Photophysical Properties and Energy Transfer Mechanism in PFO/TiO$_2$/MEH-PPV Nanocomposite Thin Films

(Sifat Fotofizikal dan Mekanisma Pemindahan Tenaga dalam Filem Nipis Nano Komposit PFO/TiO$_2$/MEH-PPV)

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ABSTRACT

Improvement in photophysical properties of poly-9,9-dioctylfluorene (PFO)/10 wt. % TiO$_2$ nanoparticle thin film as a result of systematic additions of poly(2-methoxy-5(2-ethylhexyl)-1,4-phenylenevinylene (MEH-PPV) were investigated. The nanocomposite blends were prepared with additions of MEH-PPV up to 3.0 wt. % of the total weight. All blends were prepared using the solution blending method and subsequently spin-coated onto glass substrates. The UV-V absorptions and photoluminescence characterizations showed the intensification of the primary-color emissions of the thin films with the Förster resonance as the primary energy transfer mechanism from PFO to MEH-PPV. Important photophysical parameters, such as the Förster radius ($R_o$), excited state lifetime ($\tau$), fluorescence quantum yield of the donor ($\phi$), quenching constant ($k_qv$), quenching rate constant ($k_q$), distance between the donor and acceptor ($R$), energy transfer lifetime ($\tau_{ET}$), and energy transfer rate ($k_{ET}$) display better values with increasing the contents of MEH-PPV by 2.5 wt. %, suggesting an ordered improvement on the photophysical properties of the thin film. Finally, a possible underlying mechanism describing the enhancement of the photophysical properties was proposed.

Keywords: Donor/acceptor; energy transfer properties; Förster resonance energy transfer; optical properties

ABSTRAK

Peningkatan sifat fotofizikal filem nipis adunan poli-9,9-dioktilfluorin (PFO)/10 bt. % nanozarah TiO$_2$, dengan penambahan secara sistematik poli(2-metoksi-5(2-etilheksil)-1,4-fenileenevinilene (MEH-PPV) adalah dibuktikan. Adunan nanokomposit ini disediakan dengan menambah MEH-PPV sehingga 3.0 bt. % daripada berat keseluruhan. Kesemua adunan disediakan menggunakan teknik adunan larutan dan kemudianya dimendapkan ke atas substrat kaca menggunakan teknik salutan berputar. Pencirian penyerapan UV-Vis dan fotoluminesens menunjukkan peningkatan jantaman pancaran filem nipis dengan pemindahan tenaga resonons Förster sebagai mekanisma pemindahan tenaga primer daripada PFO kepada MEH-PPV. Semua parameter fotofizikal yang penting seperti jejari Förster ($R_o$), jangka hayat keadaan teruja ($\tau$), hasilan kuantum pendarfluor oleh perderma ($\phi$), pemalar pelindapkejutan ($k_qv$), pemalar kadar pelindapkejutan ($k_q$), jarak antara penderma dan penerima ($R$), jangka hayat pemindahan tenaga ($\tau_{ET}$) dan kadar pemindahan tenaga ($k_{ET}$) menunjukkan nilai yang lebih baik dengan penambah MEH-PPV sekaligus membuktikan penambahbaikan yang teratur terhadap sifat fotofizikal filem nipis. Dengan kehadiran nanozarah, keamatan sinaran warna primer telah meningkat dengan pancaran yang seimbang antara PFO dan MEH-PPV berjaya dicapai pada kandungan MEH-PPV sebanyak 2.5 bt. %, mencadangkan peningkatan yang teratur pada sifat fotofizikal filem nipis. Kesimpulannya, mekanisma yang sesuai untuk menerangkan peningkatan sifat fotofizikal turut dicadangkan.

