \sim \log V$ where for ohmic ($m=1$), space charge limited, SCLC ($m=2$) and trap-filled space charge limited

($m > 2$). The power law model is described by (Y. Kim, Keum, Lee, Lim, & Ha, 2000):

$$J \sim \frac{V^{m+1}}{d^{2m+1}}, m = \frac{E_t}{kT} \quad (2.5)$$

On the other hand the Poole-Frenkel emission is considered reasonable for describing charge transport mechanism in the bulk.

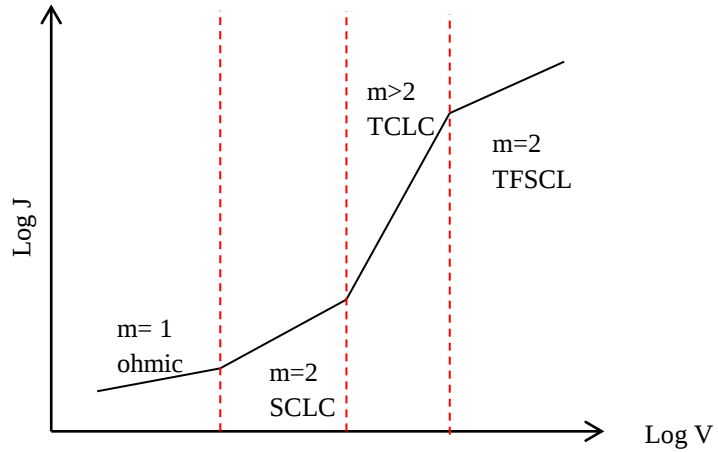


Figure 2.10 Schematic illustration of charge transport regimes consists of ohmic, SCLC, TCLC and TSFCL.

i. **Ohmic transport regime, $m=1$**

Under very low applied electric field, the charge transports are limited to the contact interface between the electrode and the organic semiconducting layer (Y. Kim & Ha, 2008). Therefore the currents typically exhibit ohmic behavior, given by:

$$J = ep\mu_h \frac{V}{d} \quad (2.6)$$

Where J is the current density, V is the dc applied voltage, p is the concentration of thermally activated holes in the valence bands, μ_h is the hole mobility and d is the thickness of the organic semiconductor layer. It is worth mentioning that the density of the electrons and holes injected into the organic semiconductor layer

is much smaller than the thermally generated electrons and holes in organic semiconductor layer (Y. Kim & Ha, 2008).

ii. **Space charge limited current regime, $m=2$ (SCLC)**

Due to the poor charge carrier mobility of the organic semiconductor, a space charge is formed at the interface between the electrode and the organic semiconductor right after the initial current flows (Y. Kim & Ha, 2008). As the applied voltage increase further, more charges has been injected than the thermally generated so that the current flow is affected by space charges either at the interface or within the organic semiconductor layer during charge transport (Y. Kim & Ha, 2008). Assuming almost no influence of traps in organic semiconductor layer at the low level of injected current, the SCLC current can be modeled using the Child's law (Mott-Gurney law) (Y. Kim & Ha, 2008). Therefore the current typically exhibits SCLC behavior given by (Matsushima & Murata, 2009):

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_0 \exp[0.89\beta \left(\frac{V}{L}\right)^{0.5}] \left(\frac{V^2}{L^3}\right) \quad (2.7)$$

Where ε_r is relative permittivity, ε_0 is vacuum permittivity, μ_0 is zero field mobility, β is field dependence parameter, V is the applied voltage and L is thickness (Matsushima & Murata, 2009).

iii. **Trap charge limited current regime, $m>2$ (TCLC)**

Upon injecting relatively large numbers of charge carriers under a high electric field, the space-charge effect is negligible and the abundant charge carriers begin to fill up the traps within the organic semiconductor layers (Y. Kim & Ha, 2008). This trap-filling process needs a large current, due to the higher trap-

energy as compared with the thermal energy ($E_t > kT$); depending upon the nature of the traps, which is indeed an intrinsic property of organic semiconductor as well as the impurities therein (Y. Kim & Ha, 2008). This is classified as being a trap-charge limited (TCL) regime.

