Long-range dipole–dipole energy transfer enhancement via addition of SiO$_2$/TiO$_2$ nanocomposite in PFO/MEH-PPV hybrid thin films

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ABSTRACT: Different weight ratios of poly(9,9-dioctylfluorene-2,7-diyl) (PFO)/poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) hybrid thin films, with and without a SiO$_2$/TiO$_2$ nanocomposite (NC), were successfully prepared using a solution blending method. All samples were deposited onto glass substrates by a spin coating technique to produce homogeneous thin films. The effect of the SiO$_2$/TiO$_2$ NC on the enhancement of the energy transfer mechanism in the PFO/MEH-PPV hybrids was investigated. The energy transfer parameters were calculated on the basis of the absorption and emission measurements. The long-range dipole–dipole energy transfer (Förster type) between the acceptor and donor molecules was enhanced in the presence of the SiO$_2$/TiO$_2$ NC in the hybrid thin films. The addition of the SiO$_2$/TiO$_2$ NC in the PFO/MEH-PPV hybrids reduced the distance between the donor and acceptor molecules more than the individual addition of SiO$_2$ or TiO$_2$ nanoparticles. Moreover, the direct relationships between the acceptor contents and energy transfer parameters, such as the energy transfer radius ($R_{DA}$), energy transfer efficiency ($\eta$), and energy transfer probability ($P_{DA}$), were estimated using theoretical fittings. © 2019 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2019, 136, 47845.

KEYWORDS: energy transfer; Förster-type; nanocomposite; PFO/MEH-PPV hybrids; thin films

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INTRODUCTION

Organic materials with good emission responses are suitable candidates for numerous optoelectronic applications such as solar cells, photovoltaic sensors, and organic light-emitting diodes (OLEDs). In the solid state, conjugated organic combinations exhibit a unique variety of electrical, optical, and photoelectric properties.1 Compared with inorganic materials, organic materials have numerous advantages, such as ease of processing and low cost. Moreover, inorganic nanostructures mixed with organic materials impart interesting and unique optoelectronic properties to nanocomposite (NC) materials.2

Although numerous conjugated organic light-emitting materials are highly luminescent in their dilute solutions, they become less emissive upon fabrication into thin films.3 This reduction in their luminescence efficiency is attributed to the molecules aggregating and then forming less emissive species, such as excimers.4 Phase separation, keto defect formation, and poor stability are other problems that can occur in the thin films of polymer blends owing to the low entropy of mixing between the dissimilar polymers and photooxidation during preparation of the film.2,4–7 Many researchers have shown that these problems can be successfully reduced through several physical, chemical, and engineering methods.8–10

The solid state of the donor/acceptor combinations emits light; therefore, such combinations have attracted significant attention as the emissive layer in optoelectronic devices.10–13 This enhancement in the emission of the solid state of the donor/acceptor combinations can be attributed to specific aggregation (J- or H-aggregation) or intramolecular planarization in the combinations.8,14 Numerous models, such as rotational deactivation, noncoplanarity, and exciton diffusion, have been suggested for enhanced emission in the solid state compared with emission quenching in solutions.15–17 Unfortunately, the intermolecular interaction occurs in the solid state of donor/acceptor blending, resulting in the quenching of the luminescence.18 As reported in our previous study, this

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problem can be diminished by incorporating inorganic nanomaterials.12

Several approaches have been utilized to enhance the OLED performance, including perfect matching between the working functions of the electrodes and the energy levels of the polymer,19 multilayer device fabrication,20 and utilization of hole and electron transporting layers.20 Another recent technique involves the enhancement of Förster energy transfer.21,22

In our previous studies, the inclusion of TiO2 NPs prevented the formation of dark quenchers and enhanced the emission performance.10,12 Moreover, in a recent study, the visible and ultraviolet emission intensities of SiO2/TiO2 were greater than that of those of pure SiO2 or TiO2 NPs.23 This enhancement in the emission intensities can be attributed the oxygen vacancies and trapped electrons at the interface of SiO2/TiO2 NC thin films.23 Based on these findings, the incorporation of SiO2/TiO2 into the blends of the emitting polymers could improve the performance of optoelectronic devices through the enhanced Förster energy transfer.