Kata kunci: Pemindahan tenaga resonon Förster; penderma/penerima; sifat optik; sifat pemindahan tenaga

INTRODUCTION

Despite great advancement in display technologies, fabrication of excellent white organic light-emitting diodes (WOLEDs) continues to attract the attention of researchers worldwide. Generally, WOLEDs can be obtained from diode emission of various wavelengths in the visible region of the electromagnetic (EM) spectrum. However, it is very challenging to produce this type of diode, particularly when using single active material. An alternative approach is the combination of primary lights produced by selective polymer-polymer blends (Lee et al. 2019; Zhang et al. 2017; Zhou et al. 2018). One of the combinations with the most potential is a blend of poly-9,9-dioctylfluorene (PFO) and
poly(2-methoxy-5 (2-ethylhexyl)-1,4-phenylenevinylene (MEH-PPV) (Cossiello et al. 2010; Madhwal et al. 2010; Prakash & Katiyar 2016). In this blend, PFO with highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of -5.8 and -2.6 eV, respectively, acts as a donor, while MEH-PPV (HOMO of -5.3 and LUMO of -2.8 eV) (Shin et al. 2009) acts as an acceptor. The energy transfer mechanism between these polymers has been confirmed to be Förster resonance energy transfer (FRET) (Cossiello et al. 2010).

Initial work on this blend focused on achieving efficient energy transfer (Liu et al. 2001). Since then, the successful fabrication of WOLEDs using this polymer combination has been reported (Huang et al. 2006; Kasperek & Blom 2017; Shen et al. 2006; Shin et al. 2009). However, optophysical issues, such as limited brightness and luminance efficiency, continue to be the major challenges related to PFO/MEH-PPV-based WOLEDs. To overcome these challenges, several approaches have been proposed such as the fabrication of multilayered polymers (Yan et al. 2015), introduction of an electron-injection and a hole-blocking layer (Yang & Zhuang 2011), as well as the addition of conducting and semiconducting nanoparticles (Al-Asbahi 2018).

The WOLEDs based on the PFO/MEH-PPV blend can only be fabricated under two conditions, that is, if incomplete energy transfer occurs and both polymers have the same emission intensity to cover the whole visible spectrum (Shen et al. 2006). To achieve these conditions, the maximum ratio of MEH-PPV in the blend was limited to 1 wt. % (Shin et al. 2009). Researchers have argued that the luminance efficiency of OLEDs can be improved by increasing the acceptor ratio (Al-Asbahi et al. 2013a; Su et al. 2005). Unfortunately, an earlier study showed that a high acceptor concentration is not favored due to the formation of dark quenchers (Thomas et al. 2014). Moreover, the addition of more acceptor only causes a dramatic reduction in the PFO emission intensity without meaningful increment in the MEH-PPV emission intensity itself (Huang et al. 2006). As a result, low-efficiency OLEDs with yellowish emission are produced. Complete quenching of the PFO emission was reported at a ratio of 4 wt. % and above (Liu et al. 2001).

The best strategy to enable the addition of more acceptor to the blend is to increase the emission intensity of the donor. Earlier studies on PFO/TiO$_2$ nanocomposite OLEDs showed that this strategy is possible (Al-Asbahi 2016; Al-Asbahi et al. 2017; Huang et al. 2018). It has been proven that the addition of 10 wt. % of TiO$_2$ nanoparticles (NPs) remarkably enhances the brightness and efficiency of PFO-based OLEDs through a mechanism known as the charge trapping effect (Jumali et al. 2012). Interestingly, in a subsequent study, the addition of 10 wt. % of TiO$_2$ NPs to a thin film of the PFO/F7GA blend not only inhibited the formation of dark quenchers but also led to an improved OLED performance (Al-Asbahi 2017). Furthermore, the high values of important FRET parameters support the argument that the energy transfer is more efficient in the presence of TiO$_2$ NPs.

