

Chapter 5. Optical properties

5.1. Introduction and overview

The main focus of this chapter is to study the optical characteristics of molecular hybrid films based on Re_3 ternary complexes which are europium and terbium chelated with bidentate ligand. Tris-(8-hydroxyquinoline) (8Hq) was used as the centre ligand whereas two bidentate ligand which are 2,2'-bipyridine (Bpy) and 1,10-Phenanthroline (Phen) were used as the neutral (secondary ligand) in the rare earth metal quinoline complexes. The significant differences in the analysis of the optical properties upon adduction of the neutral ligand to the same Re_3 metal as well as upon complexing different Re_3 metal to the same ligand are also highlighted. Each of the analysis was performed separately in two sequential sections beginning with the variations of secondary ligand but the same Re_3 ternary complexes and followed by the variations of Re_3 ternary complexes but the same secondary ligand.

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 that is involved 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 Re_3 ternary complexes which are the consequence from ligand to metal charge transfer (LMCT). The details of the LMCT process were also discussed.

5.2. UV-Vis absorption spectroscopy

5.2.1. *Euq₃bpy₃ and Euq₃phen₃*

The absorption spectra of Euq_3bpy_3 and $\text{Euq}_3\text{phen}_3$ which were measured in thin films are shown in Figure 5.1. It should be noted that both complexes contain the same metal quinoline complex which is Euq_3 but coordinated with different neutral ligands which are Bpy and Phen ligand. From the spectra, there are roughly two regions of the absorption band that could be identified. The absorption band that occurs in the UV region is known as the Soret band while the Q band occurs in the visible region. The absorption spectrum recorded for Euq_3bpy_3 exhibits two Soret band at 308 nm and 356 nm and two Q-band at 386 nm and 398 nm. The spectrum clearly shows the maximum peak exhibits at 356 nm with a shoulder at 308 nm. It should be noted that the presence of the weak band at 398 nm is the evidence of vibronic progression of the 386 nm transition. The observed absorption bands are comparable to the values obtained by Rai et. al concerning a similar ligand, which had discovered these bands at 342 nm and 382 nm (H. Wang, He, Liu, Shi, & Gong, 2009). Moreover, the broad shoulder appear at 308 nm corresponds to promotion of an electron from 8Hq ligand π -orbital to the Bpy ligand π^* -orbital. This characteristic transition can be described as $[\pi(8\text{Hq}) \rightarrow \pi^*(\text{Bpy})]$ where LLCT is referred to ligand to ligand charge transfer.

On the other hand, $\text{Euq}_3\text{phen}_3$ shows two Soret bands located at 302 nm and 334 nm and a Q-band at 386 nm. A rather different absorption feature is shown in this complex with the maximum peak appear in the UV region while less intense shoulder exhibit in the visible region. The maximum absorption peak that appear at 302 nm corresponds to the promotion of an electron from 8Hq ligand π -orbital to the Phen ligand π^* -orbital which the transition character can be described as LLCT $[\pi(8\text{Hq}) \rightarrow \pi^*(\text{Phen})]$. Interestingly, the absorption intensity regarding this transition appears to be very intense

compare to that of LLCT [$\pi(8Hq) \rightarrow \pi^*(Bpy)$] transition. This is because of the size of the Phen ligand is larger than that of Bpy ligand. This observation agrees well with the reported work which suggested that the larger secondary ligand will give rise to a stronger intensity than the smaller one in the lower energy absorption region (Kumar, Srivastava, Kumar, Kamalasanan, & Singh, 2010). The Euq_3phen_3 complex is also found to exhibit a weak shoulder in the Q-band located at 334 nm. The presence of this weak shoulder is proposed to originate from the Phen ligand. This value is closed to the value obtained experimentally by Zhong et al. at 335 nm concerning similar ligand (Zhong, Wang, Wang, & Yang, 2001).

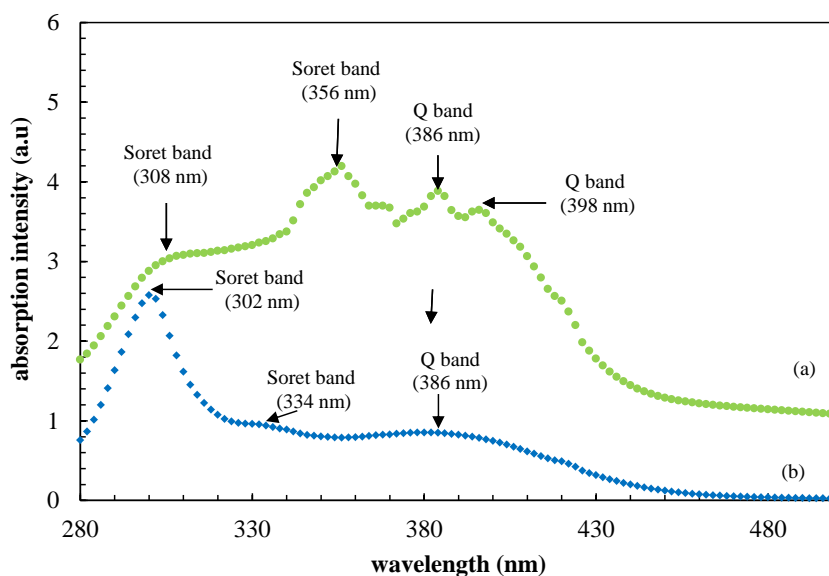


Figure 5.1 UV-Vis absorption spectra of (a) Euq_3bpy_3 and (b) Euq_3phen_3 thin films

From these absorption spectra, it is apparent that all the transitions involve are originated primarily from the electronic transition in the organic ligand. This shows that the absorption of the Euq_3 ternary complexes was mainly produced from the ligand. Since the ligand and the europium compound were unavailable for characterization, the results are compared with other related work that has been reported. The same trend was also observed by Wang et al whom have measured the absorption spectra of the

europium ion, the organic ligand and the europium complex separately (Huihui Wang, He, Yan, & Gong, 2011). Wang et al detected that absorption spectrum exhibited by the organic ligand is closely matched to the europium complexes while none of the absorption band was detected from the metal ion, confirming the role of organic ligand in the absorption process (Huihui Wang, et al., 2011). The result obtained is also consistent with the expectation that the presence of the organic ligand in the europium complexes would overcome the limitation of an intrinsically small molecular absorption coefficient for the europium metal. Such phenomenon is attributed to the “antenna effect” or the emission sensitization, a concept proposed by Lehn where a distinct absorption, energy transfer and emission sequence operates (Lehn, 1990). The concept will be discussed later in the photoluminescence result.

Another interesting observation is that both of Euq_3 ternary complexes reveal non-identical absorption characteristics in the range of 280-350 nm suggesting that the absorption process within this range is controlled by different neutral ligand. Meanwhile, the absorption shoulder in in the range of 350-440 nm shows a slightly identical feature which reflects essentially the absorption is originate from the 8Hq ligand. Therefore the overall absorption spectra of both complexes appear non identical in terms of the shape due to the effect of complexing different neutral ligand which plays the main role in absorbing the UV energy despite of the 8Hq ligand. Such behavior appears to contradict the finding of various works which proves that the absorption of the europium complexes depends on the central ligand (Biju, Raj, Reddy, & Kariuki, 2006; Kim, Lee, Kim, & Park, 2003; Turro, 1991). Therefore, the absorption spectra of the europium complexes mostly appear identical to those corresponding to the central ligand (An, Gong, Li, Zhang, & Cheng, 2005; Liu, Wen, Qi, & Liang, 2008; L. Zhang, Li, Chen, & Liu, 2009). According to Gao et al. and Guan et al., this phenomenon happen due to the dipole moment of the negatively charged

central ligand is larger than that of the neutral ligand (X.-C. Gao et al., 1999; Guan, Chen, Sun, Liang, & Zhang, 2005). This phenomenon seems not to be prominent in the Euq^{3+} ternary complexes because the dipole moment of 8Hq ligand which is 2.19 D (Filip, Humelnicu, & Ghirvu, 2009) is smaller compare to the dipole moment of both Phen and Bpy ligand which are 2.73 D (Mandal, Green, & Natarajan, 2005) and 3.80 D (Hoon-Khosla, Fawcett, Goddard, Tian, & Lipkowski, 2000) respectively. The occurrence of different absorption band and features from the UV-Vis absorption spectra also indicate that different intermolecular energy transfer process were involved due to the different secondary (neutral) ligand which may act as energy donors while 8Hq ligand will act as the energy acceptor at the first step in the sensitization process for both Euq_3bpy_3 and $\text{Euq}_3\text{phen}_3$ complexes.