Several strategies have been developed to prepare well-defined inorganic/organic hybrid NCs. The most common of these strategies are via starlike polymer as nanoreactors24–26, sol-gel,27 in situ polymerization,28 and solution blending method.29 In this study, poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO) as a donor and poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV) as an acceptor were blended at various ratios with and without a SiO2/TiO2 NC by the solution blending method. The ratio of SiO2/TiO2/20 wt. % TiO2 was used in this study. The range used provided greater emission intensities of SiO2/TiO2 were greater than that of those of MEH-PPV (acceptor). The red shift in the MEH-PPV emission was from the radiative energy transfer of the molecules of PFO (donor) with a gradual red shift. This observation represented the energy transfer from PFO to MEH-PPV, as there was no major contribution with a fixed ratio of 10% SiO2/(20% TiO2) NC. The same procedures as those of our previous study were followed to prepare PFO/0.5 wt. % MEH-PPV with an individual fixed ratio of 10 wt. % TiO2 and 10 wt. % SiO2 NPs. All materials were dissolved in a toluene solvent produced by Fluka. This solvent produced a better distribution onto a glass substrate than that of other common solvents, such as THF. Here, 100 µL from each sample was deposited onto a glass substrate with the dimensions of 1.2 cm × 2 cm using a spin coating technique (2000 rpm for 20 s), and then, the samples were annealed at 120 °C in a vacuum oven to remove the solvent.

A Perkin Elmer Lambda 900 ultraviolet–visible Spectrometer was employed to obtain the absorption spectra, and an Edinburgh Instrument FLSP920 spectrophotometer was used to obtain the PL spectra and time resolved photoluminescence. Origin software (version 8.0) was used to analyze the absorption and emission data to determine the energy transfer parameters and to design the theoretical equations by fitting the curves.

RESULTS AND DISCUSSION

Absorption and Fluorescence Spectra

Figure 2(a) shows the absorption spectra of the thin films of pristine PFO, pristine MEH-PPV, and PFO with different contents of MEH-PPV, corresponding to 0.1, 0.5, 1.0, 5.0, and 10 wt. %. The absorbance peak of pristine PFO was in the range 300–450 nm with a maximum peak at approximately 398 nm, while two peaks were observed at 342 nm and 515 nm for pristine MEH-PPV. For the blended PFO with different contents of MEH-PPV, the peak at 342 nm was hidden, while the peak at 515 nm was enhanced dramatically with an increasing MEH-PPV content. Moreover, no new absorbance peak appeared upon increasing the MEH-PPV content up to 5 wt. %, indicating that no dimers formation of the hybrids were present. When the acceptor concentration was increased to 10 wt. %, a peak located at 515 nm was clearly observed due to molecules aggregation of MEH-PPV.

Figure 2(b) shows the emission spectra of pure PFO, pure MEH-PPV, and PFO with varying contents of MEH-PPV. With an excitation wavelength at 355 nm, three main peaks for PFO were observed at 437 nm, 458 nm, and 490 nm, corresponding to the 0-0, 0-1, and 0-2 vibronic transitions, respectively. Moreover, a shoulder peak at approximately 530 nm that was detected in the emission spectrum of pristine PFO was attributed to the formation of fluorenone defects (keto defects) in the PFO backbone during the photo-oxidation process.27 Other peaks at 600 nm and 635 nm were observed for MEH-PPV, corresponding to the 0-0 and 0-1 transitions, respectively. The excitation wavelength of 355 nm was dominantly absorbed by the PFO. As MEH-PPV was added, the PFO intensity decreased significantly with a slight blue shift, while the intensity of the related peaks of MEH-PPV increased with a gradual red shift. This observation represented the energy transfer from PFO to MEH-PPV, as there was no major contribution from the MEH-PPV emission on the direct excitation at 355 nm in the region below 500 nm. The blue shift in the PFO emission was from the radiative energy transfer of the molecules of PFO (donor) to those of MEH-PPV (acceptor). The red shift in the MEH-PPV