In this study, the strategy used to enhance the photoluminescence (PL) efficiency of thin films of white PFO/MEH-PPV polymer blends were to increase the emission of the donor. Based on earlier work (Al-Asbahi 2017), all blends were prepared using a constant TiO$_2$ NP concentration (10 wt. % PFO) while systematically increasing the MEH-PPV concentration (up to 3.0 wt. % PFO). The aim of this work was to increase the limited ratio of the acceptor (MEH-PPV) in PFO/MEH-PPV blends as potential material for WOLEDs. In addition, the energy transfer properties of PFO/MEH-PPV/TiO$_2$ nanocomposite blends are investigated in more detail in this work. Finally, a suitable mechanism to describe the results is proposed.

**MATERIAL AND METHODS**

Raw materials used in this work which were PFO (Mw = 58200), MEH-PPV (Mw = 51000), and TiO$_2$ NPs (P25 Degussa) were purchased from Sigma Aldrich while toluene was bought from Fluka. The solutions were prepared using the solution blending method. Initially, PFO was dissolved in toluene and stirred at 700 rpm for 2 h to produce a solution with fixed concentration of 15 mg mL$^{-1}$. Subsequently, 10 wt. % of TiO$_2$ NPs of the total weight was added into the PFO solution before MEH-PPV with different amounts (ranging from 0.5 to 3.0 wt. % of the total weight) were added into the solution to form nanocomposite blends. Then, the blends were constantly stirred at 700 rpm for overnight and finally sonicated for 1 h to obtain homogeneous solutions.

In the present work, the spin coating technique was used to deposit the blends onto 2.4 cm$^2$ glass substrate to form thin films. The spinning rate was fixed at 2000 rpm for 30 s while each deposition used 80 µL of the prepared blends. To ensure the elimination of the solvent from the films, the thin film samples was heated on a hot plate at 90 °C for 15 min.

The optical absorption and emission characteristics of the thin film samples were determined using a Perkin Elmer Lambda 950 UV–Vis–NIR spectrometer and Edinburgh Instruments FLS920 photoluminescence spectrometer with an excitation wavelength of 370 nm, respectively. In addition, the Dektak 150 Surface Profiler was used to measure the thickness of the films.

**RESULTS AND DISCUSSION**

Figure 1 shows the UV–Vis absorption spectra of pristine PFO thin film, PFO/TiO$_2$ nanocomposite thin film, and
pristine MEH-PPV thin film. The maximum absorptions of the PFO and PFO/TiO$_2$ films are observed at 383 nm and that of MEH-PPV film is observed at 504 nm. The high similarity of the absorption spectra of PFO film and PFO/TiO$_2$ nanocomposite film suggests an insignificant absorption from TiO$_2$ NPs with large energy band gaps and an insignificant variation of the structure of the polymer. Jumali et al. (2012) reported the same characteristic. The presence of a small peak at 435 nm is attributed to the presence of β-phase chain segments in PFO (Li et al. 2017; Perevedentsev et al. 2016; Winokur et al. 2003). Despite earlier work claimed the presence of β-phase chain segments has some effect on the final optical properties of PFO, observations in the current work indicated no significant impact on the general photon absorption profile of the studied system. With fixed concentration of PFO dissolved in the same type of solvent, the presence of this small peak continues to be observed in all absorption spectra indicating no chemical reaction between the raw materials.

The absorption spectra of all blended thin films, with average thickness varies between 116 and 125 nm are shown in Figure 2. All thin films exhibited broad, intense absorption peak between 325 and 425 nm. In addition, weak absorption peak can also be seen at wavelengths between 450 and 575 nm (Figure 2 inset). The former peak is the typical absorption peak of PFO while the latter belongs to MEH-PPV. However, both absorption peaks did not exhibit any systematic enhancement in intensity. This behavior could stem from among others the nonlinear variations in the thickness of film. It is important to note the absence of any new absorption peak in the films suggesting insignificant chemical interaction particularly between the polymers (Jumali et al. 2012). Moreover, the presence of MEH-PPV has negligible effect on general absorption profile of the spectra, hence the wavelength with the maximum absorption for all thin films remain at the same value. Consequently, detailed analysis using Tauc’s equation (Hegde et al. 2019) showed that both the direct and indirect energy band gaps ($E_{gd}$ and $E_{gi}$, respectively) are essentially unchanged after the addition of MEH-PPV (Table 1). These findings are a clear manifestation of the insignificant modification of the electronic structure of the blended materials.