iv. **Trap filled space charge limited current regime, $m=2$ (TFSCLC)**

Once the injected charges fill up all of the trap-site at a very high applied voltage, additional injected charge carriers are free to move, without any influence of charge-trapping, in the presence of space-charge effects alone (Y. Kim & Ha, 2008). This regime is called trap-filled SCLC (TFSCLC) and the same mathematical expression is used as that given by Equation 2.7 for SCLC. However, it is experimentally difficult to obtain the correct physical information on this TFSCLC regime since the most actual OLED undergo a breakdown process due to the high electric field as well as the high current, so that the features of TFSCLC are significantly deformed with device degradation (Y. Kim & Ha, 2008).

v. **Poole-Frenkel (PF) emission**

PF emission is related to the trapping of the charge carrier by local traps related with bulk defects and subsequent release of the trapped charge carriers from these potential well. The current-voltage relationship for Poole-Frenkel mechanism is expressed as:

$$J = J_0 \exp\left(\frac{-\phi}{kT} + \beta_{PF} E^{\frac{1}{2}}\right) \quad (2.8)$$

Where,

$$\beta_{PF} = -\frac{E}{kT} \left(\frac{e}{4\pi\epsilon\epsilon_0 d}\right)^{1/2} \quad (2.9)$$

The PF emission can be identified by known dependence of the relation $\ln (J/E) \sim E^{1/2}$ (Deshmukh et al., 2007; Meškinis, et al.) within the organic semiconductor layer.

2.7. Rare-earth metal complexes

The rare earth metal is a group of chemical element in the periodic table that exhibit a similar chemical properties due to their common open 4f shell (Sariciftci, Koppe, & Neugebauer). The valence shell configuration of the rare earth atomic structure is expressed as 4f, 5d and 6s electrons (Sariciftci, et al.). The outer electrons ($5s^2$, $5p^6$, $6s^2$) in the rare earth elements shield effectively the 4f shell (Sariciftci, et al.) which consequently give rise to the sharp emission band which is usually less than 10 nm (Hartmut, 2007) . Normally, the trivalent rare-earth metals, Re^{3+} can be divided into two groups according to their emission properties. The first group of rare-earth metals exhibits a strong emission in the near infrared region upon irradiation of ultraviolet (UV) radiation. Their excellent emission in the near infrared region is due to the fact that the energy gap between the lowest excited state and the highest excited state is very close to each other. The rare-earth metals that belong to such group are praseodymium (Pr^{3+}), neodymium (Nd^{3+}), holmium (Ho^{3+}), erbium (Er^{3+}), thulium and ytterbium (Yb^{3+}). The second group of rare-earth metals exhibits a strong emission in the visible region and the probability of these transition are relatively high compare to the first group. Samarium (Sm^{3+}), europium (Eu^{3+}), terbium (Tb^{3+}) and dysprosium (Dy^{3+}) are the rare-earth elements that belong to the second group.

Eu^{3+} and Tb^{3+} are the well-known rare earth metals that are generally used in the OLED fabrication as the emitting layer. They are usually coordinated with the organic ligand. In coordination chemistry, a ligand is an ion or molecule that binds to a central metal

atom to form a coordination complex. Therefore, coordination between the rare earth metals with the organic ligand is known as rare earth metal complex.