EXPERIMENTAL

PFO (Mw = 58,200 and PDI~3.7) and MEH-PPV (Mw = 40,000 and PDI ~ 6) were purchased from Sigma Aldrich (Saint Louis, Missouri, USA) and were used as received, without further purification. The chemical structures of these conjugated polymers are shown in Figure 1. The (SiO2/TiO2/20 wt. % TiO2) was prepared as reported in our previous study, where the sizes of the TiO2 and SiO2 NPs were 25 and 26.4 nm, respectively.23 The solution blending method was employed to prepare the PFO/MEH-PPV hybrid with various weight ratios of MEH-PPV: 0.1, 0.5, 1.0, 5.0, and 10 wt. %, with and without a fixed ratio of 10% SiO2/(20% TiO2) NC. The same procedures as those of our previous study were followed to prepare PFO/0.5 wt. % MEH-PPV with an individual fixed ratio of 10 wt. % TiO2 and 10 wt. % SiO2 NPs. All materials were dissolved in a toluene solvent produced by Fluka. This solvent produced a better distribution onto a glass substrate than that of other common solvents, such as THF. Here, 100 µL from each sample was deposited onto a glass substrate with the dimensions of 1.2 cm × 2 cm using a spin coating technique (2000 rpm for 20 s), and then, the samples were annealed at 120 °C in a vacuum oven to remove the solvent.

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**Figure 1.** Chemical structure of PFO and MEH-PPV.
emission was attributed to the occurrence of radiative migration owing to self-absorption. However, for a higher concentration of the acceptor, the energy migration among the molecules of PFO became minimal, and a direct transfer to the molecules of MEH-PPV, through the long-range dipole–dipole energy transfer (Förster-type) mechanism, occurred.

With the addition of 10 wt. % of (SiO2/20 wt. % TiO2) NC in the hybrids of PFO/diff. wt. % MEH-PPV, the maximum absorbance peak (398 nm) contained a blue shift to 15 nm. In addition, the absorbance peak of MEH-PPV in the ultraviolet (UV) region (342 nm) contained a blue shift to 295 nm (approximately 47 nm), and its intensity was significantly enhanced, as shown in Figure 3(a). A similar trend was observed with the addition of individual TiO2 and SiO2 NPs into the PFO/MEH-PPV hybrid (as shown later in Figure 4). The increase in the absorption peak of 295 nm with the addition of the SiO2/TiO2 NC to the PFO/MEH-PPV hybrids showed that the SiO2/TiO2 assisted the light harvesting in the UV region of 285–330 nm, and the surface area could be increased more than that with the addition of individual TiO2 or SiO2 NPs. Moreover, the large blue shift of the absorbance could be attributed to the nanoparticles producing a greater hindrance, thus reducing the conjugation lengths of the PFO and MEH-PPV, as described in the Critical Concentration of the Acceptor (Ao) and Conjugation Length (Aπ) section. This was consistent with the results obtained by Yang et al., where the absorption of the conjugated polymer in the NC contained a blue shift from the SiO2 nanoparticles.

As shown in Figure 3(b), the addition of the SiO2/TiO2 NC enhanced the peak intensity corresponding to the acceptor and reduced that of the donor. Therefore, the SiO2/TiO2 NC facilitated the energy transfer between PFO and MEH-PPV. The energy transfer between the donor and the acceptor easily occurred with the SiO2/TiO2 NC owing to the stronger interactions. Thus, with the SiO2/TiO2 NC, a small quantity from the acceptor could be used to acquire a long-range dipole–dipole energy transfer.
energy transfer (Förster type) between the donor and the acceptor. This occurred even if the SiO2 or TiO2 was mixed individually with the PFO/MEH-PPV hybrid, as shown in Figure 4. However, for individual mixing, one peak related to the acceptor became dominant, while for mixing the SiO2/TiO2 NC, both peaks of the acceptor appeared. Because both peaks of the acceptor appeared for mixing the SiO2/TiO2 NC, the enhancement of the energy transfer should be greater than that of mixing individual SiO2 or TiO2 with the PFO/MEH-PPV hybrid. Even though both emission peaks were associated with the acceptor, the peaks of the donor remained at a high intensity. This enhancement in the emission intensity was attributed to the oxygen vacancies and charge trapping effect.