Unlike the band gaps, the band structure disorder estimated from the Urbach energy band tail width ($\Delta E$) (Hegde et al. 2019) displays a strong linear dependency on the MEP-PPV contents (Table 1). The steady increment in the $\Delta E$ values is commonly associated with the creation of many localized states within or near the conduction

Dominant non-radiative Förster-type energy transfer in the blended films is indicated by the huge spectral overlap between the PL spectrum of PFO/TiO₂ and the absorption spectrum of MEH-PPV (Figure 3). This argument is strongly supported by another critical element of Förster-type energy transfer, that is, the Förster radius, \( R_0 \), which can be expressed as (1) (Karthikeyan 2017):

\[
R_0 = \frac{900(\ln 10)^2\phi_0}{128\pi^3n^4N_o} \int F_D(\lambda)e_A(\lambda)\lambda^4d\lambda = \frac{900(\ln 10)^2\phi_0}{128\pi^3n^4N_o}J(\lambda),
\]

where \( n \) is the refractive index of toluene; \( N_o \) is the Avogadro number; \( \beta^2 \) is the orientation factor; \( \phi \) is the fluorescence quantum yield of pristine PFO; \( \lambda \) is the wavelength of the emitted photon; \( e_A(\lambda) \) is the molar decadic extinction coefficient of the acceptor; and \( F_D(\lambda) \) is the normalized spectral distribution of the donor (\( \int F_D(\lambda)d\lambda = 1 \)). The values for \( n, \beta^2, \) and \( \phi \) used in this work are 1.496, 2/3, and 0.72, respectively (Al-Asbahi et al. 2013a).

### TABLE 1. The thickness and optical energy properties of PFO/10 wt. % TiO₂ with addition of MEH-PPV

<table>
<thead>
<tr>
<th>MEH-PPV (wt. %)</th>
<th>Thickness ± 1(nm)</th>
<th>( E_{gd} ) (eV)</th>
<th>( E_{gi} ) (eV)</th>
<th>( \Delta E ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>117</td>
<td>2.98</td>
<td>2.846</td>
<td>0.078</td>
</tr>
<tr>
<td>0.5</td>
<td>116</td>
<td>2.98</td>
<td>2.846</td>
<td>0.082</td>
</tr>
<tr>
<td>1.0</td>
<td>120</td>
<td>2.98</td>
<td>2.846</td>
<td>0.084</td>
</tr>
<tr>
<td>1.5</td>
<td>118</td>
<td>2.98</td>
<td>2.846</td>
<td>0.091</td>
</tr>
<tr>
<td>2.0</td>
<td>123</td>
<td>2.98</td>
<td>2.846</td>
<td>0.092</td>
</tr>
<tr>
<td>2.5</td>
<td>122</td>
<td>2.98</td>
<td>2.832</td>
<td>0.093</td>
</tr>
<tr>
<td>3.0</td>
<td>125</td>
<td>2.98</td>
<td>2.825</td>
<td>0.101</td>
</tr>
</tbody>
</table>
Minor variations in the calculated values of Table 2 demonstrate that the concentration of MEH-PPV in the PFO/TiO₂ blends has an insignificant influence on the Förster radius. For effective Förster-type energy transfer, the Förster radius must range between 10 and 100 Å (Schweitzer & Schmidt 2003). Interestingly, all values for the calculated $R_o$ are between 50 and 60 Å, thus confirming the Förster-type energy transfer as the primary mechanism in PFO/MEH-PPV/TiO₂ blends. In addition, the systematic reduction in the excited state lifetime ($\tau$) and fluorescence quantum yield of the donor ($\phi$) as a function of the MEH-PPV content demonstrate the improvement in the efficiency of the Förster energy transfer in the studied films (Pandey et al. 1988).