5.2.2. *Tbq₃bpy₃ and Tbq₃phen₃*

The absorption spectra of molecular hybrid films of Tbq_3bpy_3 and $\text{Tbq}_3\text{phen}_3$ complexes are shown in Figure 5.2. It also could be seen from the spectra display characteristic absorption feature of Soret band in the UV region and Q-band in the visible region. The absorption spectrum recorded for Tbq_3bpy_3 clearly shows two Soret bands at 290 nm and 370 nm with a peak maximum in the Q-band located at 388 nm. The appearance of the absorption shoulder in the Soret band is assigned to the electronic transition from π -orbital of 8Hq ligand to π^* -orbital of Bpy ligand which can be described as LLCT [$\pi(8\text{Hq}) \rightarrow \pi^*(\text{Bpy})$]. It also should be noted that the presence of the weak band at 370 nm is the evidence of the vibronic progression of the 388 nm transition. On the other hand, a rather different behavior has been shown by $\text{Tbq}_3\text{phen}_3$ complex. A high intense peak located at 314 nm in the Soret band with a less intense shoulder located 382 nm in the Q-band was detected. The appearance of the weak band

at 370 nm is also observed indicating the vibronic progression of the 382 nm transition. Another interesting observation in the spectra is the intensity of LLCT transition in the lower wavelength absorption band. Interestingly, the absorption intensity of this transition appear to be very intense compare to the LLCT [$\pi(8Hq) \rightarrow \pi^*(Bpy)$] transition. As it was mentioned previously, such behavior occurs due to the larger size of Phen ligand compare to the Bpy ligand which will give rise to a stronger intensity than the smaller one in the lower energy absorption region (X.-N. Li et al., 2009).

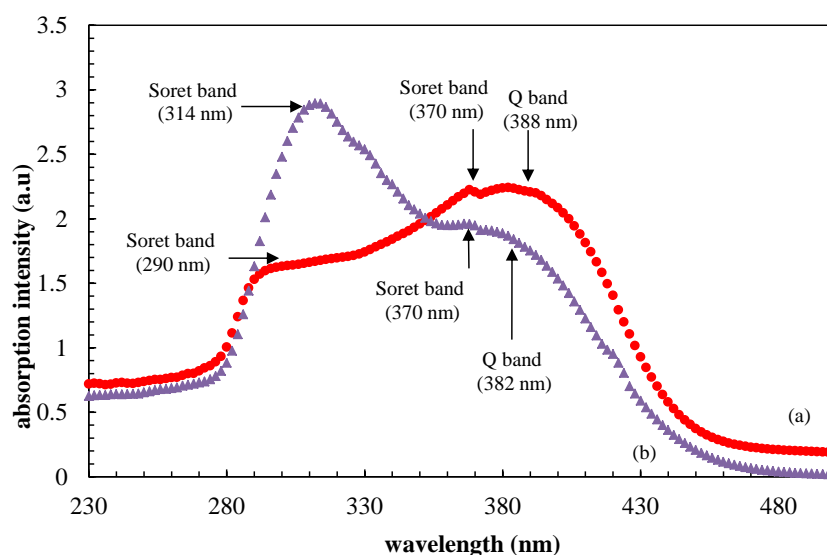


Figure 5.2 UV-Vis absorption spectra of (a) Tbq_3bpy_3 and (b) Tbq_3phen_3 thin films

Interestingly, the absorption characteristics of both Tbq_3 ternary complexes demonstrate the same behavior as the Euq_3 ternary complexes except for a non-identical characteristic in the region from 280 to 350 nm which is originated from the neutral ligand whereas the appearance of the shoulder near 350 nm is contributed from the 8Hq ligand. The similar behavior obtained from both Euq_3 and Tbq_3 ternary complexes confirms the assumption of the role of the neutral ligand in dominating the absorption process of the Req_3 ternary complexes despite of different rare earth, Re metal cations of Eu^{3+} and Tb^{3+} . It also should be highlighted that complexes reflect the effect of the

incorporation of difference bidentate ligand as the neutral ligand. This behavior appears contradict to various reports that proves the absorption of the terbium complexes is generally controlled by the central ligand (X. C. Gao et al., 1999; Xin et al., 2004). The contradiction in these Tbq₃ ternary complexes thin films may be explained by the higher dipole moment value of both Phen and Bpy ligands compare to the 8Hq ligand which consequently causes the energy absorbing process dominated by the Phen and Bpy ligands as the neutral ligand. Therefore it could be observed that both molecular hybrid films of Tbq₃bpy₃ and Tbq₃phen₃ complexes display different characteristic absorption spectra.

5.2.3. *Effect of different rare earth metals*

According to the previous section, the UV-Vis energy absorb by the Req₃ ternary complexes has been proved to produce mainly from the neutral ligand, despite of their different rare earth metal cations of Eu³⁺ and Tb³⁺. In order to evaluate the effect of different rare earth metal cations on the UV-Vis absorption behavior, a plot of the rare earth quinoline ternary complexes based on the same neutral ligand are evaluate as shown in Figure 5.3 and 5.4. It should be noted that the spectral shape of Tbq₃bpy₃ complex is identical to the spectral shape of Euq₃bpy₃ confirming the role of absorbing the energy is controlled mainly by Bpy ligand. However, there are still slight shift detected in the absorption band position where the absorption bands exhibited by Euq₃bpy show a bathochromic shift (red shift) to a higher wavelength in comparison with Tbq₃bpy. This could mainly due to the higher electronic effect of the coordinated Eu³⁺ central metal atom on the 8Hq and Bpy ligand orbitals. According to Fahmi et. al , a coordinated metal atom with a higher atomic radius, will give a strong electronic effect on ligand molecular orbital (Muhammad & Sulaiman, 2011). At the radius of

1.99Å for Eu^{3+} which is higher than 1.80Å for Tb^{3+} , the electronic effect of Eu^{3+} seems to be stronger compare to that of Tb^{3+} . This stronger bonding result in more π - π orbital stacking and thereby lowering the HOMO-LUMO space (Yu & Su, 2003) to produce a bathochromic shift in the absorption spectra of Euq_3bpy_3 compared to that of Tbq_3bpy_3 .

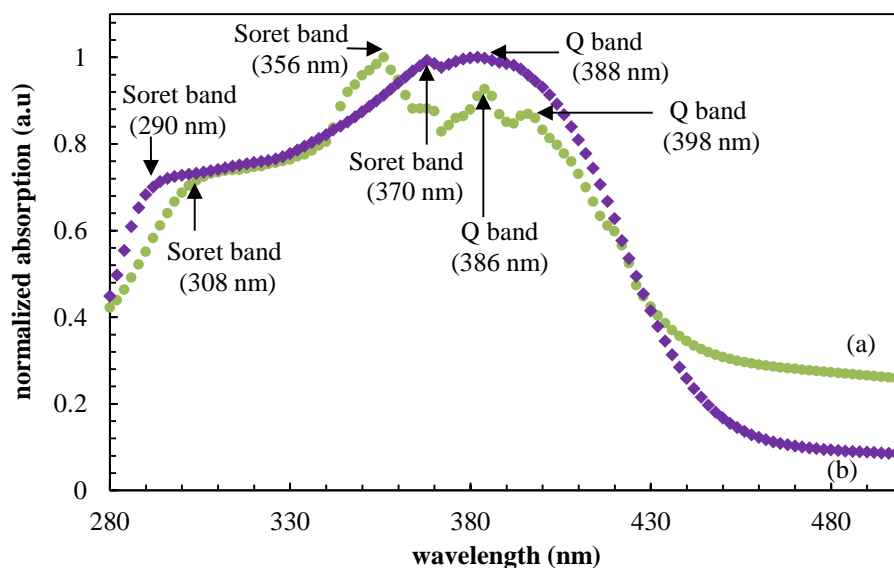


Figure 5.3 UV-Vis absorption spectra of (a) Euq_3bpy_3 and (b) Tbq_3bpy_3 thin films

On the other hand, the absorption spectra of $\text{Euq}_3\text{phen}_3$ is also found to display identical spectra with $\text{Tbq}_3\text{phen}_3$ resulting from the absorption by the Phen ligand. This observation is consistent with the aforementioned UV-Vis behavior of rare-earth quinoline ternary complexes with Bpy ligand in which it clearly showed that the absorption process does not affected by the rare earth metals. It also can be noticed that the absorption of band positions of the $\text{Euq}_3\text{phen}_3$ shows a hypsochromic shift (blue shift) in comparison with $\text{Tbq}_3\text{phen}_3$. This behavior is found to be in accordance with the abovementioned behavior of the rare earth ternary complexes with Bpy as the neutral ligand which attributed this phenomenon to the strong electronic effect experienced by Eu^{3+} compare to that Tb^{3+} as the rare earth metal due to the radius of Eu^{3+} radius which is higher than Tb^{3+} . However this effect seems not to be prominent in

this case. The deviation of this behavior is probably due to the coordination complex of $\text{Euq}_3\text{phen}_3$ which is not as stable as the $\text{Tbq}_3\text{phen}_3$ complex. On the other hand, the other factors such as the variations in the stoichiometric of the involved synthesis methods and the purity degree of the complex also may contribute to this deviation. [Hidalgo et al., 2007; Hossain et al., 2008]. Therefore, $\text{Tbq}_3\text{phen}_3$ will experience stronger electronic effect and cause more π - π overlap leading to the reduction in the band gap to produce a bathochromic shift.