An exciting phenomenon was observed at 10 wt. % MEH-PPV, where the emission intensity of the acceptor decreased instead of increasing, and the donor emission was simultaneously quenched. This quenching showed that the energy transfer process was completed, whereas the reduction in the emission intensity of the acceptor showed that the energy transfer from the donor to the significant number of acceptor molecules was not emitted as fluorescence. Instead the transferred energy was converted into heat, suggesting that some of the MEH-PPV molecules acted as dark quenchers without any fluorescence. The dominant formation of the dark quenchers was attributed to the creation of non-fluorescent ground state complex dimers, as shown by the formation of the absorption peak (approximately 515 nm) at 10 wt. % in the absorption spectrum.

Table I lists the optical properties of the donor/acceptor thin films with and without 10 wt. % SiO2 NC and TiO2 NPs.

Long-Range Dipole–Dipole Energy Transfer Parameters
As shown in the emission spectra [Figure 2(b)], the energy transfer effect was clearly observed in the PFO/MEH-PPV hybrids when the acceptor content exceeded 0.1 wt. %. Moreover, this effect became more apparent when the SiO2/TiO2 NC was added into these hybrids, even with an acceptor content of 0.1 wt. % [Figure 3(b)]. To compare the energy transfer parameters for the PFO/MEH-PPV hybrids with and without the SiO2/TiO2 NC, an excitation wavelength of 355 nm was used, for which direct MEH-PPV excitation was insignificant, and energy transfer from PFO to MEH-PPV occurred. The possibility of long-range dipole–dipole energy transfer (Förster type) could be evidenced by (1) the strong overlap (not shown here) between the absorption spectrum of pristine MEH-PPV and the emission spectrum of pristine PFO, (2) the strong decrease in the emission intensity of PFO with the addition of MEH-PPV, and (3) the effective enhancement of the emission intensity of MEH-PPV. Several parameters, in the sections below, were evaluated to describe the energy transfer mechanism with and without the SiO2/TiO2 NC. Moreover, the ratio of PFO/0.5 wt. % MEH-PPV was employed to evaluate the effect of the individual addition of TiO2 and SiO2 on the energy transfer mechanism.

Quantum Yield and Lifetime of the Donor in the Hybrids. In homogeneous dynamic quenching, the following equation can be used to determine the quantum yield (\(\phi_{DA}\)) and lifetime (\(\tau_{DA}\)) values of the donor in the hybrid thin films:

\[
\frac{I_D}{I_{DA}} = \frac{\phi_D}{\phi_{DA}} = \frac{\tau_D}{\tau_{DA}}
\]

where \(I_D\) and \(I_{DA}\) are the emission intensity of donor in the absence and presence of acceptor, respectively. Table I lists the \(\phi_{DA}\) and \(\tau_{DA}\) values of PFO in the hybrid thin films, which decreased with the addition of MEH-PPV. This suggested the possibility of radiative energy transfer. The significantly shorter values of \(\phi_{DA}\) and \(\tau_{DA}\) than those of the pristine PFO thin film (\(\phi_D = 0.72\) and \(\tau_D = 346\) ps) provided theoretical evidence of the efficient energy transfer from PFO to MEH-PPV. The values in Tables I and II were shorter with SiO2 and TiO2, as a mixture or an individual component, compared with those without SiO2 and TiO2 NPs. Moreover, this suggested that the efficient energy transfer with the SiO2 and TiO2 NPs was greater than that without the NPs, as discussed in the sections below.

