Junction properties and conduction mechanism of new terbium complexes with triethylene glycol ligand for potential application in organic electronic device

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Abstract: Terbium-picrate triethylene glycol (EO3-Tb-Pic) complex was prepared in thin film and single layer device structure of ITO/EO3-Tb-Pic/Al, using spin coating technique. The UV-Vis absorption spectroscopy analysis was performed to evaluate the electronic molecular transition of the complex. The optical band gap, \( E_g \) estimated from the Tauc model revealed that EO3-Tb-Pic thin film exhibited a direct transition with \( E_g \) of 2.70 eV. The electronic parameters of the ITO/EO3-Tb-Pic/Al device such as the ideality factor \( n \), barrier height \( \Phi_b \), saturation current \( I_o \), and series resistance \( R_s \), were extracted from the conventional \( \ln(I)-V \) plot, Cheung’s functions and Norde’s method. It was found that the evaluated parameters calculated from Norde’s and Cheung’s methods were consistent with those calculated from the conventional \( I-V \) method. In the double logarithmic \( I-V \) plot, three distinct regions based on the slope were identified, and the conduction mechanisms were discussed and explained. The mobility, \( \mu \) value was estimated from SCLC region as 2.58×10⁻⁷ cm²/(V·s). This newly obtained lanthanide complex may be potentially utilized in electronic devices.

Keywords: terbium-picrate complex; triethylene glycol; Tauc model; optical band gap; current-voltage; rare earths

Lanthanide complexes are one type of optoelectronic functional material that has been used in the organic semiconductor application, especially in organic light emitting devices (OLED)\(^\text{[1]}\). Their attractive features that offer nearly monochromatic luminescent emitters with emission peaks covering a broad spectral range in the visible region have fascinated researchers for decades\(^\text{[1–3]}\). The excellent pure emission possessed by these materials is known to originate from their specific electronic structure that is due to the f-f transitions in the 4f orbitals which is well shielded by closed 5s and 5p shells\(^\text{[2–4]}\).

Therefore, the emission characteristic from these materials is expected to be very narrow and leads to the high radiative quantum yield. This particular property makes lanthanide complexes, especially europium (Eu) and terbium (Tb) attractive candidates employed as an electroluminescence emitter in OLED\(^\text{[3]}\).

Terbium-picrate triethylene glycol (abbreviated hereafter as EO3-Tb-Pic) is of special interest to many researchers. It is because the acyclic polyether ligands possess a pseudo-cyclic like crown ether conformation which will provide greater stability for the complexes\(^\text{[5]}\). Moreover, the ability of the triethylene glycol (EO3) ligand to satisfy the coordination requirements of the Ln(III) center with a high coordination number is an important criterion in the design of a green emitter center for applications associated with organic light emitting diodes (OLEDs)\(^\text{[6]}\). The promising result from photoluminescence reported from our previous work indicated that EO3-Tb-Pic is a suitable candidate as organic semiconductors, especially in OLED application\(^\text{[5]}\). However, the previous research on EO3-Tb-Pic focuses mainly on the innovations in crystallography, structural and photoluminescence properties. Less attention has been paid on the electrical properties, despite the fact that they are the main factors that affect the device characteristics of an OLED. Moreover, a comprehensive knowledge regarding the electrical behavior of metal/organic semiconductor and charge conduction mechanism at an interface is essential as it is among the main factors that will also reflect and influence the device behavior.

Current-voltage (\( I-V \)) measurement plays an important role in characterization of device parameters. It has been proven to be one of the techniques for identifying and characterizing the charge conduction phenomenon in various organic semiconductor materials. Moreover, the various electronic parameters of electrical behavior of EO3-Tb-Pic/Al interface may lead to the estimation of several electronic parameters such as the ideality factor, \( n \), barrier height, \( \Phi_b \), saturation current, \( I_o \) and series resistance, \( R_s \).

As an extension of this work, the optical behavior of
EO3-Tb-Pic in the thin film form was further analyzed by assessing the UV-Vis absorption measurement. Their band gap transition and optical band gap, $E_g$ was determined by using the Tauc model. The electrical behavior and device characteristic of ITO/EO3-Tb-Pic/Al were evaluated by means of current-voltage measurement. The charge conduction mechanism was predicted through the double logarithmic $I$-$V$ plot according to the power law relation whereas the estimation of the electronic parameters was made via the well-known modified Shockley equation by assuming the thermionic model. Three different methods which are the conventional $\ln$ $I$-$V$ method, the Cheung’s function and the modified Norde’s function are utilized to extract these electronic parameters.