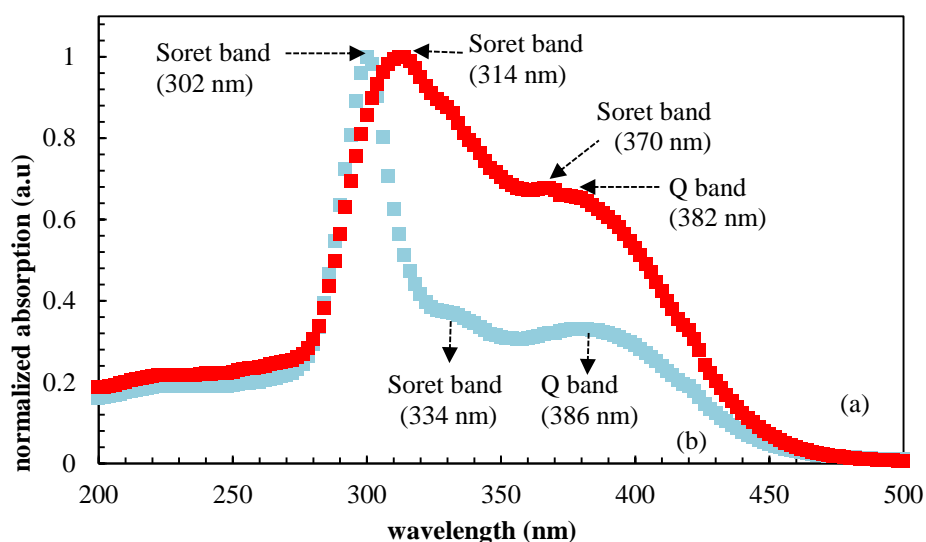


Figure 5.4 UV-Vis absorption spectra of (a) $\text{Tbq}_3\text{phen}_3$ and (b) $\text{Euq}_3\text{phen}_3$ thin film

5.3. Band gap analysis

5.3.1. Euq_3bpy_3 and $\text{Euq}_3\text{phen}_3$

One of the important parameter in determining the optical band gap of the thin films is the absorption coefficient, α . The absorption coefficient, α which defines the amount of light absorbed by a material, is calculated according to the Beer Lambert law with following relation; $I=I_0e^{-\alpha t}$ and consequently $\alpha=2.30\log(I_0/I)/t$ (Lin, 2010). Since the transmission is related to the absorbance, this relation is written as follow;

$\alpha = 2.30 \log A/t$, where I and I_o are the incident and transmitted intensities, A is the absorbance and t is the thickness (Lin, 2010). The thickness for Euq_3bpy_3 and $\text{Euq}_3\text{phen}_3$ thin films are approximately 74.00 ± 0.01 nm and 72.00 ± 0.01 nm respectively. The thicknesses of both thin films were measured by using KLA Tencor profilometer.

By taking assumption from the Tauc model that the absorption edge has a parabolic variation with photon energy (Dridi et al., 2009), the optical band gap can be estimated by the relation:

$$\alpha h\nu = \alpha_o (h\nu - E_g)^n \quad (5.1)$$

where α_o 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 ($n=2$). However it is difficult to determine the transition by direct absorption measurement. The value of n can be obtained mathematically from the logarithm and derivation of Equation (5.1) as explained by F.F. Mohammed *et al* (Muhammad, Abdul Hapip, & Sulaiman, 2010). Equation (5.1) is rearranged and can be expressed as:

$$\frac{d \ln(\alpha h\nu)}{d h\nu} = \frac{n}{h\nu - E_g} \quad (5.2)$$

Referring to Equation (5.2), a plot of $d \ln(\alpha h\nu)/d h\nu$ vs. $h\nu$ for both compound is presented in Figure 5.5 with the maximum occurring at a point where $h\nu = E_g$. It can be clearly observed that the maximum point of the graph yields the approximation values of E_g for Euq_3bpy_3 and $\text{Euq}_3\text{phen}_3$ are 2.93 ± 0.02 eV and 2.77 ± 0.02 eV, respectively. It should be noted that these initial values are only the estimated value used to plot a graph of $\ln(\alpha h\nu)$ vs $\ln(h\nu - E_g)$ as shown in Figure 5.6, in relation from Equation (5.1) to obtain the value of n (Muhammad & Sulaiman, 2011). The slope of the graph gives the estimate value of $n \sim 0.51 \pm 0.08$ for Euq_3bpy_3 and $n \sim 0.5 \pm 0.1$ for $\text{Euq}_3\text{phen}_3$.

These values are found to be close to $n \sim 0.5$. Therefore it is reasonable to prove that these Euq_3 ternary complexes experience a direct band gap from this estimation.

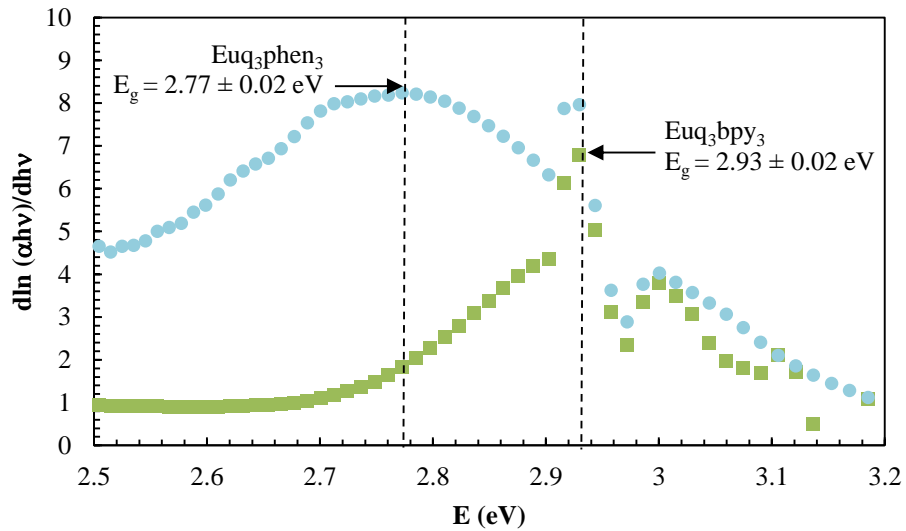


Figure 5.5 Graph of $d\ln(\alpha h\nu)/d(h\nu)$ vs. $h\nu$ of Euq_3bpy_3 and $\text{Euq}_3\text{phen}_3$ thin films that is used to determine the estimate value of E_g .

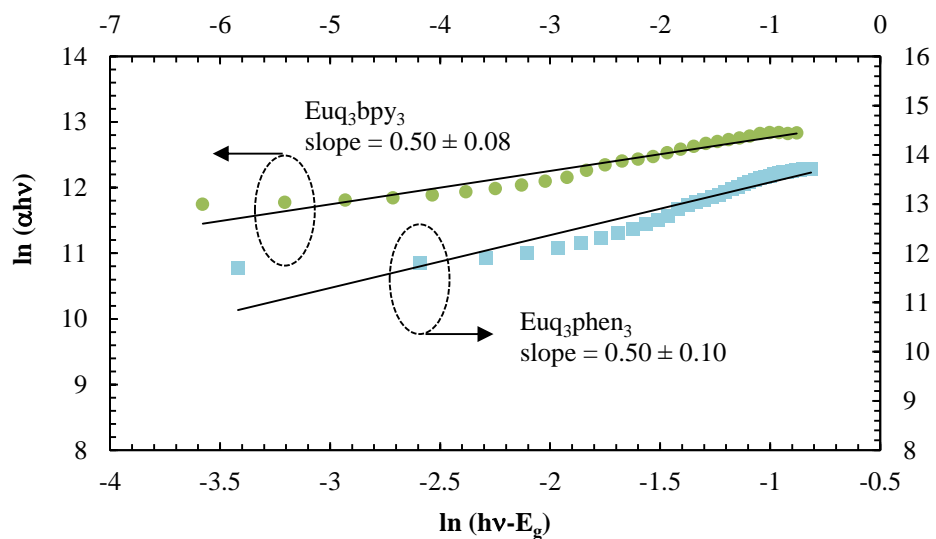


Figure 5.6 Graph of $\ln(\alpha h\nu)$ vs $\ln(h\nu - E_g)$ of (a) Euq_3Bpy_3 (b) $\text{Euq}_3\text{phen}_3$ thin films. The slope of the graph gives the estimation value of n which indicates the transition of the band gap.

By applying equation (5.1), the optical band gap of both compounds is evaluated from a plot of $(\alpha h\nu)^{1/n}$ against $h\nu$ as shown in Fig. 5.7. From the plot, the band gap can be

extrapolated by fitting a straight line to $h\nu = 0$ as illustrated in Figure 5.7. The band gap obtained for Euq_3bpy_3 and $\text{Euq}_3\text{phen}_3$ are 2.86 ± 0.02 eV and 2.84 ± 0.02 eV respectively. From these findings, it is obvious that the band gap of Euq_3bpy_3 is slightly higher compare to that of $\text{Euq}_3\text{phen}_3$ which is probably due to the higher conjugation length of Phen ligand that may result in π - π stacking enhancement leading to the reduction of the band gap.