### Table I. Optical Properties of the Donor/Acceptor Thin Films with and without 10 wt. % (SiO2/20 wt. % TiO2)

<table>
<thead>
<tr>
<th>Acceptor content (wt. %)</th>
<th>(\phi_{DA})</th>
<th>(K_{pr}) (ns(^{-1}))</th>
<th>(A_{ex}) (Å)</th>
<th>(\tau_{DA}) (ps)</th>
<th>In presence of SiO2/TiO2 NC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\phi_{DA})</td>
<td>(K_{pr}) (ns(^{-1}))</td>
<td>(A_{ex}) (Å)</td>
<td>(\tau_{DA}) (ps)</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>0.521</td>
<td>1.905</td>
<td>0.087</td>
<td>251</td>
<td>0.354</td>
</tr>
<tr>
<td>0.5</td>
<td>0.318</td>
<td>4.460</td>
<td>-0.764</td>
<td>153</td>
<td>0.195</td>
</tr>
<tr>
<td>1.0</td>
<td>0.243</td>
<td>6.470</td>
<td>-1.135</td>
<td>117</td>
<td>0.207</td>
</tr>
<tr>
<td>5.0</td>
<td>0.057</td>
<td>7.430</td>
<td>-2.801</td>
<td>27.53</td>
<td>0.035</td>
</tr>
<tr>
<td>10</td>
<td>0.021</td>
<td>9.630</td>
<td>-3.842</td>
<td>10.08</td>
<td>0.004</td>
</tr>
</tbody>
</table>
Table II. Energy Transfer Parameters of the PFO/0.5 wt. % MEH-PPV Hybrid Thin Film with SiO2 and TiO2

<table>
<thead>
<tr>
<th>Dopant (1.0 wt. %)</th>
<th>$\phi_{DA}$</th>
<th>$\tau_{DA}$ (ps)</th>
<th>$R_0$ (Å)</th>
<th>$R_{DA}$ (Å)</th>
<th>$k_{ET}$ (ns$^{-1}$)</th>
<th>$A_\alpha$ (Å)</th>
<th>$A_D$ (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2</td>
<td>0.144</td>
<td>69.2</td>
<td>84.2</td>
<td>66.8</td>
<td>11.5</td>
<td>-1.782</td>
<td>0.75</td>
</tr>
<tr>
<td>SiO2</td>
<td>0.216</td>
<td>104</td>
<td>84.7</td>
<td>73.5</td>
<td>6.74</td>
<td>-1.289</td>
<td>0.73</td>
</tr>
</tbody>
</table>

Stern–Volmer ($k_{SV}$) and Quenching Rate ($k_q$) Constants. The homogeneity of the dynamic quenching of PFO by MEH-PPV with and without the SiO2/TiO2 NC was determined from the linear Stern–Volmer plot (Figure 5). The values of $k_{SV}$, with and without the SiO2/TiO2 NC, were 4.21 and 0.78 (µM$^{-1}$), respectively. These values implied that 50% of the fluorescence was quenched for the MEH-PPV concentrations of approximately 0.24 and 1.28 µM with and without the SiO2/TiO2 NC, respectively.

The value of $k_q$ with the SiO2/TiO2 NC was $1.22 \times 10^{15}$ M$^{-1}$ s$^{-1}$, approximately five times greater than that without the SiO2/TiO2 NC (2.25 $\times 10^{13}$ M$^{-1}$ s$^{-1}$). The high values of $k_q$ are indicative of how well mixing between the conjugated polymers and the SiO2/TiO2 NCs.

Förster Radius, Energy Transfer Rate, and Energy Transfer Lifetime. The critical distance (Förster radius), $R_0$, is calculated from the following formula:

$$R_0^2 = \frac{9000(\ln 10)\beta^2\phi_D}{128\pi^2n^4N_o} \int F_D(\lambda)e_\lambda(\lambda)\lambda^2d\lambda = \frac{9000(\ln 10)\beta^2\phi_D}{128\pi^2n^4N_o} J(\lambda)$$

The parameter $\beta^2$ is the orientation factor (2/3 for isotropic media), and $n$ is the refractive index of the solvent. The parameter $N_o$ is Avogadro’s number and $\lambda$ is the wavelength. The parameter $e_\lambda(\lambda)$ is the molar decadic extinction coefficient of the acceptor, and $F_D(\lambda)$ is the normalized spectral distribution of the donor (i.e., $\int F_D(\lambda)d\lambda = 1$). The values of $R_0$ and $J(\lambda)$ with and without the SiO2/TiO2 NC are listed in Table III. The values of $R_0$ with and without the SiO2/TiO2 NC were slightly larger than those without the NC. The Förster radii with and without the SiO2/TiO2 NC were in the ranges of 48–89 and 43–87 Å, respectively. These values confirmed the dominant long-range dipole–dipole energy transfer (Förster type) in the hybrid.