Table 2. Förster radius, quantum yield, and lifetime of PFO/10 wt. % TiO₂/MEH-PPV

<table>
<thead>
<tr>
<th>MEH-PPV content (wt. %)</th>
<th>$R_o$ (Å)</th>
<th>$\phi$</th>
<th>$\tau$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>55.8</td>
<td>0.680</td>
<td>326</td>
</tr>
<tr>
<td>1.0</td>
<td>53.4</td>
<td>0.479</td>
<td>230</td>
</tr>
<tr>
<td>1.5</td>
<td>53.1</td>
<td>0.417</td>
<td>200</td>
</tr>
<tr>
<td>2.0</td>
<td>53.4</td>
<td>0.258</td>
<td>124</td>
</tr>
<tr>
<td>2.5</td>
<td>58.9</td>
<td>0.186</td>
<td>89</td>
</tr>
<tr>
<td>3.0</td>
<td>52.2</td>
<td>0.124</td>
<td>60</td>
</tr>
</tbody>
</table>

Figure 4 shows the photoluminescence spectra of all PFO/TiO₂/MEH-PPV-blended films. The efficiency of MEH-PPV as acceptor was demonstrated by orderly declining intensities of the PFO peaks. As a result, the emission intensity of MEH-PPV gradually increases before exhibiting a downward trend when its content exceeds 2.0 wt. %.

Based on Figure 4, additional evidence of the efficient energy transfer, that is, the Stern–Volmer constant (quenching constant; $k_q$) and quenching rate constant ($k_q$), can be extracted using the following relations (2) and (3) (Ciotta et al. 2019):

$$\frac{I_o}{I} = 1 + k_{SV} [A]$$  \hspace{1cm} (2)

$$k_q = \frac{k_{SV}}{\tau_o}$$  \hspace{1cm} (3)
where \( I_0 \) and \( I \) are the fluorescence intensities in the absence and presence of an acceptor, respectively, and \([A]\) is the acceptor concentration. The excited state lifetime of the pristine donor (\( \tau_0 \)) is fixed at 346 ps (Al-Asbahi et al. 2013b). The linear Stern-Volmer plot for the blends is presented in Figure 5. The \( k_{sv} \) value obtained from the gradient of the line implies that 2.07 µM MEH-PPV are required to halve the fluorescence of PFO. On the other hand, the value calculated for \( k_q \) is \( 1.40 \times 10^{15} \) M\(^{-1}\)s\(^{-1}\), that is, five orders of magnitude higher than the minimum value for efficient energy transfer (Albrecht 2008).

Other important parameters related to the energy transfer, such as the energy transfer lifetime, \( \tau_{ET} \), and energy transfer rate, \( k_{ET} \), have been calculated using the following (4) and (5) (Albrecht 2008):

\[
\tau_{ET} = \frac{1}{[A]k_q} \quad (4)
\]

\[
k_{ET} = \frac{1}{\tau_0} \left( \frac{R_o}{R} \right)^6 \quad (5)
\]

where \([A]\) is the molar concentration of the acceptor in the blend. In addition, the distance between the donor and acceptor, \( R \), was estimated using (6) (Albrecht 2008):

\[
\delta = \frac{R_o^6 + R^6}{R^6} \quad (6)
\]

where \( \delta \) is the energy transfer efficiency, which equals \( (1 - I / I_0) \) (Albrecht 2008).
All calculated values are presented in Table 3. Except for 0.5 wt. % MEH-PPV, all other values for $R$ are in the range of the Förster radius. More importantly, the distance between the donor and acceptor systematically decreases as more MEH-PPV is added to the blend. Remarkably, the $\tau_{ET}$ also decreased with the MEH-PPV content, while $k_{ET}$ positively enhances as the distance between donor and acceptor shortens. Interestingly, all trends of these parameters support the above-mentioned findings about the excited state lifetime ($\tau$) and fluorescence quantum yield ($\phi$), confirming the highly efficient energy transfer in current blend films (Albrecht 2008).