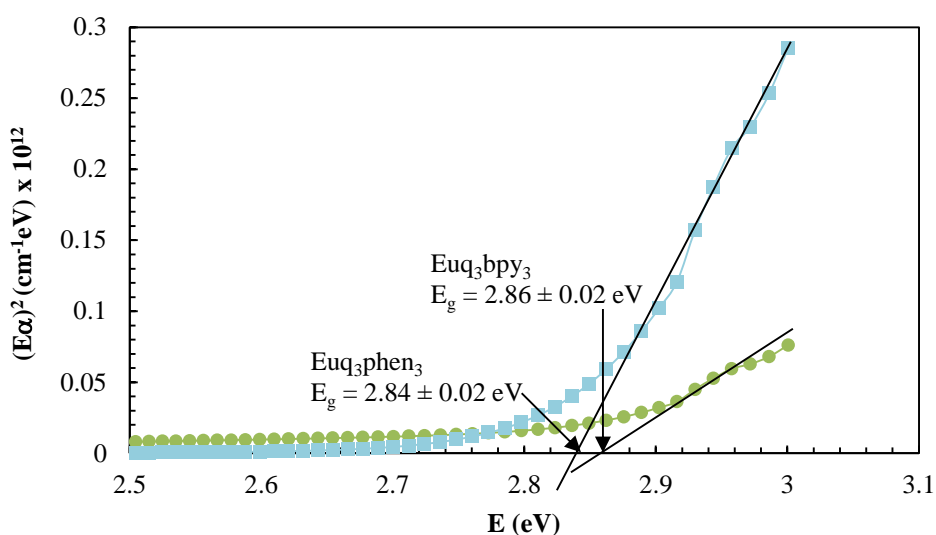


Figure 5.7 Graph of $(\alpha h\nu)^2$ vs $h\nu$ of (a) Euq_3bpy_3 and (b) $\text{Euq}_3\text{phen}_3$ thin films thin film. The band gap can be extrapolated from a straight line to $h\nu = 0$

5.3.2. Tbq_3bpy_3 and $\text{Tbq}_3\text{phen}_3$

The optical band gap for Tbq_3 ternary complexes has been estimated by using Tauc model. The thickness for each terbium complexes is determined by using profilometer. The thickness of Tbq_3bpy_3 and $\text{Tbq}_3\text{phen}_3$ thin films are estimated to be 77.00 ± 0.01 nm and 78.00 ± 0.01 nm respectively. It should be noted that a similar method as the previous section has been applied in order to determine the estimation of the band gap transitions in the Tbq_3 ternary complexes. A graph of $d\ln(\alpha h\nu)/d h\nu$ vs. $h\nu$ are plotted as shown on Figure 5.8 in order to obtained the approximation values of E_g .

It is apparent that the maximum peak of the graph exhibits the value of 2.82 ± 0.02 eV and 2.70 ± 0.02 eV for Tbq_3bpy_3 and $\text{Tbq}_3\text{phen}_3$. By applying this initial value of E_g , graph of $\ln(\alpha hv)$ vs $\ln(hv - E_g)$ was illustrated as in Figure 5.9. The value of n can be derived from the slope of the graph. It was found that the estimate value of n for Tbq_3bpy_3 and $\text{Tbq}_3\text{phen}_3$ are 0.50 ± 0.10 and 0.61 ± 0.10 respectively. This estimation suggests the presence of the direct band gap in the Tbq_3 ternary complexes.

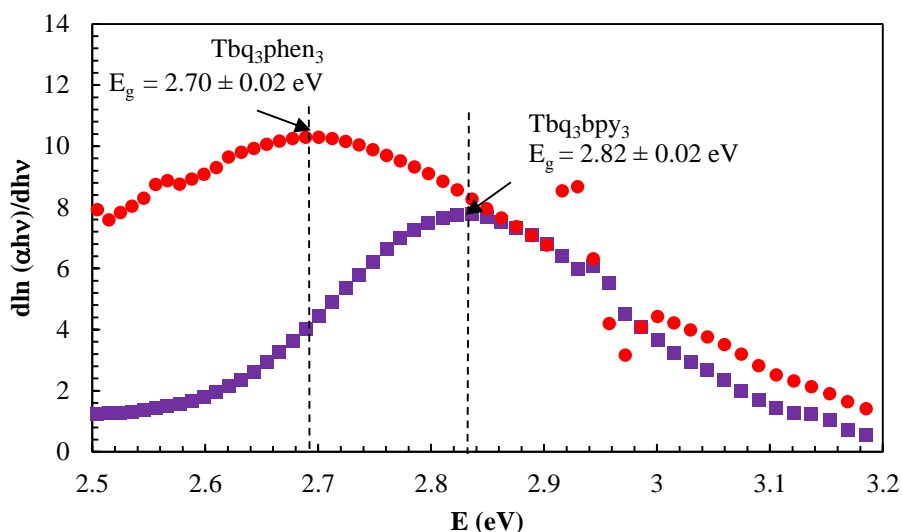


Figure 5.8 Graph of $d\ln(\alpha hv)/dhv$ vs. $h\nu$ of Tbq_3bpy_3 and $\text{Tbq}_3\text{phen}_3$ thin films that is used to determine the estimate value of E_g

The exact value of the band gap is calculated by extrapolating the straight line portion of the plot of $(\alpha hv)^{1/n}$ against $h\nu$ graph against $h\nu$ axis by using the n value determine previously. Figure 5.10 illustrate a graph of $(\alpha hv)^2$ against $h\nu$. The correct band gap value obtained for Tbq_3bpy_3 and $\text{Tbq}_3\text{phen}_3$ are 2.87 ± 0.02 eV and 2.85 ± 0.02 eV respectively. It is observed that the band gap of Tbq_3bpy_3 is slightly higher compare to that of $\text{Tbq}_3\text{phen}_3$ as the conjugation of the Bpy ligand is somewhat lower compare to the Phen ligand and thereby increases the energy gap between the HOMO and LUMO state. These results are found to be in good agreement with the previous case of Euq_3

ternary complexes in which the higher band gap is obtained from the complexes with Phen as the neutral ligand.

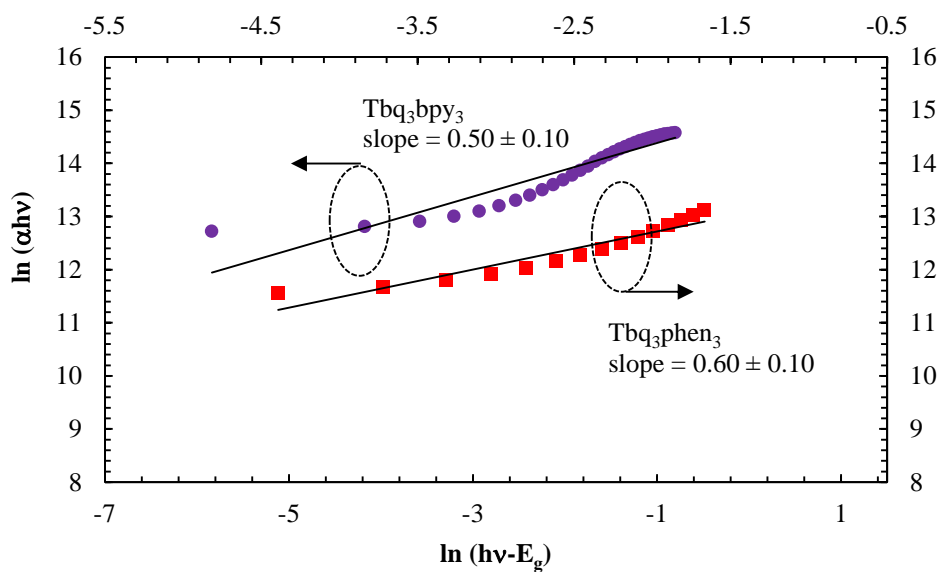


Figure 5.9 Graph of $\ln(\alpha hv)$ vs $\ln(hv-E_g)$ of (a) Tbq_3phen_3 and (b) Tbq_3bpy_3 thin films. The slope of the graph gives the estimation value of n which indicates the transition of the band gap.