Consequently, the Förster theory is suitable for calculating the Förster energy transfer parameters, as previously reported. Moreover, the values of $R_0$ with individual SiO2 and TiO2 in the hybrid of PFO/0.5 wt. % MEH-PPV were 84.7 and 84.2 Å, respectively. This was because the particle sizes of SiO2 and TiO2 were approximately the same, and thus, the surface area was similar. The decreasing of $R_0$ (approximately 77.7 Å) when mixing PFO/0.5 wt. % MEH-PPV with the SiO2/TiO2 NC could be attributed to the defect formation and the surface area increase, as discussed previously in the Absorption and Fluorescence Spectra section. Based on the $R_0$ values, the mechanism of the Förster energy transfer is suitable in the PFO/MEH-PPV system with SiO2 and TiO2 as a mixture or individual compounds.

The calculation of the distance between the donor and acceptor molecules ($R_{DA}$) was based on the Förster radius and fluorescence intensities of the donor without ($I_{DA}$) and with ($I_{DA}$) the acceptor. Figure 6 shows that as the acceptor content increased from 0.1 to 10 wt. %, the $R_{DA}$ decreased from 105 to 24 Å and from 87 to 22 Å, without and with the SiO2/TiO2 NC, respectively. This implied that the distance between the molecules of PFO and MEH-PPV became smaller with the SiO2/TiO2 NC. Furthermore, a reduction in the values of $R_{DA}$ was detected even if the SiO2 or TiO2 NPs were added individually in the PFO/MEH-PPV hybrid (Table II); however, this reduction was not less than that of the hybrid with the mixture of SiO2/TiO2.

Figure 5. Stern–Volmer plots for emission quenching of PFO by various weight ratios of MEH-PPV: (a) without SiO2/20 wt. % TiO2 and (b) with 10 wt. % (SiO2/20 wt. % TiO2). [Color figure can be viewed at wileyonlinelibrary.com]
The reduction in RDA with the NPs was consistent with previous results of PFO/Fluorol 7GA with TiO2 NPs. Moreover, by fitting the data of Figure 6, theoretical equations were obtained to provide the relationships between RDA and the acceptor content as follows.

\[
R_{DA} = 0.00387 + 0.0143X0.418 \quad (3)
\]

The parameter X is the acceptor weight ratio (wt. %) without the SiO₂/TiO₂ NC.

\[
R_{DA} = 0.006 + 0.0127X0.506 \quad (4)
\]

The parameter X is the acceptor weight ratio (wt. %) with the SiO₂/TiO₂ NC.

The energy transfer rate (kET) between a single donor/acceptor pair separated by a distance between the donor and acceptor (RDA) can be expressed in terms of the Förster distance (R₀).
As listed in Table III, the $R_{DA}$ values were significantly smaller than those without the SiO$_2$/TiO$_2$ NC; whereas, the changes in the $R_0$ values were insignificant compared with those without the SiO$_2$/TiO$_2$ NC. Consequently, the energy transfer rate ($k_{ET}$) values were enhanced with SiO$_2$ and TiO$_2$, as a mixture or individual compounds, in the hybrids (Tables II and III).

The variations in the values of the energy transfer lifetime ($\tau_{ET}$), energy transfer rate ($k_{ET}$), and total decay rate (TDR) of the donor ($k_{ET} + \tau_D^{-1}$) with the addition of the SiO$_2$/TiO$_2$ NC in the hybrid thin films with various acceptor contents are listed in Table III. As shown in previous studies,$^{11,33,34}$ an efficient energy transfer in the donor/acceptor hybrids is shown by an increase in the $k_{ET}$ and TDR and a decrease of $\tau_{ET}$ with an increasing acceptor content. These findings were observed in the current system of the donor/acceptor hybrids. In the presence of the SiO$_2$/TiO$_2$ NC, the values of $\tau_{ET}$ were approximately five times smaller, whereas the values of $k_{ET}$ and the TDR were larger than those without the SiO$_2$/TiO$_2$ NC. This showed the positive effect of the SiO$_2$/TiO$_2$ NC on the enhancement of the long-range dipole–dipole energy transfer (Förster type) between PFO and MEH-PPV.