1 Experimental

1.1 Device fabrication and measurement

The molecular structure of EO3-Tb-Pic compound is shown in Fig. 1(a)\textsuperscript{5} and details on the synthesis method employed were similar to those described elsewhere\textsuperscript{5}. In order to fabricate the organic semiconductor device, the EO3-Tb-Pic thin film was spin coated to an overall of 330.6±0.1 nm over the glass and indium tin oxide (ITO) coated glass substrates. Consequently, top contact aluminium (Al) electrode was thermally evaporated on top of the EO3-Tb-Pic thin film at a pressure of approximately $10^{-3}$ Pa with a deposition rate of 0.5 A/s. The schematic diagram of the single-layer device configuration, ITO/EO3-Tb-Pic/Al, is shown in Fig. 1(b). Analysis of the optical properties of EO3-Tb-Pic thin film was performed using UV-VIS/NIR Spectrometer (model Jasco 570). The electrical properties of ITO/EO3-
Tb-Pic/Al were evaluated from the current-voltage (I-V) using a Keithly 236 Source Measurement Unit (SMU).

1.2 Determination of optical band gap transition $n$ and band gap $E_g$

One of the important parameters that govern the optical characteristics of organic semiconductor materials is the optical band gap, $E_g$. It is commonly used to estimate the energy separation between HOMO and LUMO of the organic semiconductor materials. According to Fujii et al., optical band gap, $E_g$ can be well analyzed at the absorption edge in terms of band-to-band transition concept\([7]\). Absorption coefficient, $\alpha$ is well known to play an important role in determining the optical band gap, $E_g$. It can be calculated by exploiting Beer Lambert law equation:

$$I = I_0 \exp(-\alpha t)$$  \hspace{1cm} (1)

In Eq. (1), $I_0$ is the intensity of the incident light and $t$ is the material thickness. The value of the absorption coefficient, $\alpha$ is generated from $\alpha = 2.303A/h\nu$ where $A$ is the absorbance intensity. By assuming that the absorption edge tends to possess a parabolic variation with the photon energy, $\nu$, optical band gap, $E_g$ can be estimated by the Tauc relation\([8]\):

$$\alpha \nu = \alpha_0 (\nu - E_g)^n$$ \hspace{1cm} (2)

in which $\alpha_0$ is the energy independent constant and $m$ is the value to determine type of $E_g$ transition either is direct transition ($m=1/2$) or indirect transition for ($m=2$). In order to estimate $m$, a new equation is generated by applying the natural logarithm and the derivation of Eq. (2). This equation is expressed as below:

$$\frac{d \ln(\alpha \nu)}{d \nu} = \frac{m}{\nu E_g}$$ \hspace{1cm} (3)

From Eq. (3), graph of $d \ln(\alpha \nu)/d \nu$ is plotted in order to obtain the initial value of $E_g$. It is worth noting that these values are just the initial values that will be utilized for plotting a graph of $\ln(\alpha \nu)$ vs $\ln(\nu - E_g)$. The slopes of the graph enable the estimation value of $m$. A graph of $(\alpha \nu)^2/E$ is then plotted in order to evaluate the value of $E_g$ more precisely. The extrapolated intercept of the linear portion of the graph at $(\alpha \nu)^2=0$, yield the value for optical band gap, $E_g$.

1.3 Method of diode parameter extraction from current-voltage (I-V) characteristics

1.3.1 Conventional $\ln I$-$V$ method

The Schottky junction that formed between the organic semiconductor materials, and the metal contact enable the extraction of some important diode parameters such as the ideality factor $n$, barrier height $\Phi_b$, saturation current $I_s$ and series resistance $R_s$. Under forward bias and within the lower voltage region, current, $I$ obey the thermionic emission. The general equation describing the current, $I$ is given by Sze et al.\([9]\) as

$$I = I_s (\exp(\frac{qV}{nkT}) - 1)$$ \hspace{1cm} (4)

where $V$ is the voltage, $I$ is the current, $I_s$ is the saturation current, $n$ is the ideality factor, $k$ is the Boltzmann constant, $T$ is the absolute temperature and $q$ is the electronic charge. In Eq. (4) the saturation current, $I_s$ can be expressed as\([10,11]\),

$$I_s = A A' \exp(-\frac{q \Phi_b}{kT})$$ \hspace{1cm} (5)

In Eq. (5), $A$ is the geometrical area of the diode, $\Phi_b$ is the Schottky barrier height and $A'$ is the effective Richardson constant. The Schottky barrier height, $\Phi_b$ is obtained from Eq. (5), and can be expressed as:

$$q \Phi_b = kT (\frac{A A' T^2}{I_s})$$ \hspace{1cm} (6)