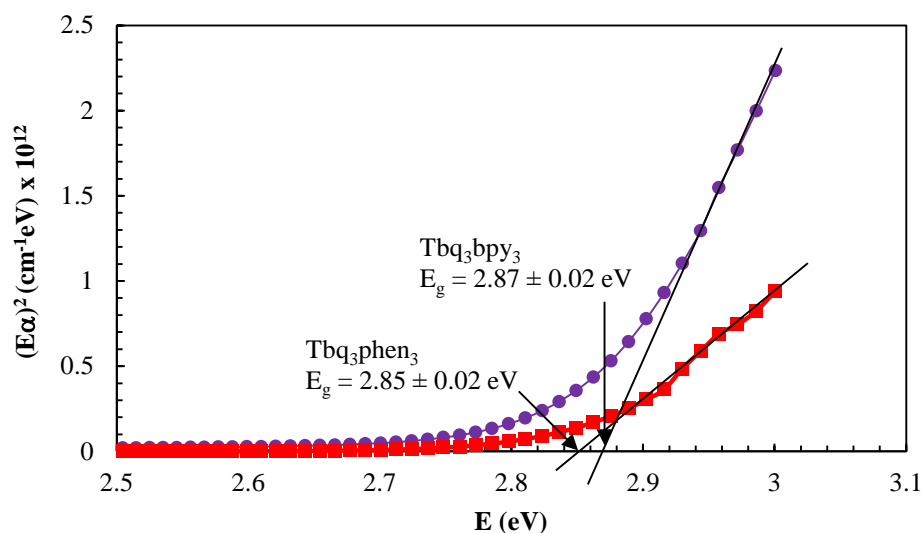


Figure 5.10 Graph of $(\alpha hv)^2$ vs hv of (a) Tbq_3bpy_3 and (b) Tbq_3phen_3 thin film. The band gap can be extrapolated from a straight line to $hv = 0$

5.3.3. Effect of different rare earth metals

Previous section has proven that the energy gap of the Req_3 ternary complexes is reduced as the conjugation length of the neutral ligand increases. Due to this fact, it is reasonable to conclude that the neutral ligand has played a significant role in determining the optical band gap. However the role of the rare earth metals on the optical band gap of the rare earth ternary complexes is not fully clarified. In order to evaluate such effect, a plot of $(\alpha h\nu)^2$ against $h\nu$ for the Req_3 ternary complexes based on the same neutral ligand are evaluate as shown in Figure 5.11 and 5.12. The band gap is determined by extrapolating the straight line portion of the plot to $\alpha h\nu=0$. As indicated in Figure 5.11, the band gap value obtained for Euq_3bpy_3 is slightly lower in comparison to that of Tbq_3bpy_3 .

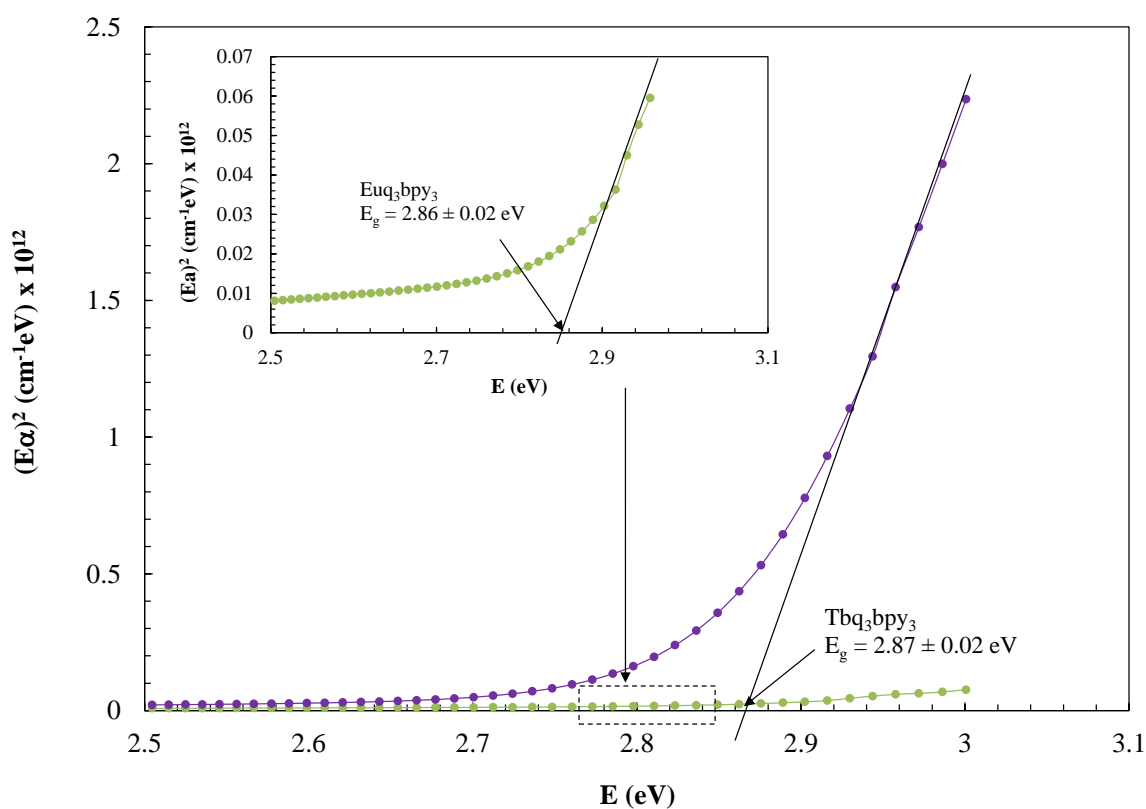


Figure 5.11 Graph of $(\alpha h\nu)^2$ vs $h\nu$ of (a) Euq_3bpy_3 and (b) Tbq_3bpy_3 thin film. The band gap can be extrapolated from a straight line to $h\nu = 0$

On other hand, the same trend was also observed for Req_3 ternary complexes with Phen as the neutral ligand in which the Eu^{3+} as the metal centre resulting a lower band gap compare to that of Tb^{3+} (Figure 5.12). The effect of the rare earth metals on this optical band gap is in accordance to the aforementioned analysis on the UV-Vis absorption spectroscopy in which the reduction of the band gap exhibited by Eu^{3+} is attribute to its stronger bonding that will result in higher π - π overlap and thereby lowering the band gap (Muhammad, et al., 2010).

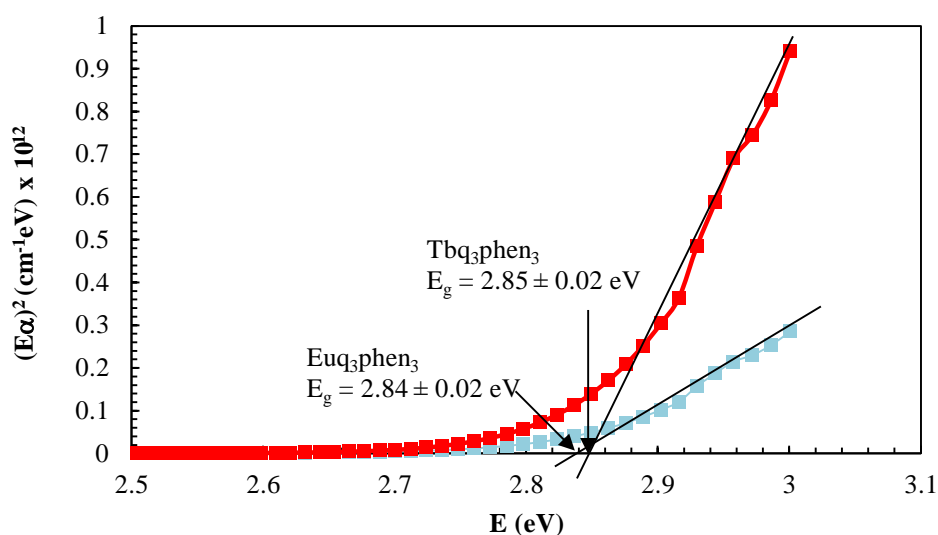


Figure 5.12 Graph of $(\alpha h\nu)^2$ vs $h\nu$ of (a) $\text{Euq}_3\text{phen}_3$ and (b) $\text{Tbq}_3\text{phen}_3$ thin film. The band gap can be extrapolated from a straight line to $h\nu = 0$

5.4. Photoluminescence study

The photoluminescence (PL) spectra of Euq_3bpy_3 , $\text{Euq}_3\text{phen}_3$, Tbq_3bpy_3 and $\text{Tbq}_3\text{phen}_3$ thin films are shown in Figure 5.13. Interestingly, all the complexes yields almost identical spectra with only small different detected in the intensity. With the excitation of 400 nm, it can be seen clearly that all complexes show broad and strong emission from the ligand in the range of 330-530 nm. The expected sharp Eu^{3+} luminescence peak at 580 nm, 590 nm, 615 nm, 650 and 690 nm that is due to the ($^5\text{D}_0 \rightarrow ^7\text{F}_0$), ($^5\text{D}_0 \rightarrow ^7\text{F}_1$), ($^5\text{D}_0 \rightarrow ^7\text{F}_2$), ($^5\text{D}_0 \rightarrow ^7\text{F}_3$) and ($^5\text{D}_0 \rightarrow ^7\text{F}_4$) transitions is absent (Zheng et al.).

The luminescence characteristics for Tb^{3+} metal ion that should be observed at 491, 549, 582 and 618 nm correspond to the f-f electronic transition of $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_3$ and $^5D_4 \rightarrow ^7F_2$ (Figure 5.13) is also not detected (Zheng, et al.). The absent of the luminescence characteristics of these complexes will be discussed later.