### The Probability ($P_{DA}$) and Efficiency ($\eta$) of the Donor/Acceptor Energy Transfer.

Figures 7 and 8 show the relationship of the acceptor content with $P_{DA}$ and $\eta$, respectively. A gradual increase occurred for $P_{DA}$ with the addition of the acceptor with and without the SiO$_2$/TiO$_2$ NC. The larger increase in the $P_{DA}$ values in the presence of the SiO$_2$/TiO$_2$ NC was attributed to the systematic reduction in the emission intensity (I$_{DA}$) that was greater than that without the SiO$_2$/TiO$_2$ NC. Moreover, by fitting the data of Figure 7, the relationships between $P_{DA}$ and the acceptor content with and without the SiO$_2$/TiO$_2$ NC were as follows.

$$P_{DA} = e^{22.07 \times 0.57X - 0.024X^2}$$

The parameter $X$ is the acceptor weight ratio (wt. %) without the SiO$_2$/TiO$_2$ NC.

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**Figure 7.** Probability of the energy transfer from PFO to MEH-PPV for various weight ratios: (a) without SiO$_2$/20 wt. % TiO$_2$ and (b) with 10 wt. % (SiO$_2$/20 wt. % TiO$_2$).

**Figure 8.** Efficiency of the energy transfer from PFO to MEH-PPV for various weight ratios: (a) with SiO$_2$/20 wt. % TiO$_2$ and (b) without 10 wt. % (SiO$_2$/20 wt. % TiO$_2$).
The parameter $X$ is the acceptor weight ratio (wt. %) with the SiO$_2$/TiO$_2$ NC.

A systematic increase in the energy transfer efficiency ($\eta$) was observed until the acceptor content reached 5 wt. % with and without the SiO$_2$/TiO$_2$ NC, as shown in Figure 8. The maximum energy transfer efficiencies without and with the SiO$_2$/TiO$_2$ NC were 0.97 and 0.99, respectively. This also showed the positive effect of the SiO$_2$/TiO$_2$ NC in the blends to enhance the mechanism of the energy transfer between PFO and MEH-PPV. By fitting the data of Figure 8, the relationship between $\eta$ and the acceptor content with and without the SiO$_2$/TiO$_2$ NC was estimated as follows.

$$\eta = \frac{1.11X^{0.67}}{0.64 + X^{0.67}}$$

(8)

The parameter $X$ is the acceptor weight ratio (wt. %) without the SiO$_2$/TiO$_2$ NC.

$$\eta = \frac{1.51X^{0.29}}{0.98 + X^{0.29}}$$

(9)

The parameter $X$ is the acceptor weight ratio (wt. %) with the SiO$_2$/TiO$_2$ NC.

As shown in Figure 9, an inflection point in $\eta$ was observed at $R_{DA} = R_o$. The parameter $\eta$ was close to unity at $R_{DA} < 0.5 \ R_o$ and dramatically decreased for $R_{DA} > R_o$. Therefore, the long-range dipole–dipole energy transfer (Förster type) from PFO, with and without the SiO$_2$/TiO$_2$ NC, to MEH-PPV occurred at a higher probability for $10 \ \AA < R_o < 100 \ \AA$. Moreover, the distance between the PFO and MEH-PPV molecules was less than 1.5 $R_o$. These results are consistent with previous reports.$^{11,34,42}$

Critical Concentration of the Acceptor ($A_o$) and Conjugation Length ($A_\pi$).

The concentration of the acceptor with 76% energy transfer is the critical concentration ($A_o$).$^{33}$ The concentration of the acceptor should be much lower than $A_o$ to suppress the intermolecular

![Figure 9](https://example.com/figure9.png)

Figure 9. Dependence of the efficiency of the energy transfer ($\eta$) on the distance between the molecules of the donor/acceptor: (a) without SiO$_2$/20 wt. % TiO$_2$ and (b) with 10 wt. % (SiO$_2$/20 wt. % TiO$_2$).