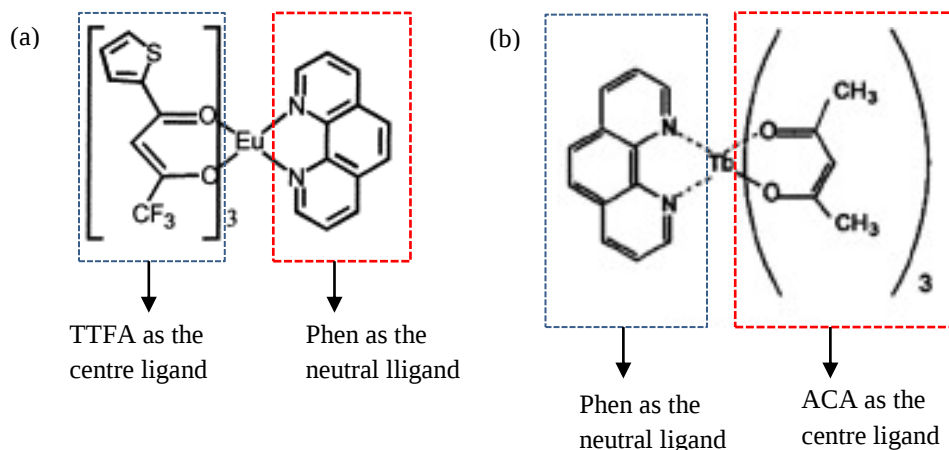


Figure 2.11 Molecular structures of (a) $\text{Eu}(\text{TTFA})_3\text{phen}$ and (b) $\text{Tb}(\text{ACA})_3\text{phen}$ (He et al., 2008; Male, Salata, & Christou, 2002)

Basically two organic ligand known as central and neutral ligand will coordinate to the rare earth metal to form the rare earth metal complex. The central ligand will responsible for the energy absorption and transfers to the excited levels (Santos et al., 2008) whereas the role of the neutral ligand (sometimes known as secondary ligand) is not only to saturate the coordination number of the rare-earth metal ion, Re^{3+} but also to improve the volatility and stability of the europium complex (Guan, Chen, Sun, Liang, & Zhang, 2005; Santos, et al., 2008). The rare earth metal complex with these two organic ligands is also known as rare earth ternary complexes in which the ternary term is refer to the three different molecules that are bound together. The example of various rare earth ternary complexes that has been synthesized and applied as the emitting material by researchers is shown in Figure 2.11. It should be noted that the selection of the centre and neutral ligand is depends on the triplet and singlet energy level of each

ligand. The luminescence properties of Eu^{3+} and Tb^{3+} are described in the following section.

2.7.1. Eu^{3+} luminescence

Of the rare-earth complexes reported, europium complexes appear to be the most studied due to the ability to emit strong red light that are widely exploited in OLED (Li et al., 2010; Liu et al., 2011; Xin et al., 2007). Several europium complexes have been employed as red emitters in electroluminescent devices (Bian & Huang, 2010; De Silva, Li, Huang, & Zheng, 2008; Kusrini et al., 2012; Zhang, Hou, Du, & Wu, 2009).