To produce white OLEDs, it is desirable that the emitting materials produce photons covering the whole visible region of the EM spectrum. Alternatively, the materials should produce a suitable combination of primary colors with balanced intensities (Shen et al. 2006). A precise ratio between the emitting materials is crucial to achieve a balanced intensity.

### Table 3. Critical energy transfer distance, energy transfer rate and energy transfer lifetime

<table>
<thead>
<tr>
<th>MEH-PPV content (wt. %)</th>
<th>$R (\AA)$</th>
<th>$k_{ET}$ ($ns^{-1}$)</th>
<th>$\tau_{ET}$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>89.2</td>
<td>0.2</td>
<td>374</td>
</tr>
<tr>
<td>1.0</td>
<td>59.9</td>
<td>1.4</td>
<td>187</td>
</tr>
<tr>
<td>1.5</td>
<td>52.4</td>
<td>3.1</td>
<td>125</td>
</tr>
<tr>
<td>2.0</td>
<td>48.5</td>
<td>5.2</td>
<td>93</td>
</tr>
<tr>
<td>2.5</td>
<td>49.4</td>
<td>8.3</td>
<td>75</td>
</tr>
<tr>
<td>3.0</td>
<td>40.2</td>
<td>13.9</td>
<td>62</td>
</tr>
</tbody>
</table>

Balanced emission intensities were successfully achieved at an acceptor concentration of 2.5 wt. % (Figure 4). This value is 2.5 times greater than earlier reported data, signifying the importance of the TiO$_2$ NPs in the blends (Shin et al. 2009). It is notable that more acceptor can be added to the blends because of the presence of NPs, which is desirable for a more efficient energy transfer. Earlier studies successfully proved that the addition of TiO$_2$ to PFO enhances the emission intensity through the charge trapping effect (Al-Asbahi et al. 2013b; Jumali et al. 2012). This is possible because TiO$_2$ has a stronger electron affinity as well as an energy band diagram that is compatible with the polymer. Hence, more excitons are created in the PFO, which in turn allows intense emission during electron–hole recombination. Consequently, more acceptors can be added to the blends.

Because the Förster energy transfer efficiency improves with the addition of MEH-PPV, more acceptor molecules can be excited, which leads to intense emission. Above a concentration of 2.0 wt. %, the emission intensity of MEH-PPV starts to drop. However, this reduction does not imply that the energy transfer from the donor to the acceptor slows down. In fact, the efficient energy transfer from the PFO continues, as manifested by the detection of lower emission. However, instead of fluorescence, the energy received by the MEH-PPV is converted to heat via the formation of dark quenchers (Nedumpara et al. 2008). This observation indicates the preferential energy loss via heat. A similar observation has been reported for PFO/TiO$_2$/F7GA blend film (Al-Asbahi 2017).

### Conclusion

In conclusion, the influence of different MEH-PPV concentrations on the photophysical properties of PFO/10 wt. % TiO$_2$/MEH-PPV nanocomposite thin films have been investigated. The decrease in the donor emission intensity, increase in the acceptor emission intensity, and high $R_o$ and $k_{ET}$ values with increasing MEH-PPV content are the major indicators for efficient Förster resonance energy transfer in the blend. In addition, all $\tau$, $\phi$, $k_{q}$, $R$, $\tau_{ET}$, and $k_{ET}$ calculations indicate an improvement in the emission efficiency. Because of the charge trapping effect provided by the TiO$_2$ NPs, more acceptor molecules can be added to the blend to improve energy transfer efficiency and to achieve balanced emissions, which are the two prerequisites for high-efficiency WOLEDs.

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