The ideality factor, $n$ is given by relation\([10,11]\),

$$n = \frac{q}{kT} \frac{dV}{d(\ln I)}$$ \hspace{1cm} (7)

1.3.2 Cheung’s method

The Cheung’s function is expressed as follows:

$$\frac{\partial V}{\partial (\ln I)} = \frac{I R_s + n kT}{q}$$ \hspace{1cm} (8)

$$H(I) = V - \frac{kT}{q} \ln \frac{I_s}{AA'T^2}$$ \hspace{1cm} (9)

and,

$$H(I) = IR_s + n \Phi_b$$ \hspace{1cm} (10)

where $R_s$ is the series resistance, $n$ is the ideality factor and $\Phi_b$ is the effective barrier height. A linear plot of $dV/d(\ln I)$-$dV$ will give the approximate value of $R_s$ while the $y$-axis intercept will give the $nkT/q$ value\([12,13]\). Similarly the plot of $H(I)$-$I$ determines series resistance, $R_s$ and the effective barrier heights, $\Phi_b$, values\([12,13]\).

1.3.3 Norde’s method

The Norde’s method is expressed mathematically as:

$$F(V) = \frac{V - \frac{kT}{q} \ln \frac{I(V)}{AA'T^2}}{\gamma}$$ \hspace{1cm} (11)

where $\gamma$ is the integer (dimensionless) greater than $n$. $I(V)$ is the current obtained from the $I$-$V$ characteristic measurement.

The value of the barrier height, $\Phi_b$ is evaluated by exploiting the minimum point of $F(V)$ using the following equation:

$$\Phi_b = F(V_0) + \frac{V_0}{\gamma} \frac{kT}{q}$$ \hspace{1cm} (12)

where $F(V_0)$ is the minimum value of $F(V)$ and $V_0$ is the corresponding voltage. The series resistance, $R_s$ is estimated by means of

$$R_s = \frac{kT(\gamma - n)}{qI}$$ \hspace{1cm} (13)

1.4 Charge conduction mechanism analysis

The conduction mechanism in these devices can be predicted from the double logarithmic $I$-$V$ characteristics
with the current following the power law exponent in the form of $I/V^l$ where the value of $l$ defines the type of conductions and the fitted slope determines the value of $l$. The charge transport through the organic semiconductor layer can be divided into three different regimes as shown in Fig. 1(c) where for ohmic ($l=1$), space charge limited, SCLC ($l=2$) and trap-filled space charge limited ($l>2$).

The current, under SCLC is expressed as\cite{14}

$$I = \frac{9\varepsilon_0 \mu t V^2}{8d^2}$$

where $\varepsilon_0$ is the permittivity of the organic film, $\mu$ is the charge carrier mobility, $d$ is the gap between the electrodes and $V$ is the applied voltage. In Eq. (14), $\theta$ is the ratio of free to trapped charges and is related to the density of the charge carrier, $P_0$ and trapped carrier, $P_t$ are given as\cite{13}:

$$\theta = \frac{P_0}{P_0 + P_t}$$

The value of the trapped factor, $\theta$ may be calculated as\cite{13}:

$$\theta = \frac{I_1}{I_2}$$

$I_1$ and $I_2$ are the ratio of the current densities at the beginning and the end of region II.

2 Results and discussion

2.1 Optical properties

The electronic transitions of EO3-Tb-Pic thin films on a glass substrate are evaluated from the UV-Vis absorption spectrum as shown in Fig. 2(a). It can be observed that a peak appeared at 360 nm in the Soret band. This absorption peak corresponds to the promotion of an electron from EO3 ligand $\pi$-orbital to the HPic ligand $\pi^*$-orbital. Such transition can be described as LLCT [$\pi$(EO3) $\rightarrow \pi^*$(HPic)] where LLCT is defined as a ligand to ligand charge transfer. On the other hand, the presence of the Q-band, with the peak maximum at 420 nm, is ascribed to the LLCT [$\pi$(HPic) $\rightarrow \pi^*$(EO3)] transition.

From the above analysis, it is apparent that the absorption process is controlled mainly by the organic ligand. The result obtained is also consistent with the expectation that the presence of the organic ligand in the EO3-Tb-Pic thin film would overcome the limitation of an intrinsically small molecular absorption coefficient for the Tb$^{3+}$. This phenomenon can be explained from the sensitization process or “antenna effect”, a concept proposed by Lehn where a distinct absorption, energy transfer and emission sequence operate\cite{15}.