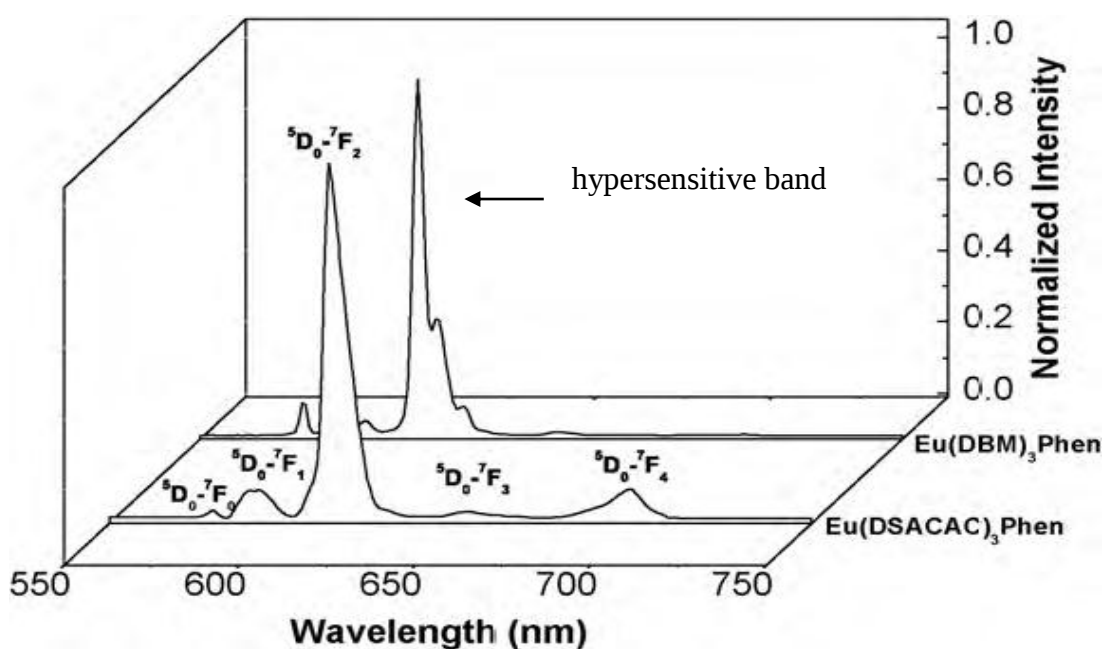


Figure 2.12 Typical emission spectrum of europium complexes (Liang & Xie, 2010)

Due to the unique mechanism of excitation, europium complexes used in electroluminescent devices emit red light at the same frequency, although the ligands on the europium center are different to each other (Duan, Sun, & Cheng, 2005). The photoluminescence spectra of europium complexes displayed the characteristic of

narrow bands from $^5D_0 \rightarrow ^7F_j$ transitions (Figure 2.12) and exhibited a pure red color emission. The induced electric dipole transitions have an additional selection rule if the initial level has $J = 0$, as is the case for Eu^{3+} (5D_0): transitions to odd J are forbidden (Klink, 2000). This generally results in the following emission spectrum (Klink, 2000):

- i. $^5D_0 \rightarrow ^7F_0$ (580 nm): extremely weak, induced electric dipole ($J = 0$ to $J = 0$ is forbidden).
- ii. $^5D_0 \rightarrow ^7F_1$ (590 nm): magnetic dipole emission.
- iii. $^5D_0 \rightarrow ^7F_2$ (613 nm): hypersensitive induced electric dipole emission, which is usually dominating.
- iv. $^5D_0 \rightarrow ^7F_3$ (650 nm): extremely weak, induced electric dipole emission.
- v. $^5D_0 \rightarrow ^7F_4$ (~700 nm): weak, induced electric dipole emission.

2.7.2. Tb^{3+} luminescence

Various terbium complexes also have been employed as green emitters in electroluminescent devices (Bechtold et al., 2011; Chen et al., 2009; Katkova et al., 2009; Lepnev et al., 2009). Compared to the europium complexes, terbium complexes reported for OLED are not as enormous as the development of europium complexes in OLED. However, they opened an area for green emission material from rare-earth metal complexes. The photoluminescence spectra of terbium complexes displayed the characteristic of narrow bands from $^5D_4 \rightarrow ^7F_j$ transitions (Figure 2.13) and exhibited a pure green color emission. The luminescence of Tb^{3+} complexes is characterized by emission from the 5D_4 state resulting in green luminescence. Its peaks at 491, 549, 582 and 618 nm correspond to the f-f electronic transition of $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3$ (Figure 2.13) (Zheng et al.). Among them, the $^5D_4 \rightarrow ^7F_5$ emission band at

545 nm is hypersensitive, but is not as sensitive to the changes in the environment as the $^5D_0 \rightarrow ^7F_2$ emission of Eu^{3+} .