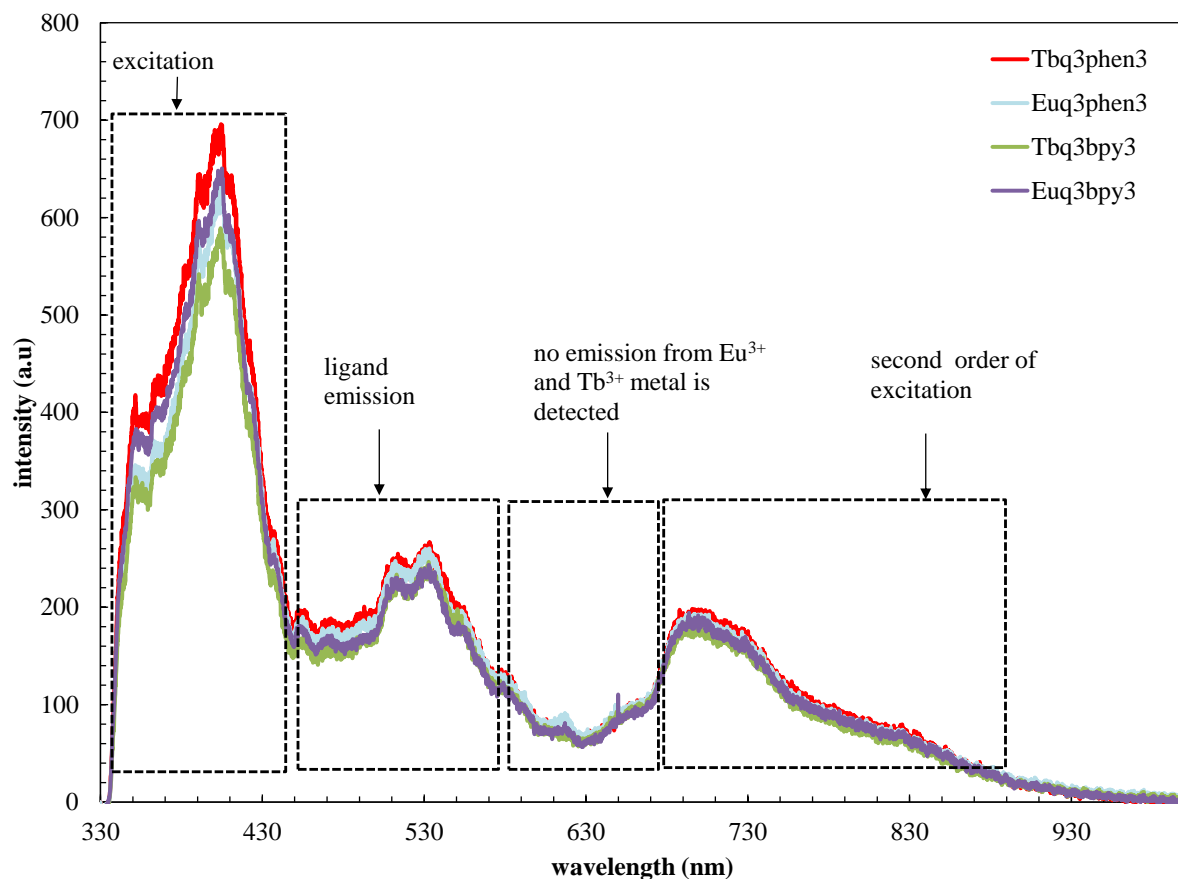


Figure 5.13 Re_q3 ternary complexes luminescence characteristics

A close inspection on the ligand emission in Figure 5.13 reveals that the emission characteristics demonstrated by all these Re_q3 ternary complexes resemble the emission characteristics of Alq_3 thin films. The same behavior was also observed by Thompson et al. which measured various rare earth quinoline, Re_q3 complexes and observed the PL arises solely from the ligand (Thompson, Blyth, Gigli, & Cingolani, 2004). The domination of the ligand emission in the photoluminescence spectra indicates that the intramolecular energy transfers from the ligand to the rare earth metals ion are

ineffective. This may be due to the fact that the triplet state of the 8Hq as the central ligand does not match with the energy of Eu^{3+} and Tb^{3+} in order to allow efficient energy transfer. The details of this inefficient energy transfer between these rare earth metals and the ligands will be discussed in the section 5.5.

On the other hand, it is also observed that all of these complexes exhibit the maximum PL peak at 530 nm. This value is found to be close to the value obtained by Fahmi et.al at 535 nm for Alq_3 thin films (Muhammad & Sulaiman, 2011). Therefore it is reasonable to attribute the ligand emission to contribution from the 8Hq ligand. It should be noted that the emission peak appearing at around 670- 830 nm is due to the undesired artifact originating from the second order of the excitation peak.

5.5. Energy transfer study

5.5.1. *Euq₃bpy₃ and Euq₃phen₃*

It is well known that the importance of the rare earth metal complexes is related to their interesting luminescence emission which arises from the electronic transition of the rare-earth metal (Belian, De Sa, Alves Jr, & Galembeck, 2010). The organic ligand that is coordinated to the rare earth metal play as the antenna role to absorb the energy and subsequently transferred it to the rare earth metals leading to the extremely sharp f-f transition (Evans, Douglas, & Winscom, 2006). Nevertheless such effect does not occur in these Req_3 ternary complexes as the PL spectra does not show any luminescence characteristics contribute from the rare earth metal. This undesired efficient deactivation of the rare earth metal luminescence can be explained from the energy transfer mechanism in more detail. The schematic diagram that represents the photosensitization mechanism which produced Eu^{3+} luminescence characteristic is depicted in Figure 5.14. Generally, the luminescence process can be explained as follow. Upon absorption of the

UV light by the ligand, the electron will excite from the ground state, S_0 to the singlet excited state, S_1 . After that, the excited electrons will either fall down to S_0 state and appears as the fluorescence or the ligand undergo a intersystem crossing (ISC) process through a non-radiative path to the lowest triplet state, T_1 of the ligand. It is noteworthy that direct energy transition from the S_0 to T_1 is spin forbidden. Therefore the energy transfer from S_0 is required to undergo an ISC process from S_1 to T_1 . The excited electrons in the T_1 will then either return to S_0 state and undergo non-radiative relaxation by emitting the phosphorescence produced by the ligand or the absorbed energy is transferred to the lowest excited state, 5D_0 of the central Eu^{3+} ion in the complex. These are the steps that are involved during the sensitization process where the ligand acts as an “antenna” or sensitizer to transfer the energy to the metal ion. The ligand to metal charge transfer (LMCT) process which transfer the energy of the triplet excited state of the ligand to the lowest excited state of the metal Eu^{3+} ion will consequently followed by an internal conversion to the emitting 5D_0 state. Then a transition from the excited state of 5D_0 to the 7F_j ($J=0-4$) occurs and thus the characteristics of red emission appear in the visible region.

In order to give an insight into the detailed of the energy transfer mechanism of the Euq_3bpy_3 and Euq_3phen_3 complexes, the energy level of the higher excited of 5D_j ($J=0,1,2,3$), singlet excited state, S_1 and triplet excited state, T_1 of 8Hq, Bpy and Phen ligand is listed in Table 5.1 and shown as a schematic energy diagram as in Figure 5.14. It is noteworthy that the singlet state of the central ligand can be estimated from the wavelength of the UV-Vis absorption edges of the europium complexes. However, this estimation is only valid if the energy absorption process is originated mainly from the central ligand. Since it has been proven in the previous UV-Vis absorption result that the neutral ligand in the Euq^{3+} ternary complexes dominates the absorption process, therefore it is invalid to estimate the value of singlet excited state of the 8Hq ligand

from the UV-Vis absorption spectra. Thus, the value is taken from the literature. Nevertheless, a direct estimation of the singlet excited state of the neutral ligand from the UV-Vis absorption edge is still consider inaccurate. This is because of the absorption process of a europium complexes is always governed by both central and neutral ligands. Therefore it is incorrect to say that the value of the singlet excited state determine in the spectra is the value of the singlet excited of these neutral ligand since the energy absorption is not solely produced from the neutral ligand as the central ligand also plays a role in absorbing the energy. Thus the singlet excited values of both Phen and Bpy ligands are also obtained from the literature.

Since the ligand triplet energy level cannot be directly identified from the absorption and photoluminescence spectra, as an approximation, the value from the literature is used. According to the literature, the triplet energy level for both ligands can be obtained from the phosphorescence spectra of $Gd(l)_3 \cdot 2H_2O$ where l , is referred to the corresponding ligand (Pan et al., 2011). This was explained in terms of the energy of the lowest excited state ${}^6P_{7/2}$ of Gd^{3+} ion is too high to accept energy from a ligand , therefore the data obtained from the phosphorescence spectra of the complexes actually reveal the triplet energy level of the corresponding ligand (Pan, et al., 2011). On the basis of the data above, the energy transfer process of both Euq_3phen_3 and Euq_3bpy_3 is explained as follow.

