Non-Radiative Energy Transfer Mechanism and Optoelectronic Properties of (PFO/TiO$_2$)/Fluorol 7GA Hybrid Thin Films

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Abstract— **Energy transfer between poly (9,9'-di-n-octylfluorenyl-2,7-diyl) (PFO)/TiO2 nanoparticles (NPs), as a donor, and Fluorol 7GA as an acceptor has been studied. The energy transfer parameters were calculated by using mathematical models. The dominant mechanism responsible for the energy transfer between the donor and acceptor molecules was Förster-type, as evidenced by large values of quenching rate constant and critical distance of energy transfer as well as fluorescence quantum yield and excited state lifetime of donor in the presence of acceptor. Moreover, these composites, which were used as an emissive layer in organic light emitting diodes, were investigated in terms of current– voltage and electroluminescence spectra.**

Keywords- Energy transfer parameters; Förster-type; Electroluminescence; Organic light emitting diodes

I. INTRODUCTION

Emitting conjugated polymers exhibit themselves as active materials in thin film technology due to their application in photovoltaic [1, 2] and electroluminescent [3, 4] devices. The devices performance is strongly influenced by the polymer's photophysical and electronic properties.

Polyfluorene (PF)-based LEDs performance is limited by their poor stability as well as low luminance efficiency [5, 6]. However, it is still receiving remarkable attention due to several merits such as: low cost, easy fabrication, low operating voltage and flexibility. In another aspect, several strategies were implemented to improve the performance of polymer light emitting diodes (PLEDs), including proper matching of the polymer's energy levels with electrodes' working functions, the employment of transporting layers for both holes and electrons, multi-layer device fabrication, etc. Another possible approach is via polymers blending [7]. The later approach was reported to successfully improve the performance of optoelectronic devices, enhance quantum efficiency as well as offer possibility for color tuning [8, 9]. Tremendous enhancement in both photoluminescence (PL) and electroluminescence (EL) characteristics has been attributed mainly on the formation of bulk heterojunctions resulted from homogenous dispersion of emissive material in a polymeric matrix [10].

In general, the energy transfer mechanism in polymer blend is a complex competing

process between Forster-type energy transfer and Dexter-type energy transfer. While both mechanism may simultaneously take place in the blend, the former mechanism is dominantly used to describe energy transfer event in polymer blend systems [11, 12], molecular dye systems [13, 14] and photosynthetic aggregates [15, 16]. Although the exact energy transfer mechanism can be determined using suitable equipments [17], the theoretical approach is conveniently used to provide supporting arguments [18].

This work is intended to present a theoretical investigation on the photophysical and energy transfer properties and suggests a possible mechanism for the energy transfer between poly (9,9'-di-n-octylfluorenyl-2.7-diyl) (PFO)/TiO$_2$ nanocomposite and Fluorol 7GA. In addition, the using of these materials as a single emitting layer in OLED is also demonstrated.

II. EXPERIMENTAL PROCEDURES

The poly (9,9'-di-n-octylfluorenyl-2,7-diyl) (PFO) (M$_W$ = 58200) and TiO$_2$ powder (mean size of 25 nm) were purchased from Sigma-Aldrich, USA; whereas the Fluorol 7GA (M$_W$ = 324.41) was purchased from Exciton. These materials were dissolved in toluene solvent produced by Fluka. The glass and indium tin oxide (ITO) substrates were purchased from Merck Balzers.

The thin films were prepared on glass substrate for the photoluminescence (PL) and optical absorption measurements, while it prepared on ITO substrate for current–voltage (J-V) and electroluminescence (EL) measurements.

Different weight ratios of Fluorol 7GA (0.3, 1.0 and 3.0 wt. %) were added into fixed ratio of PFO: TiO$_2$ (90:10 wt. %) under sonication for 1 h. The concentration of the PFO was fixed at 15 mg/ml for all samples. By spin coating technique, 100 μL of (PFO/TiO$_2$)/Fluorol 7GA composite was deposited onto a substrate (glass and ITO) with dimensions of 2 cm × 1.2 cm. The thickness and active area of the aluminium cathode prepared were 150 nm and 0.076 cm^2, respectively, for OLED characterizations.

Perkin Elmer Lambda 900 UV–VIS Spectrometer and Perkin Elmer (LS55) Luminescent Spectrophotometer were employed to obtain the absorption and PL spectra, respectively. The I–V and EL measurements were obtained using a Keithley 238 measurement system and HR2000 Ocean Optic Spectrometer, respectively.