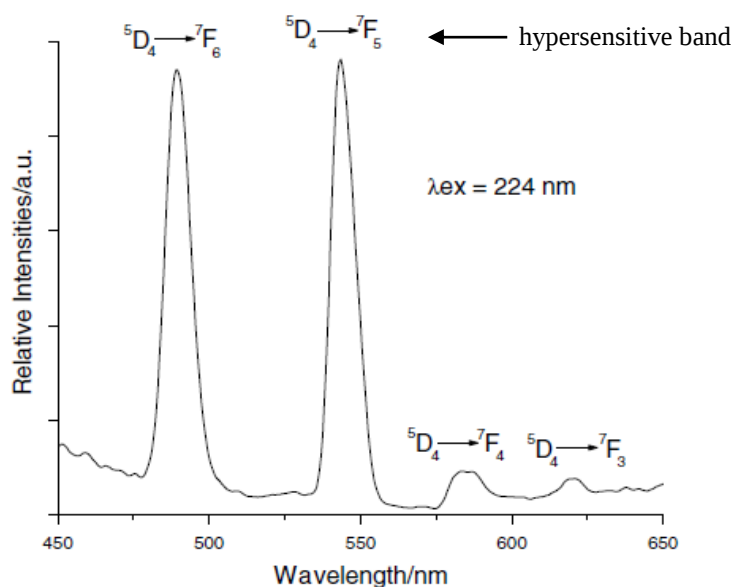


Figure 2.13 Typical emission spectrum of terbium complexes (Yan & Wang, 2007)

2.7.3. Energy transfer mechanism (sensitization)

Generally, all the rare-earth metals show very weak absorption from the UV region due to the smaller molar absorption coefficient, ϵ which is usually less than 10 Lmol^{-1} (Binnemans, 2009). Therefore, a very limited amount of radiation is absorbed by the rare-earth metals (Binnemans, 2009). This may be overcome by the sensitization process (Binnemans, 2009). According to Weismann, an intense metal centered luminescence characteristics can be observed by coordinating a high absorbing organic ligand with the rare-earth metal complexes coordination sphere (H. J. Kim, Lee, Kim, & Park, 2003). In coordination chemistry, a ligand is an ion or molecule that binds to a central metal atom to form a coordination complex. In this case, organic ligand will take the responsibility of absorbing the light and they are known as sensitizers. The role of the sensitizers is to excite the rare earth metal ion, Re^{3+} via an energy transfer from the

sensitizer to the rare-earth ion. This process is sometimes referred as the “antenna effect”. The commonly accepted energy transfer mechanism (sensitization process) from the organic ligand to the rare-earth metal ions which is proposed by Crosby and Whan (Gunnlaugsson, Harte, Leonard, & Nieuwenhuyzen, 2003) is schematically depicted in Figure 2.14.