![Figure 10](https://example.com/figure10.png)

Figure 10. Fluorescence quantum yield ($\Phi_{DA}$) versus the conjugated length ($A_\pi$): (a) without SiO$_2$/20 wt. % TiO$_2$ and (b) with 10 wt. % (SiO$_2$/20 wt. % TiO$_2$).
transfer in the donor. Based on the $R_0$ values, the $A_o$ values of MEH-PPV were approximately 0.62 and 0.67 mM, without and with the SiO$_2$/TiO$_2$ NC, respectively, while these values increased to 0.73 and 0.75 mM with SiO$_2$ and TiO$_2$, respectively.

The conjugation length ($A_\pi$) value in the excited singlet state is defined as the distance between the dipoles arising from the ground state ($S_0$) to the excited singlet state ($S_1$) transition, derived from the radiative rate constant ($k_r$) and radiationless rate constant ($k_{nr}$). There was no significant modification in the value of $k_r$ (approximately 2.08 ns$^{-1}$) with the increase of the acceptor content, even in the presence of the SiO$_2$/TiO$_2$ NC. However, the value of $k_{nr}$ significantly increased with an increasing acceptor concentration, and it was greater with the SiO$_2$/TiO$_2$ NC. Consequently, $A_\pi$ decreased with an increasing acceptor concentration, with a smaller value with the SiO$_2$/TiO$_2$ NC than that without the NC. The values of $A_\pi$ with and without the SiO$_2$ and TiO$_2$ NPs, as a mixture and individual components, are listed in Tables I and II.

The existence of one, two, or three lifetimes can be interpreted by the presence of one, two, or three conformers.44 This allows a comparison between the various decays and the realization of the lifetime decays obtained at 440 nm for the PFO/MEH-PPV hybrids with and without the SiO$_2$/TiO$_2$ NC, corresponding to the emission region of PFO, are shown in Figure 11(a,b), respectively. The acceptor decays for the PFO/MEH-PPV hybrids with and without the SiO$_2$/TiO$_2$ NC at a collection wavelength of 560 nm are shown in Figure 11(c,d), respectively. A global analysis including the data obtained at 440 and 560 nm was also carried out, confirming the general trends of the data in Tables IV and V. In these tables, the lifetime decays were calculated by the following expression.

\[
\tau = \frac{\sum (\tau_i B_i)}{\sum (\tau_i B_i)}
\]

The parameters $B_i$ and $\tau_i$ are the fitting parameters, which are strongly dependent on the conformer geometries and environment. The existence of one, two, or three lifetimes can be interpreted by the presence of one, two, or three conformers.44 This allows a comparison between the various decays and the realization.
The offset between the energy levels for the MEH-PPV and PFO46,47 suggested an exciplex formation between the donor and the acceptor. Therefore, the long decay component in the MEH-PPV emission decay at 560 nm was attributed to the presence of the exciplex, which is in agreement with a previous report for the PFO/MEH-PPV blend.45 As shown in Figures 2(b) and 3(b), the overlapping of the exciplex and the MEH-PPV emission.45

Table IV. Main Fitting Parameters And Lifetime Decays of the Thin Films of PFO at 0.1, 0.5, 1.0, 5.0, and 10 wt. % of MEH-PPV

<table>
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<tr>
<th>Acceptor content (wt. %)</th>
<th>Relative amplitude</th>
<th>Donor lifetime (τ1 ps)</th>
<th>χ²</th>
<th>Accepter lifetime (τ2 ps)</th>
<th>Relative amplitude</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>B</td>
<td>τ1</td>
<td></td>
<td></td>
<td>B1</td>
</tr>
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<tr>
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</table>

<table>
<thead>
<tr>
<th>Acceptor content (wt. %)</th>
<th>Relative amplitude</th>
<th>Donor lifetime (τ1 ps)</th>
<th>χ²</th>
<th>Accepter lifetime (τ2 ps)</th>
<th>Relative amplitude</th>
</tr>
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<tbody>
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<td>B</td>
<td>τ1</td>
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<td></td>
<td>B1</td>
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<td>0.460</td>
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REFERENCES

7. Chen, C.-T.