The energy transfer mechanism of Euq_3phen_3 and Euq_3bpy_3 complexes are illustrated in Figure 5.14. From the schematic diagram, it can be observed that both singlet excited, S_1 states and triplet excited states, T_1 of Phen/Bpy ligand are higher than that of 8Hq ligand. Therefore, two possible energy transfer mechanism in this complex is proposed since the participation of the neutral ligands (Phen and Bpy ligands) and the central ligand (8Hq) in this process are separated. The first possible mechanism involves the energy transfer from ground state, S_0 of the Phen/Bpy ligand to its own S_1 state. Then

the energy in the S_1 state is transferred to the S_1 state of 8Hq or to its own triplet level and subsequently to the T_1 state of 8Hq and finally to the 5D_0 level of Eu^{3+} . The second possible mechanism involves the energy transfer from 8Hq ligand. Specifically, the 8Hq ligand is excited to its S_1 state, and subsequently transfers the S_1 state to the T_1 state by intersystem crossing and finally transfers to the 5D_0 level of Eu^{3+} .

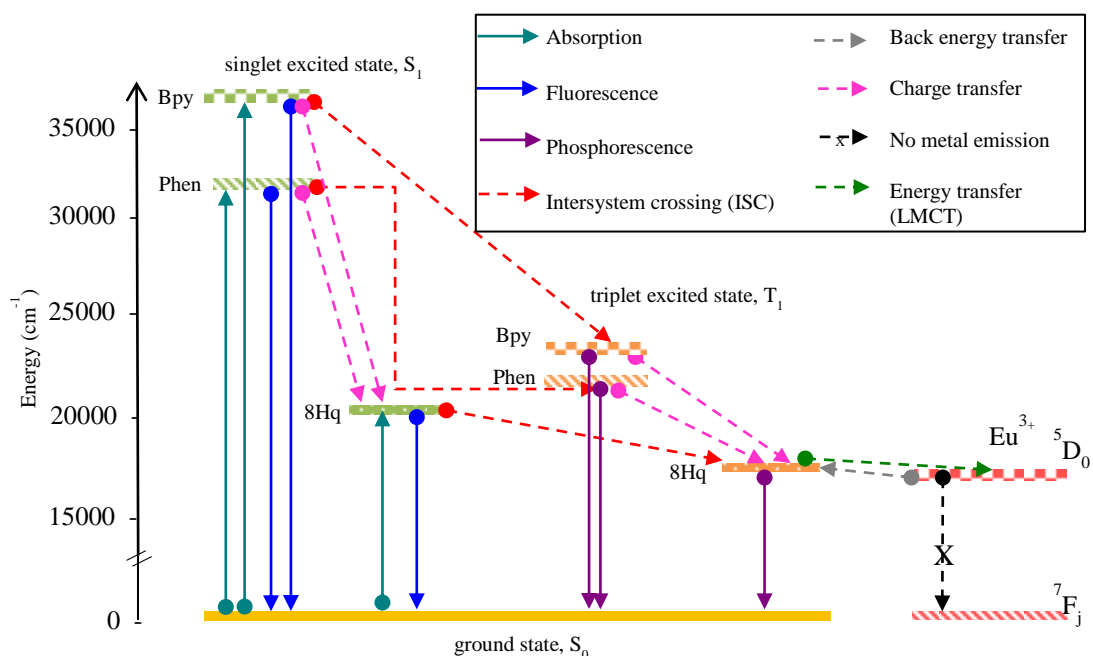


Figure 5.14 A schematic diagram of the proposed energy transfer process in the $\text{Euq}_3\text{phen}_3$ and Euq_3bpy_3 ternary complexes

It should be noted that none of the energy transfer occur between the 8Hq and Phen/Bpy ligands since the S_1 and T_1 states of Phen/Bpy ligands is too high to allow the transfer process. From these two proposed mechanism, it is obvious that the sensitization of 5D_0 state which is responsible for the emission characteristic of Eu^{3+} is performed by 8Hq ligand not the Phen/Bpy ligand. Therefore the T_1 state of 8Hq ligand is known as LMCT (ligand to metal charge transfer) state. Referring to the data listed in Table 5.1 and 5.2, it can be observed that 8Hq can only sensitized the 5D_0 state but not the other 5D_j ($j=1,2,3$) state. This is because the triplet energy of the 8Hq ligand lying at the value

below 5D_j ($j=1, 2, 3$) state but above 5D_0 state (Biju, et al., 2006). The higher emission level of Eu^{3+} in the 5D_j ($j=1, 2, 3$) state compare to LMCT state of 8Hq will cause a back energy transfer process. However the energy gap between the 8Hq ligand and the lowest excited state of Eu^{3+} is too low to allow an efficient sensitization process. The ineffective energy transfer can be explained from the Latva empirical rule that enquire $\Delta E ({}^3\pi\pi^*-{}^5D_0) > 2500 \text{ cm}^{-1}$ in order to have an optimal energy transfer process between the ligand and the metal (Latva et al., 1997). It should be noted that the denotation ${}^3\pi\pi^*$ means a transition from ${}^3\pi$ (ground state of the triplet) to π^* (excited state of the triplet). The energy gap $\Delta E ({}^3\pi\pi^*-{}^5D_0)$ between the 8Hq and 5D_0 state of Eu^{3+} which is approximately equal to $\sim 411 \text{ cm}^{-1}$ cause a strong influenced of back energy transfer and consequently defines the quenching of the Eu^{3+} emission. Therefore it is observed from the emission spectra of both Euq_3bpy_3 and $\text{Euq}_3\text{phen}_3$ complexes are mainly from the central ligand. These features present the nature of the dominating non-radiative emission. For instance, the lack of Eu^{3+} luminescence is ascribed due to the low energy gap that is unable to prevent back energy transfer from the Eu^{3+} excited state to the triplet state of the 8Hq ligand. Therefore, no Eu^{3+} luminescence should be observed from these complexes. From this analysis, it is obvious that the central ligand plays a very important role in sensitizing Eu^{3+} . Even though the adduction of Phen and Bpy ligand as the secondary ligand in the Euq^{3+} ternary complexes can provide a higher T_1 level to assist the sensitization, but it still cannot take the role of the 8Hq ligand in sensitizing the 5D_0 state of Eu^{3+} since the difference, $\Delta E ({}^3\pi\pi^*-{}^5D_0)$ is less than 2500 cm^{-1} . In fact, the role of the neutral ligand which is absorbing and transporting energy to the other ligand and central metal ion that consequently will enhance the Eu^{3+} is only valid if the energy difference between the emission level of Eu^{3+} and T_1 state of the central ligand, $\Delta E ({}^3\pi\pi^*-{}^5D_0)$ should be more than 2500 cm^{-1} . Therefore it is important to design a central ligand with the T_1 level is somewhat higher than the

emission level of Eu^{3+} with the optimal difference ΔE (${}^3\pi\pi^* - {}^5\text{D}_0$) should be more than 2500 cm^{-1} .

Table 5.1 Electronic transition of Eu^{3+} and Tb^{3+} from higher excited state with their assignments. These values are obtained from literature (Biju, Reddy, & Freire, 2007; T. Li et al., 2011)

Rare earth metal	Higher excited state (cm^{-1})	Assignments
Eu^{3+}	24800	${}^5\text{D}_3$
	21200	${}^5\text{D}_2$
	19000	${}^5\text{D}_1$
	17500	${}^5\text{D}_0$
Tb^{3+}	20500	${}^5\text{D}_4$
	24800	${}^5\text{D}_3$
	21200	${}^5\text{D}_2$
	19000	${}^5\text{D}_1$

Table 5.2 Triplet and singlet excited values for 8Hq, Bpy and Phen ligand

Ligand	Singlet state (cm^{-1})	Triplet state (cm^{-1})
8Hq	21834 (Maffeo & Williams, 2003)	17667 (Maffeo & Williams, 2003)
Bpy	36166 (Manas & Chen, 2000)	22900 (T. Li, et al., 2011; Yu & Su, 2003)
Phen	31250	22100 (T. Li, et al., 2011; Yu & Su, 2003; F. Zhang, Hou, Du, & Wu, 2009)

5.5.2. Tbq_3bpy_3 and $\text{Tbq}_3\text{phen}_3$

Generally, the photosensitization pathway that represents the photoluminescence process in Tbq_3 ternary complexes is similar as described in section 5.5.1 for Euq^{3+} ternary complexes. Basically, the photoluminescence process in the Tbq^{3+} ternary complexes involves four main process which are absorption that subsequently excite the energy from $S_0 \rightarrow S_1$, follow by intraligand charge transfer (ILCT) then intersystem crossing (ISC) or sometimes known as ligand to metal charge transfer (LMCT) and lastly an internal conversion to the emitting ${}^5\text{D}_4$ state which the Tb^{3+} emission characteristics will result in a green emission. In order to give insight the detailed of the energy transfer mechanism in the $\text{Tbq}_3\text{phen}_3$ and Tbq_3bpy_3 complexes, the schematic

diagram that represents the sensitization pathway is proposed and depicted in Figure 5.15.