III. RESULTS AND DISCUSION

As shown in Fig. 1, the large spectral overlap between the emission spectrum of PFO/TiO$_2$ and absorption spectrum of Fluorol 7GA gives good evidence to efficient energy transfer between monomers of PFO (donor) and molecules of Fluorol 7GA (acceptor). Therefore, Förster-type energy transfer is possible in this system. Moreover, the radiative energy transfer between PFO (donor) and Fluorol 7GA (acceptor) is weak as supported by low concentration level of the acceptor. This finding is compatible with previous reported studies in which Förster-type is the prominent mechanism for energy transfer in most polymer-dye blends [19, 20].
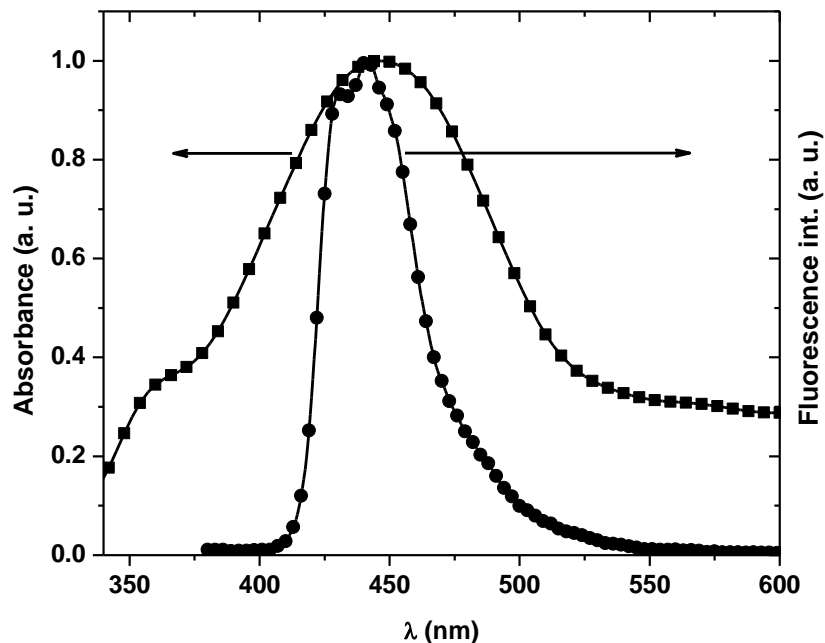
Fig. 1: Normalized absorption spectrum of Fluorol 7GA and fluorescence spectrum of PFO/TiO$_2$.

Fig. 2 illustrates that the maximum emission intensities exhibited a red-shift with increasing acceptor concentration which may be attributed to radiative migration due to self-absorption [21, 22]. As the acceptor content exceeded 3 wt. %, the emission of donor was almost completely quenched; resulting in the complete energy transfer from the PFO to the Fluorol 7GA. This proved the efficient non-radiative energy transfer from donor monomers to acceptor molecules in present of TiO$_2$ nanoparticles (NPs) [23]. Once the weight ratio of the acceptor was 1.0 wt. %, the emission intensity from Fluorol 7GA reached a maximum, and then decreased when the weight ratio in the blends was higher than this ratio. This reduction may be due to aggregation of the Fluorol 7GA molecules [24].
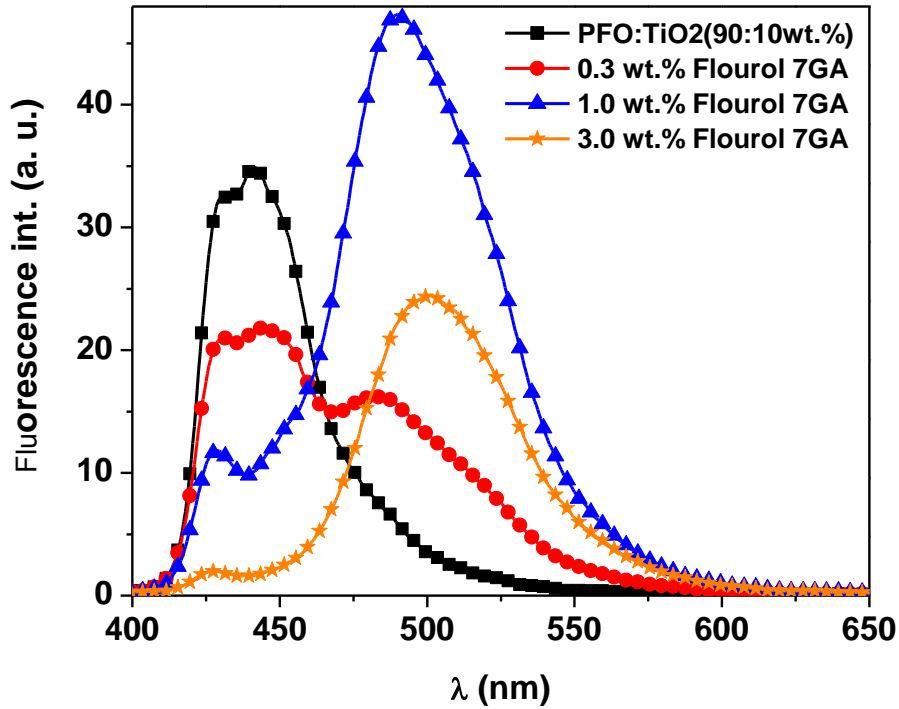
Fig. 2: Emission spectra of PFO/TiO$_2$ in absence and presence of Fluorol 7GA. (λ_{ex} = 355 nm).

