Chapter 7. Conclusions and future works

7.1. Conclusions

Four molecular hybrid compound based on the rare earth metal quinoline complexes (Req_3) chelated with 2,2-bipyridine (Bpy) and 1,10-Phenanthroline (Phen) as neutral ligand namely Euq_3bpy_3, Euq_3phen_3, Tbq_3bpy_3 and Tbq_3phen_3 have been successfully deposited as thin films by a simple spin coating technique. Since Req_3 ternary complexes are very insoluble complex which can only be dissolved in DMSO, 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. All Req^{3+} complexes with fixed concentration of 10 mg/ml is spin coated with spinning speed of 2500 rpm at 30 s. The thickness of the resultant Euq_3bpy_3, Euq_3phen_3, Tbq_3bpy_3 and Tbq_3phen_3 complexes thin films which are 74.00 ± 0.01 nm, 72.00 ± 0.01 nm, be 77.00 ± 0.01 nm and 78.00 ± 0.01 nm are measured by using KLA TENCO P-6 profilometer. The structural, thermal, optical and electrical properties were investigate according to the same rare-earth metal but different central and neutral ligands in order to highlight the effect of the neutral ligand to these properties.

The structural properties of the molecular hybrid compound based on the rare earth metal quinoline complexes (Mq_3) chelated with 2,2-bipyridine (Bpy) and 1,10-Phenanthroline (Phen) as neutral ligand are characterized by using FTIR and XRD analysis. FTIR shows the presence of the possible chemical bonding that was involved upon complexation of the Bpy and Phen ligands to the Req_3 ternary complexes in a thin film form. The identical features in the FTIR spectra reveal that both complexes are chemically similar to each other due to the same quinoline (8Hq) ligand that have been chelated to the metal Eu^{3+}, whereas the minimal but significant changes in the band position proves the involvement of Phen or Bpy ligands in the coordination. It was also

observed that the intermolecular metal ion bonding which are Eu-O, Tb-O, Eu-N and Tb-N correspond to the complexes were exhibited at smaller wavenumbers due to the greater mass of both Eu^{3+} and Tb^{3+} rare earth metal centre that are attached to the nitrogen and oxygen atoms. The XRD analysis reveal a broad diffraction hump located at around $2\theta \approx 25^{o}$ attribute to the amorphous structure of all Req_3 ternary complexes. Therefore it is expected that photoluminescence properties of the Req_3 ternary complexes is expected to be high as the weak interaction that presence in the disordered thin films leads to a dominance of radiative decay. The thermal properties of the Req_3 complexes are analyses by using the thermogravimetric (TGA) and differential thermogravimetric (DTG). The Req_3 ternary complexes are found to exhibit different thermal decomposition behavior despite of similar rare-earth metal and the center ligand (8Hq ligand). A thorough thermal analysis on the Req_3 ternary complexes analysis reveal that the Req_3 ternary complexes with Phen ligand as the neutral ligand shows the higher thermal stability compare to the Req_3 ternary complexes with Bpy ligand. The first decomposition steps which only start at 300ºC imply that the Req_3 ternary complexes with Phen ligand as the neutral ligand present no degradation on its structure until 300ºC. The high thermal stability exhibits by this complexes indicate that this complex is favorable for potential material in OLEDs fabricated by vacuum deposition (Li et al., 2010). However, the Req_3 ternary complexes with Bpy ligand have been found to degrade below 100ºC. The first step of decomposition for these complexes can be easily degraded if the thin films is prepared using thermal evaporation process at relatively high temperature (Teixeira et al., 2011)

The optical properties of the molecular hybrid compound based on the rare earth metal quinoline complexes Req_3 chelated with 2,2-bipyridine (Bpy) and 1,10-Phenanthroline (Phen) as neutral ligand are analysed using UV-Vis and photoluminescence (PL)

spectroscopy. In summary, the UV-Vis absorption results reveals that the absorption process of the Req_3 ternary complexes are dominated by the neutral ligand (secondary ligand) indicating that chelated ligand has overcame the limitation of an intrinsically absorption coefficient for the rare earth metals. Therefore, the occurrence of different absorption band and features is observed from the absorption spectra. The LLCT transition intensity was found to be linearly dependent to the neutral ligand size. Thus, the intensity of the LLCT transition of Req_3 ternary complexes with Phen ligand as the neutral ligand (secondary ligand) is higher compare to the Req_3 ternary complexes with Bpy ligand as the neutral ligand (secondary ligand). The optical band gap that is estimated from Tauc analysis reveals that band gap of the of Req_3 ternary complexes with Bpy ligand as the neutral ligand (secondary ligand) is somewhat lower compare to the Req_3 ternary complexes with Phen ligand as the neutral ligand (secondary ligand). The presence of the direct band gap in all Req_3 ternary complexes are also predicted from the derivation of the Tauc model.