2.2 Band gap analysis

The plot of $d\ln(\alpha hv)/dhv-E$ from Eq. (3) is shown in Fig. 2(b). It is apparent that the maximum peak of the graph exhibits the initial values of $E_g=2.62\pm0.02$ eV. By utilizing this initial value of $E_g$, graph of $\ln(\alpha hv)$ vs $\ln(hv-E_g)$ as shown in Fig. 3(a) is plotted to assess the optical band gap transition, $m$. The slope of the graph allows one to obtain the value of $m=1/2$. This suggests that EO3-Tb-Pic undergoes direct allowed optical transitions. This estimation also successfully provides evidence for the existence of a direct band gap between the energy bands and is in agreement with other findings of metal complexes\cite{16}. A graph of $(\alpha hv)^2-E$ as illustrated in Fig. 3(b) is then plotted in order to evaluate the value of $E_g$ more precisely. The extrapolated intercept of the linear portion of the graph at $(\alpha hv)^2=0$, yield the value for optical band gap, $E_g=2.70\pm0.02$ eV.

2.3 Current voltage ($I-V$) characteristics

Fig. 4(a) shows $I-V$ characteristic of ITO/EO3-Tb-Pic/Al. Apparently, there is a considerably large turn on voltage of 8 V observed in the forward bias region. This behavior is believed to be related to the wide-band gap of the EO3-Tb-Pic. It is known that wide-band gap material requires large enough electric field to generate charge

\[\text{Fig. 2 UV-Vis absorption spectrum (a) and dln(\alpha hv)/dhv-E plot (b) of EO3-Tb-Pic thin film}\]
 carriers and further induced the electronic transition energy into the range of visible light. Therefore, EO3-Tb-Pic is found to exhibit well-defined luminescent characteristics as evidence from our previous published report\[^{5}\]. However, there is no light emitted from this device even when observed at 10 V. This is possibly attributed to the triplet-triplet annihilation and quenching effects associated with the relatively long excited state lifetimes due to the phosphorescence nature of the EO3-Tb-Pic\[^{5}\].

The semi-logarithmic plot of the forward bias characteristic is shown in Fig. 4(b). The characteristic shows an exponential behavior at the lower voltage region (0–0.8 V) and then deviates from the exponential at the higher voltage region (V>0.8 V). The characteristic of the linear part of the exponential region is known to depend on the three important electrical parameters which are the ideality factor, \( n \), saturation current, \( I_0 \) and barrier height, \( \Phi_b \).

The extrapolated intercept of the linear portion in Fig. 4(b) with the \( I \) axis at \( V=0 \) V, yields the value for \( I_0=1.39\times10^{-9} \) mA. It is worth noting that this saturation current, \( I_0 \) describes the number of charge carriers that are able to overcome the barrier\[^{10–12}\].

Using the graphically obtained value for saturation current, \( I_0 \) and a value of Richardson constant, \( A'\sim10^{-2} \) A/cm\(^2\)/K\(^2\) (as derived for organic semiconductor in literature\[^{17}\]), the Schottky barrier height, \( \Phi_b \) calculated from Eq. (6) yields a value of 0.40 eV. The ideality factor, \( n \) determined from the slope of the exponential regime of semi-logarithmic I-V characteristics (Fig. 4(b))\[^{18,19}\] yields a value of 3.4. The deviations of the diode ideality factors from unity signify the presence of the trap-assisted recombination that often occurs in organic semiconductor devices\[^{20}\]. Moreover, the high turn-on voltage exhibited by this device may also contribute to the large ideality factor, \( n \). The other factors such as the fabrication-induced defects at the interface, the recombination of holes and electrons in the depletion region as well as the increase of the diffusion current due to the applied voltage may also cause the ideality factor, \( n \) to deviate from unity\[^{21}\].
It is known that the non-linear behavior at the high-voltage region $V > 0.8$ V, which is reflected in the downward curvature of the forward bias semi-logarithmic $I-V$ plot is an evidence of series resistance, $R_s$ effect. The value of series resistance, $R_s$ can be evaluated by using a method developed by Cheung’s expressed as Eqs. (8, 9 and 10). It is evident from Eq. (8), that the experimental value for series resistance, $R_s$ and ideality factor, $n$ can be obtained by plotting the forward bias, $I-V$ characteristic in the form of $dV/d\ln I$. The differentiated characteristic as function of voltage, displayed in Fig. 5(a) clearly shows a linear behavior. From Eq. (8), a slope of the plot yields the value for series resistance, $R_s=924$ Ω whereas the intercept of the plot, yields the value for ideality factor, $n=3.5$. In order to identify the consistency of the Cheung’s method in the case of series resistance, $R_s$, a $H(I)-I$ plot has been realized. Using the above-mentioned value of the ideality factor, $n$, together with the forward bias, $I-V$ data in Eq. (9), values of $H(I)$ are calculated. $H(I)$-I Characteristics is shown in Fig. 5(b). Similar to the $dV/d\ln I$ characteristics of Fig. 5(a), Fig. 5(b) also exhibits a straight line. It is well established that the value of series resistance, $R_s$ can be calculated from the slope of Fig. 5(b) yielding a value $R_s=926$ Ω. On the other hand, a value of Schottky barrier height, $\Phi_b$ is also calculated from the $y$-axis intercept, which is equal to $n\Phi_b$. Considering the same value of the ideality factor, $n$ and the $y$-intercept in Fig. 5(b), a value of $\Phi_b=0.45$ eV is obtained. Through these results, it is seen that the extracted parameters are in agreement with those obtain from conventional $I-V$ method.