The absorption and fluorescence spectra of the blends can be employed to determine the non-radiative energy transfer parameters of the system. According to Eqs. 1 and 2 [25, 26], the Stern-Volmer (k_{SV}) and the quenching rate (k_q) constants can be obtained from the slopes of the Stern-Volmer plots (Fig. 3).

$$\frac{I_D}{I_{DA}} = 1 + k_{SV}[A] \tag{1}$$

$$k_q = \frac{k_{SV}}{\tau_n} \tag{2}$$

where I_D and I_{DA} represent the fluorescence intensities of donor in the absence and presence of acceptor, respectively, [A] is the concentration of acceptor, and τ_D (~ 346 ps) [24] is the excited state lifetime of donor in absence of acceptor.
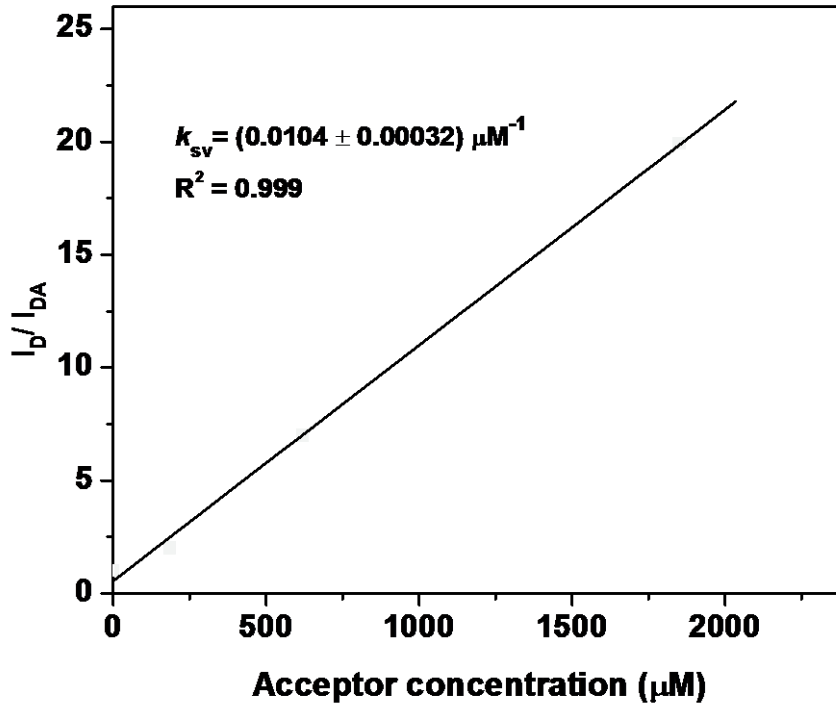
Fig. 3: Stern-Volmer plots for fluorescence quenching of PFO/TiO$_2$ by Fluorol 7GA.

The linear Stern–Volmer plot obtained, as shown in Fig. 3, indicates homogeneous dynamic quenching of the PFO by the Fluorol 7GA in present of the TiO$_2$ NPs. The value of k_{SV} obtained was ~ 0.0104 (μM)$^{-1}$, which means that 50 % of the fluorescence was quenched at Fluorol 7GA concentration of approximately 96.2 μM. The k_q has been evaluated as 3.01×10^{13} M^{-1}.S^{-1}, which is significantly greater than

the minimum value for efficient quenching (1×10^{10} M^{-1}.S^{-1}) [27]. The high k_q value indicates the good combination between the PFO and the Fluorol 7GA in present of TiO$_2$ NPs, and thus excellent quality of the interface between them.

Due to the homogeneous dynamic quenching of the PFO by the Fluorol 7GA, the Stern-Volmer equation can also be written as:

$$\frac{I_D}{I_{DA}} = \frac{\tau_D}{\tau_{DA}} = \frac{\emptyset_D}{\emptyset_{DA}} \qquad (3)$$

where $\emptyset_D$ (~ 0.72) [24] is fluorescence quantum yield of donor in the absence of acceptor, whereas $\emptyset_{DA}$ and τ_{DA} are the fluorescence quantum yield and excited state

lifetime of donor in the presence of acceptor [27].