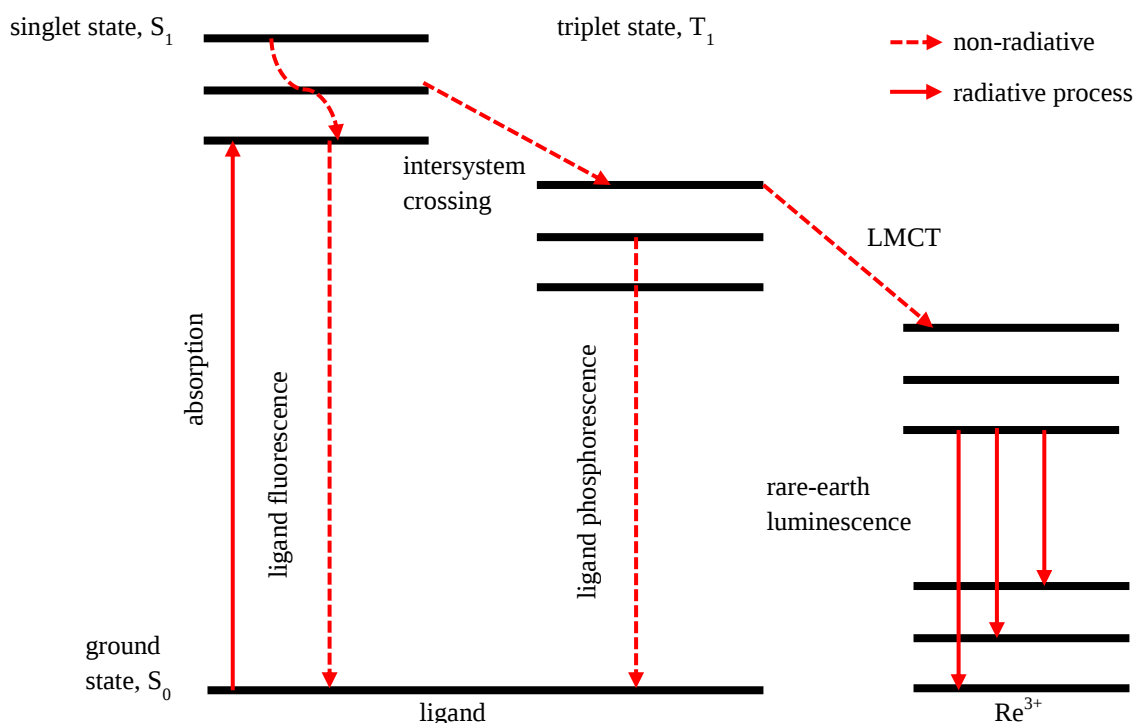


Figure 2.14 Energy transfer process of rare-earth metal complexes

The organic ligand will absorb the light and excited it to the singlet excited state, S_1 . From S_1 state, the energy is transfer to the triplet state, T_1 through intersystem crossing (ISC) or can decay to the ground state either radiatively by fluorescence or non-radiatively by dissipation of heat (Hebbink, 2002). From the T_1 state, the energy is transferred to the rare-earth metal ion, Re^{3+} through charge transfer process (ligand to metal charge transfer, LMCT) which finally emits luminescence or the T_1 state decays to the ground state as phosphorescence. It is worth noting that the energy transfer from S_1 state directly to the rare-earth metal ion, Re^{3+} is not allowed as it is spin forbidden.

The observed luminescence from the Re^{3+} is dependent mainly on the position of the triplet state, T_1 of the ligand and the emitting levels of the Re^{3+} . If the energy level between the lowest triplet state; T_1 lie above the 5D_j level of rare-earth metal ion, the energy can be transferred efficiently to this level. (Sariciftci, et al.)

2.7.4. Ligand

In order to ensure efficient energy absorption, the rare-earth metal ions, Re^{3+} is required to coordinate with high absorbing ligand systems (Binnemans, 2009). Different types of chelating ligands like β -diketones (Lis et al., 2008; Reisfeld, 2004; Yan & Kong, 2010), pyridines (Bao, Tang, & Tang, 2011), bipyridines (Freidzon, Scherbinin, Bagaturyants, & Alfimov, 2011), cryptands (Seth & Aravindakshan, 2011), calixarenes (Comby & Bünzli, 2007), cyclodextrins (Brunet, Juanes, & Rodriguez-Ubis, 2007), crown ethers (Brunet, et al., 2007) and some others are known. 2,2'-Bipyridine (bpy) ($\text{C}_{10}\text{H}_8\text{N}_2$) and 1,10-Phenanthroline (phen) ($\text{C}_9\text{H}_7\text{NO}$) are the examples of the a bidentate ligand in coordination chemistry that forms strong complexes with most metal ions. In terms of its coordination properties, phen is similar to bpy. On the other hand, 8-Hydroxyquinoline (8Hq) is a monoprotic bidentate chelating agent in which the reaction of 8-hydroxyquinoline with aluminium(III) results in Alq_3 , a very popular emitter in organic light-emitting diodes (OLED)