It is also proven that the different degree in the green coloured fluorescence detected in the PL spectra is due to the fact that the energy transfer between the triplet state and the rare earth metal is inefficient since the calculated energy gap between the ligand and the metal centered did not comply with the Latva empirical rule. The energy transfer study reveals the sensitization mechanism which the central ligand plays a very important role in sensitizing the rare earth metals (Eu^{3+} and Tb^{3+}). Even though the adduction of Phen and Bpy ligand as the secondary ligand in the Req_3 ternary complexes can provide a higher T_1 level to assist the sensitization, but it still cannot replace the role of the 8Hq ligand to sensitized the $^5D_0$ state of Eu^{3+} as well as the $^5D_4$ state of Tb^{3+}. In fact, the role of the neutral ligand which is transporting energy to the other ligand and central metal ion that consequently will enhance the rare earth metals is

only valid if the energy difference between the emission level of Eu^{3+} and Tb^{3+} and T_1 state obey the Latva rule. These analyses also explain the radiation less emission in the electroluminescence of the device containing this metal complex which is explained and discussed in the next chapter.

The electrical properties of the Req_3 ternary complexes as organic semiconductor devices are characterized by measuring the I-V characteristics with the configuration of ITO/ Req_3/Al. The I-V curves demonstrates by ITO/Tbq_3bpy_3/Al and ITO/ Tbq_3phen_3/Al are found to be more stable compare to that of ITO/Euq_3bpy_3/Al and ITO/ Euq_3phen_3/Al which exhibits anomalous behavior as a result of an abrupt current jump at certain voltage. However there is no obvious light emission captured in these single layer devices since the device structure consists of only an emitting organic layer causes an imbalance in the carrier transport that lead to charge accumulation at the interface, which leads to exciton quenching.

In addition, the transport mechanisms that dominate the devices are also evaluated. The presence of the bulk-limited transport mechanism has been evaluated using the power law relation, whereas the contact-limited mechanism is evaluated using the Richardson-Schottky thermionic emission (R-S model). From the evaluation, it was found that the contact-limited model dominates the transport mechanism. The proposed model is then utilized in order to extract the electronic parameters from the conventional ln I-V characteristics and Cheung's functions. The non-ideal behavior demonstrates from the ln I-V characteristics permits the extraction of the electronic parameters of the diode such as the ideality factor, n, effective barrier height, Φ_b and saturation current, I_0. However, all the ideality factors was found to deviate from unity indicating the presence of the series resistance, interface states and the voltage drop across the interfacial layer .The ideality factor, n is found to be inversely dependence to the effective barrier

height, Φ_b in which is reflected by the increment of the barrier height, Φ_b with reduction of the ideality factor, *n*. Moreover, the ideality factor, n is also found to reduce as the series resistance decrease.

The electronic parameters that have been extracted from the conventional ln I-V characteristics is found to be close to the values obtained from Cheung's functions indicating the validity of the parameters. However, the conventional ln I-V method is considered to be more accurate compare to the Cheung's function since the Cheung's functions is just a derivation from the Schottky diode equation. The other significant finding that should be emphasized is the correlation of the electrical parameters obtained from previous analysis with the device performance. The estimated saturation current, I_0 and the barrier height, Φ_b actually explained the failure operation of the device as OLED which also supports the domination of the contact limited model in these devices. The estimated barrier height is also utilized to estimate the HOMO and LUMO values of the Req_3 ternary complexes. The schematic band diagram for all devices is then proposed.

Another thing that should be highlighted is that the adduction of different neutral ligand with the same rare earth metals is found to slightly affect the electrical properties of these devices. Therefore it can be observed that the electronic parameters extracted from the I-V measurement is different as the adduction of the neutral ligand is changed. Other than that, it was also obvious that the adduction of different rare earth metals with the same neutral ligand is also affecting the electronics parameters. However there are some deviations detected from the non-linear relationship between the barrier height, Φ_b and the ideality factor, *n* which may be contributed by the defect exist in these devices. On the other hand, the adductions of different rare earth metals despite of the same organic ligand are also found to affect the electrical properties of these devices. From

this finding, ITO/Euq_3 ternary complexes/Al is found to exhibit better device performance compare to that of ITO/Tbq_3 ternary complexes/Al. The result also established the linear relationship between the barrier height, Φ_b and the ideality factor, *n*.

Even though Req_3 ternary complexes has the appropriate structure to produce high photoluminescence efficiency and thermal stability, the devices containing these materials are still lack of electroluminescence properties. The absence of this property is coincides with the inefficient energy transfer in the LMCT state as proven from the optical analysis, making the device inherently inefficient. This established that the efficiency of an OLED is crucially dependence on the optical and electrical properties.

7.2. Future works

On the basis of the conclusion as mentioned earlier, some suggestions for the future works are proposed. Since Req_3 ternary complexes are newly synthesized material, a thorough investigation should be taken in order to fulfill the requirement for fabrication of OLED. Therefore the following suggestion should be undertaken as future works

- Modified the 8Hq ligand to tune their triplet energy so that it will able sensitized the $^5D_0$ state of Eu^{3+} and obtain a red electroluminescence as well as $^5D_4$ state of Tb^{3+} to obtain a pure green electroluminescence
- Fabricate a multilayer OLED with the Req_3 ternary complexes as the emissive layer sandwiched between the electron and hole transport layer in order to enhance the recombination rate in the emissive layer.
- Characterize the Req_3 ternary complexes thin films by using impedance spectroscopy and capacitance voltage measurement to obtain more information on electrical properties as well as the mobility's

- Fabricate the OLED according to several parameter such as thickness and temperature to further analyzed the transport mechanism