The ϕ_{DA} and τ_{DA} in present of the TiO_2 NPs with different Fluorol 7GA weight ratios have been determined and tabulated in Table 1. It can be clearly seen that, the ϕ_{DA} values dramatically decreased upon addition the Fluorol 7GA. This reduction gives another evidence for that the possibility of radiative energy transfer is weak. Meanwhile, the significant lower of the τ_{DA} than that for the PFO in present of TiO_2 NPs is additional evidence of efficient the non-radiative energy transfer from the PFO/TiO_2 nanocomposite to Fluorol 7GA [28].

Table 1: Quantum yield and lifetime of donor in the presence acceptor.

Acceptor content	ϕ_{DA}	τ_{DA} (ps)
0.3 wt. %	0.46	224
1.0 wt. %	0.26	126
3.0 wt. %	0.044	21.2

The critical transfer distance (R_o) can be determined using the Förster theory [29]. The large value of R_o (~ 66 Å) indicates that the dominant mechanism responsible for energy transfer is Förster type, where this type is effective only in the range of R_o typically between 10 Å and 100 Å [30, 31].

Fig. 4 illustrates the effect of Fluorol 7GA on current (I) of PFO/TiO_2 nanocomposite under forward bias (V). It can be seen that the current decreased with increasing the Fluorol 7GA content due to the resistivity enhancement of the light emitting layer [32]. Moreover, the reduction in current of the devices indicates an increment in electron-hole (exciton) confinement as well as exciton recombination efficiency, which are crucial for the enhancement of device performance [33, 34].The charge trapping process can occur together with energy transfer in the ITO/(PFO/TiO_2)/Fluorol 7GA/Al devices as proved by the J-V behavior (Fig. 4).
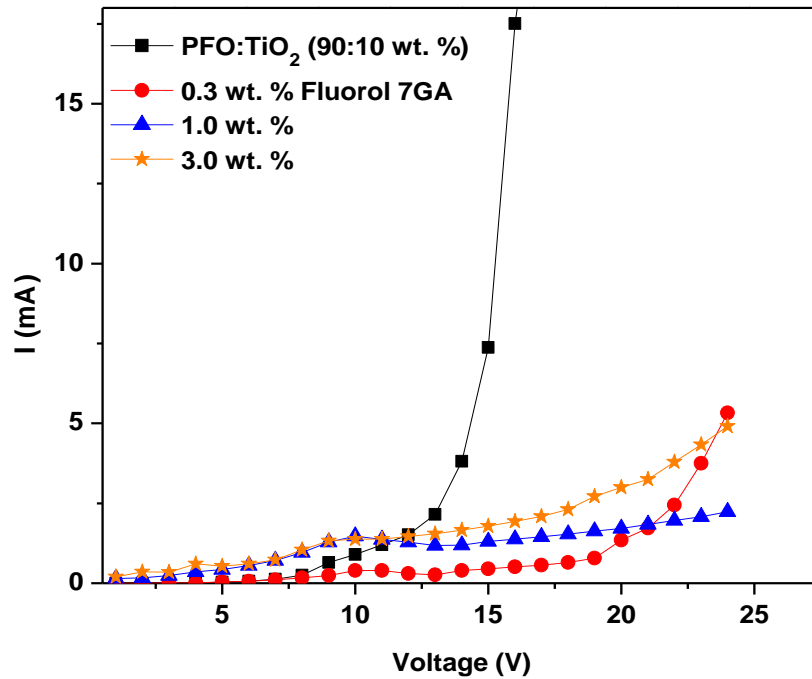
Fig. 4: Current -Voltage characteristic of the OLEDs.

EL spectra of all devices exhibited broad visible emission extending from 400 nm up to 750 nm (not shown). The EL spectra of PFO/TiO$_2$ displayed peaks at 425, 450, 519 and 555 nm. The first two blue emission bands are related to PFO [35], while the other two green emission bands can be attributed to the electrochemical degradation of PFO and the keto defect during device operation and fabrication, respectively [35, 36]. New shoulder peak at 590 nm was observed, upon addition of Fluorol 7GA, together with the previous peaks of the PFO/TiO$_2$ ascribed to the Förster energy transfer and carrier trapping processes, which can work together in the device.

IV. CONCLUSION

Energy transfer mechanism and optoelectronic properties of (PFO/TiO$_2$-)/Fluorol 7GA thin films have been investigated. Each of strong overlap between the emission band of PFO/TiO$_2$ and the absorption band of Fluorol 7GA, higher values of R_o and k_{SV} indicate that the dominant mechanism of the energy transfer is Förster type. In addition, an enhancement in intensity of Fluorol 7GA and a quenching in intensity of PFO/TiO$_2$ with addition Florol 7GA confirmed the efficient Förster energy transfer from the PFO to the Fluorol 7GA in present of TiO$_2$ NPs. Both Förster energy transfer and charge trapping process in the device led to a raise in the electron-hole recombination, and thus improved the device performance. In future work, optoelectronic properties of this device will be investigated in detail.

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