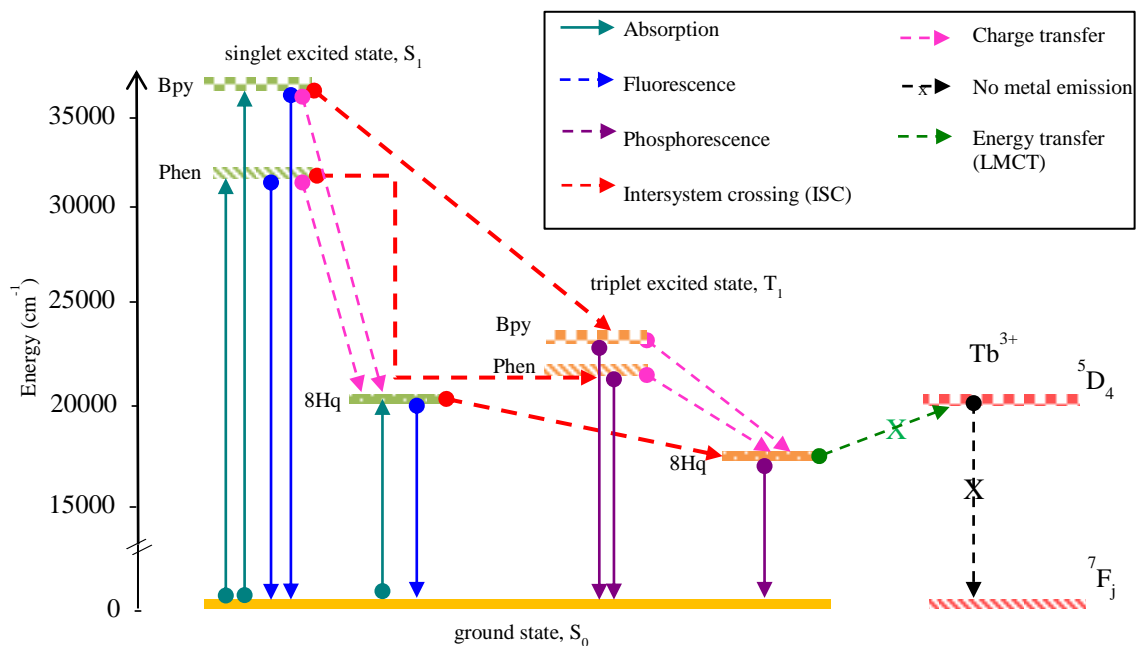


Figure 5.15 A schematic diagram of the proposed energy transfer process in the $\text{Tbq}_3\text{phen}_3$ and Tbq_3bpy_3 ternary complexes

The energy difference between the triplet level, T_1 state of the central ligand and the emission level of Tb^{3+} , ΔE (${}^3\pi\pi^* - {}^5\text{D}_4$) should be more than 2500 cm^{-1} in order to comply the Latva rule. Therefore it is important to design a central ligand with the T_1 level is somewhat higher than the emission level of Tb^{3+} with the optimal difference ΔE (${}^3\pi\pi^* - {}^5\text{D}_4$) should be more than 2500 cm^{-1} .

The energy level of the higher excited of ${}^5\text{D}_j$ ($J=1,2,3,4$) is listed in Table 5.1 while the singlet excited state, S_1 and triplet excited state, T_1 of 8Hq, Bpy and Phen ligand is listed in Table 5.1. On the basis of the data above, the energy transfer process of both $\text{Tbq}_3\text{phen}_3$ and Tbq_3bpy_3 is explained. It should be noted that the energy transfer pathway in the Tbq_3 ternary complexes is similar as the Euq^{3+} ternary complexes except

for the sensitization process that occur in the LMCT state is rather different. From the schematic diagram, it can be observed that the triplet excited state, T_1 of 8Hq (17667 cm^{-1}) ligand is slightly lower than 5D_4 level of Tb^{3+} (20500 cm^{-1}). Therefore no energy transfer from LMCT state to the Tb^{3+} could occur that will lead to the lack of Tb^{3+} emission. As was mentioned in section 5.5.1, in order to have an efficient LMCT process, the energy level of T_1 state must be somewhat higher than the emission level of Tb^{3+} and the optimal difference ΔE ($^3\pi\pi^*-^5D_4$) should be around 2500 cm^{-1} as complied in Latva rule. Therefore it is observed from the emission spectra of both Tbq_3bpy_3 and Tbq_3phen_3 complexes are mainly from the ligand since there is no energy transfer occurs at the LMCT state. These features present the nature of the dominating non-radiative process. Therefore, no Tb^{3+} luminescence should be observed from these complexes as evidence in the PL spectra.

From this analysis, it is obvious that the central ligand plays a very important role in sensitizing Tb^{3+} . Even though the adduction of Phen and Bpy ligand as the secondary ligand in the Tbq^{3+} ternary complexes can provide a higher T_1 level to assist the sensitization, but it still cannot take role of the 8Hq ligand to sensitize 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 Tb^{3+} is only valid if the energy difference between the emission level of Tb^{3+} and T_1 state obey the Latva rule.

5.5.3. Effects of the rare earth metals on the energy transfer mechanism of Req_3 ternary complexes

The variation on the energy transfer process between Euq_3 ternary complexes and Tbq_3 ternary complexes arises during the LMCT process. Since the LMCT process involve only energy transition from the T_1 state of the central ligand to the emissive state of the

rare earth metals, the schematic diagram that represents the sensitization process is focused on the energy transfer pathway from T_1 state and the emissive state of the rare earth metals depicted in Figure 5.16. The most significant aspect that is seen is that the emissive state of Eu^{3+} lies slightly below the T_1 state of 8Hq ligand, whereas the emissive state of Tb^{3+} lies higher than T_1 state of 8Hq ligand. Even though both complexes do not experience any metal luminescence, the effect of this occurrence is relatively different. The LMCT process from the 8Hq ligand to the Eu^{3+} experience a back energy transfer due to the lower energy gap ΔE (${}^3\pi\pi^*$ - 5D_0) between the triplet state of 8Hq and 5D_0 state of Eu^{3+} which is approximately equal to $\sim 411 \text{ cm}^{-1}$. However, the energy transfer from LMCT state to the Tb^{3+} could not occur due to the triplet excited state, T_1 of 8Hq (17667 cm^{-1}) ligand is slightly lower than 5D_4 level of Tb^{3+} (20500 cm^{-1}).

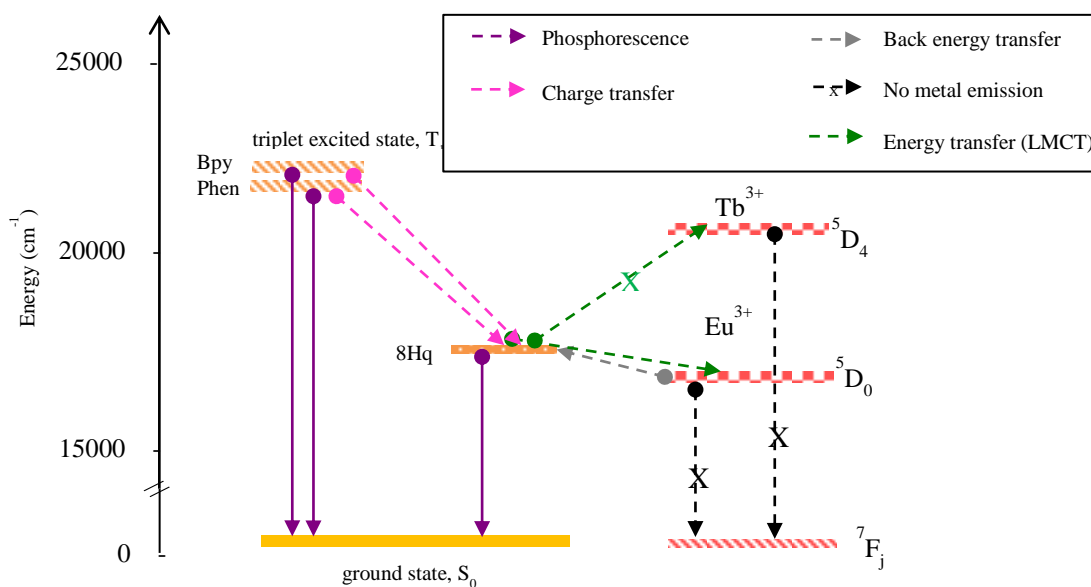


Figure 5.16 A schematic diagram of the proposed energy transfer process in Req_3 ternary complexes

5.6. Conclusion

Euq₃ and Tbq₃ ternary complexes have similar UV-Vis absorption spectra which confirm that assumption that the neutral ligand dominates the absorption process of the Req₃ ternary complexes despite of different rare earth metal cations of Eu³⁺ and Tb³⁺. However, Tbq₃ ternary complexes will experience stronger electronic effect and cause more π - π overlap leading to the reduction in the energy band gap compared to that of Euq₃ ternary complexes. From Tauc relation it can be prove that the electronic transitions for these complexes are direct with the energy band gap of Euq₃ ternary complexes are slightly lower compared to that of Tbq₃. Photoluminescence study indicates that the ligand emission is dominant in all Euq₃ and Tbq₃ ternary complexes implying that the intermolecular energy transfer from the ligand to the rare earth metal ions are ineffective. The energy transfer process for all Euq₃ and Tbq₃ are then explained schematically. It can be concluded that the energy transfer from LMCT state to the Eu³⁺ and Tb³⁺ could not occur as the Latva rule is not complied.