Generally, a high series resistance can hinder an accurate evaluation of barrier height, $\Phi_b$. Due to this fact, an alternative method known as the modified Norde’s method is proposed to deduce the value of Schottky barrier height, $\Phi_b$ [22]. The plot of $F(V)-V$ of the device is shown in Fig. 6(a). The value of the barrier height, $\Phi_b$ and series resistance, $R_s$ can also be evaluated by exploiting the minimum point of $F(V)$ using Eqs. (12 and 13). The Schottky barrier height, $\Phi_b$ for ITO/EO3-Tb-Pic/Al is calculated to be 0.47 eV. Meanwhile, the series resistance, $R_s$ is found to be 928 Ω. It is worth noting that
these parameters are in agreement with those obtained by the ln-I-V and Cheung’s method. The ideality factor, $n$, Schottky barrier height, $\Phi_b$, and series resistance, $R_s$, are evaluated from the conventional I-V method, the Cheung’s function and Norde’s method are tabulated in Table 1.

### 2.4 Charge conduction mechanism

Information about the proposed charge conduction mechanism in the device can be obtained from the double logarithmic $I$-$V$ characteristics. In order to explain the possible conduction mechanisms of the ITO/EO3-Tb-Pic/Al device, the double logarithmic $I$-$V$ plot in Fig. 6(b) is marked with regions I, II and III. It can be seen that the slope of the region I is equal to 1.1. Such behavior indicates the predominance of ohmic conduction.

As the voltage increases, the slope of region II is found to increase to 2.2, suggesting the current, $I$, experiences a phenomenon known as space charge limited current (SCLC). In this region, the number of carriers injected into the sample will exceed the number of acceptor charge in the sample which in turn will form a space charge to limit the current flow. Using the value of the trapped factor, $\theta$, obtained from Eq. (16), the mobility, $\mu$, can be estimated from Eq. (14) as $2.6 \times 10^{-7}$ cm$^2/(V\cdot s)$. The obtained mobility of EO3-Tb-Pic thin film is comparable to the values obtained by the other organic semiconductor materials which are usually $<10^{-2}$ cm$^2/(V\cdot s)^{[23]}$.

As the applied voltage is further increased, the slopes in region III become more abrupt with the value of 7.7. Such behavior is in accordance with the characteristics of a trap charged limited current (TCLC) conduction. In this region, the current, $I$, is controlled by exponential distribution of trap levels where the trap sites start to be filled by electrons.

### 3 Conclusions

The electronic properties of ITO/EO3-Tb-Pic/Al were studied by means of $I$-$V$ measurement. The derived electronic parameters were summarised. The EO3-Tb-Pic/Al showed a behavior consistent with Schottky diode. It was established that the values of the ideality factor, $n$, saturation current, $I_o$ and barrier height, $\Phi_b$ were extracted according to thermionic emission theory in the region of low forward voltage from I-V characteristic. It was evident that series resistance, $R_s$ was significant in the downward curvature of the forward I-V characteristic, however ideality factor, $n$, saturation current, $I_o$ and barrier height, $\Phi_b$ were significant in the both regions. The evaluated parameters calculated from Norde’s and Cheung’s methods were consistent with those calculated from the conventional I-V method. The charge conduction mechanism was proposed at different voltage regions from double logarithmic I-V plot which in the low-voltage region, charge conduction was dominated by ohmic conduction while at higher voltages, conduction mechanism changed to SCLC conduction with exponential trap distribution.

### References:


