Exciton diffusion lengths of organic semiconductor thin films measured by spectrally resolved photoluminescence quenching

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We demonstrate spectrally resolved photoluminescence quenching as a means to determine the exciton diffusion length of several archetype organic semiconductors used in thin film devices. We show that aggregation and crystal orientation influence the anisotropy of the diffusion length for vacuum-deposited polycrystalline films. The measurement of the singlet diffusion lengths is found to be in agreement with diffusion by Förster transfer, whereas triplet diffusion occurs primarily via Dexter transfer. © 2009 American Institute of Physics. [DOI: 10.1063/1.3079797]

I. INTRODUCTION

Although organic semiconductors have been employed in a variety of thin film photonic devices,12 including organic photovoltaics (OPVs) and organic light emitting diodes (OLEDs), the optimization of such devices requires understanding of and control over energy transport.3,4 For example, the accurate determination of the exciton diffusion length (LD) and diffusivity (D) is important in optimizing the design of solar cells and OLEDs. Accordingly, a variety of methods have been used to extract these fundamental electronic parameters. Most notable of these techniques include thickness dependent photoluminescence (PL) quenching, and spectrally resolved photocurrent response of Schottky diodes. These techniques have significant drawbacks, however, that limit their accuracy. In this work we demonstrate that spectrally resolved PL quenching (SR-PLQ) can be used to accurately measure the exciton diffusion length of a variety of archetype organic semiconductors including amorphous N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (α-NPD), boron subphthalocyanine (SubPc), and 4′-bis(9-carbazolyl)-2,2′-biphenyl (CBP), and polycrystalline 2,3,7,8,12,13,17,18-octaethyl-21H23H-porphine platinum(II) (PtOEP), di-indenoperylene (DIP), and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA).

Ghosh and Feng5 introduced a widely used technique for extracting the diffusion length by measuring the photoresponse of an organic thin film Schottky diode. The diffusion length is found by assuming that the spatial distribution of excitons near the dissociating metal/organic interface is determined by the extent of optical penetration into the film arising from the wavelength dependent absorption coefficient. The accuracy of this method depends on the consideration of optical interference near a metal surface. Enhanced quenching of excitons at the metal interface can also complicate the measurement due to long range (5–50 nm) energy transfer,7 resulting in an overestimation of the exciton diffusion length. This problem is further compounded by metal penetration of up to several tens of nanometers into the organic layers during deposition.8 Corrections for transmission losses through metal contacts can also introduce errors due to surface plasmon effects. It is not surprising, therefore, that the extracted LD often exceeds 100 nm,9–15 while independent support for such large values has not been independently verified.

Another commonly used means for measuring LD from luminescent materials is thickness dependent PL quenching (TD-PLQ), where the luminescence of organic films of various thicknesses is measured both with and without an exciton quenching layer positioned adjacent to the material under study. The PL intensity from optical pumping increases as the thickness increases to greater than the exciton diffusion length due to diffusion away from the quenching interface.4,12,13 However, the growth of the thinnest films needed for these measurements does not always result in continuous layers. Also, different degrees of optical interference must be taken into account for samples with and without quenching layers; an effect that can be further complicated by thin incomplete films. Finally, the boundary condition (BC) of perfect exciton blocking has been shown to be invalid when the film thickness is ~LD, leading to uncertainties in the analysis.15,16

Here, we employ SR-PLQ. In this method, the spatial exciton distribution is extracted from the absorption spectrum to determine the PL efficiency near a quenching interface. This method allows the use of a single continuous film sample, where interference effects are negligible over a particular wavelength range, and the BCs can be simplified as compared to the thickness dependent measurement. Since SR-PLQ employs only a single thin film sample, it is particularly useful for measuring the diffusion length as a function of material purity or crystalline order, which are often thickness dependent and can vary from growth to growth. Measurements of LD using an analogous method have been reported on single crystals of tetracene18 and anthracene,19 where quenching occurred at an oxidized free surface. The

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luminescence was then normalized to the lamp intensity, which requires accurate measurement of the total number of emitted photons. Since this normalization procedure is difficult for materials with low PL efficiency, in this work we replace the free surface with organic films that serve as either exciton quenching or blocking (i.e., nonquenching) layers. Using this modified procedure, we eliminate the need for potentially complex and inaccurate measurement of the absolute incident light intensity.

This paper is organized as follows. In Sec. II we discuss the exciton diffusion model utilized to extract $L_D$ from SR-PLQ measurements. Förster transfer-mediated singlet diffusion and Dexter transfer of triplets are also discussed. Experimental methods are provided in Sec. III, and in Sec. IV the results are presented for several amorphous and polycrystalline organic thin films grown by vacuum deposition. We discuss these results in Sec. V, and provide conclusions in Sec. VI.

II. THEORY

The experimental configuration for the SR-PLQ measurement is shown in Fig. 1 (inset). A wavelength dependent exciton distribution $n(x)$, where $x$ is the distance from the sample surface facing the incident illumination] in a thin film is generated using a monochromated light source. The material under study is capped with either a transparent exciton blocking or exciton quenching layer, where the corresponding BCs are $\partial n(0)/\partial x = 0$ (BC1) or $n(x=0)=0$ (BC2). For sufficiently thick films, $n \rightarrow 0$ as $x \rightarrow t$ (BC3), where $t$ is the film thickness. The exciton distribution is then described by the one-dimensional steady state exciton diffusion equation,

$$\frac{L_D^2}{\tau} \frac{\partial^2 n(x)}{\partial x^2} - \frac{n(x)}{\tau} + \frac{I_0 \alpha}{\cos(\theta_k)} \exp\left( - \frac{\alpha x}{\cos(\theta_k)} \right) = 0,$$

where the first term describes the diffusive transport, the second term accounts for the natural decay of excitation, and the last term is the exciton generation rate. Accordingly, the diffusivity $D=L_D^2/\tau$, $\tau$ is the exciton lifetime, $I_0$ is the incident photon flux, $\alpha$ is the absorption coefficient, and $\theta_k$ is the incidence angle at $x=0$, accounting for wavelength dependent refraction through the blocking or quenching layer.\textsuperscript{20}

In Fig. 1 we show $n(x)$, for example, the case of $L_D$ = 15 nm and $\alpha=0.005$ and 0.05 cm$^{-1}$, in the presence of either a blocking or quenching layer. At large $\alpha$, there is significant exciton generation near the quenching interface, and hence increased exciton quenching. Comparing the PL intensity of the sample with a blocking layer to that with a quenching layer, we obtain the normalized quenching ratio $\eta$ by integration of the corresponding exciton densities over all $x$ as follows:

$$\frac{\text{PL}_{Q}(\alpha)}{\text{PL}_{B}(\alpha)} = \frac{\int_0^\infty n_Q(x,\alpha)dx}{\int_0^\infty n_B(x,\alpha)dx}.$$

Here, $n_Q$ is the exciton density in the film with the quenching layer, $n_B$ is the density in the film with the blocking layer, and $\text{PL}_Q$ ($\text{PL}_B$) is the PL emission intensity for the sample with the quenching (blocking) layer at a given excitation wavelength. Solving for $n(x)$ in Eq. (1), Eq. (2) then becomes

$$\eta(\alpha) = \frac{\alpha(\lambda)L_D}{\cos(\theta_k)} + 1 = \alpha'(\lambda)L_D + 1.$$

Thus, the slope of a plot of PL$_B$/PL$_Q$ versus $\alpha'(\lambda)$ yields the diffusion length in cases where energy transfer between the film and the quenching layer can be neglected.

For situations where there is an overlap in the absorption spectrum of the quenching layer with the emission spectrum of the layer under study, nondiffusive Förster energy transfer to the quenching layer must be considered.\textsuperscript{14} In this case, Eq. (1) is modified for a sample with a thin quenching layer as

$$\frac{L_D^2}{\tau} \frac{\partial^2 n(x)}{\partial x^2} - \frac{n(x)}{\tau} + I_0 \alpha' \tau \exp(-\alpha' x) - n(x) \times \left[ \rho_A \int \left( \frac{R_0^6}{R(x)^6} \right) dA \right] = 0,$$

where the Förster transfer rate is integrated over the entire quenching interface of area $A$, $R_Q$ is the Förster radius,\textsuperscript{21} $R(x)$ is the distance from a point in the film to any molecule within the quenching layer, and $\rho_A$ is the number of quenching molecules per unit area.\textsuperscript{22} Equation (4) is then
The transition dipole factor for crystalline materials is given as:

\[ L_D^2 \frac{\partial^2 n(x)}{\partial x^2} - n(x) + L_D^2 \alpha' \exp(-\alpha' x) - \rho a^2 \frac{2\pi}{3} \frac{R_0^6}{\chi^2} n(x) = 0. \]  

(5)

Both Eq. (1) (with BC1 and BC3) and Eq. (5) (with BC2 and BC3) can be solved numerically for the samples with blocking and quenching layers, respectively, at every \(\alpha(\lambda)\). These solutions are then iteratively fit to \(\text{Pl}_{\text{Lh}}/\text{Pl}_{\text{Q}}\) versus \(\alpha(\lambda)'\) using Eq. (2), from which \(L_D\) is extracted.

To understand the relationship between the microscopic process of Förster transfer (dipole-dipole interactions) and the macroscopic diffusivity, we consider a simple cubic lattice of lattice constant \(a\), where diffusion is assumed to be isotropic and limited to the six nearest neighbor molecule interactions. Since the coherence time for exciton motion is generally much smaller than the exciton hopping time at room temperature,\(^{21}\) we have\(^{16}\)

\[ D = \frac{4}{3} \tau_H \frac{\alpha}{\tau}, \]

(6)

where \(\tau_H\) is the hopping time. Then, \(1/\tau_H\) is the Förster rate, \(k_F\), given by:\(^{25}\)

\[ k_F = \frac{1}{\tau} \frac{3}{4 \pi} \frac{\kappa^2 \Phi_F}{n^4 \sigma} \frac{1}{\alpha} \frac{1}{\tau} \left( \frac{R_0}{a} \right)^6, \]

(7)

where \(\Phi_F\) is the fluorescence yield, \(\kappa\) is the transition dipole orientation factor, \(\sigma\) is the overlap integral between the emission and absorption spectra,\(^{21,25}\) \(n\) is the index of refraction at the wavelength where \(\sigma\) is at a maximum, and \(R_0\) is the corresponding Förster radius within a film of homogeneous composition (i.e., the self-transfer radius). For amorphous films with randomly oriented rigid dipoles,\(^{24}\) \(\kappa = 0.845 \frac{2}{3}\). The transition dipole factor for crystalline materials is\(^{21}\) \(\kappa = \cos(\phi_{AD}) - 3 \cos(\phi_D)\cos(\phi_D)\), where \(\phi_{AD}\) is the angle between donor and acceptor dipole moments, and \(\phi_D\) and \(\phi_{AD}\) are the angles between the molecular stacking direction and the transition dipole moment of donor \((D)\) and acceptor \((A)\) molecules. Because the crystalline materials studied here generally form parallel stacks, \(\phi_{AD} = 0^\circ\) and \(\phi_D = \phi_D\). From Eqs. (6) and (7), the diffusion length can thus be written as:

\[ L_D = \sqrt{\frac{\kappa^2 \Phi_F \sigma}{8 \pi n^4 \alpha^2}} = \frac{R_0}{\sqrt{6} \alpha^2}. \]

(8)

For the nearest neighbor diffusion by hopping (i.e., electron exchange interactions) expected for triplet excitons, the transfer rate is described by Dexter theory, viz.,\(^{25}\)

\[ \frac{1}{\tau_H} = k_D = \frac{2\pi}{h} \frac{K}{\alpha^2} \exp\left(-\frac{2a}{\chi}\right) \sigma_D, \]

(9)

where \(\hbar\) is Planck’s constant, \(\sigma_D\) is the normalized overlap of the molecular emission and absorption spectra,\(^{23,25}\) \(\chi\) is the effective orbital radius of the final and initial electronic states which depends on the transfer direction relative to the molecular axes, and \(K\) is a normalization constant. From Eqs. (6) and (9), the Dexter-mediated diffusion length is simply

\[ L_D = \sqrt{\frac{\pi K \sigma_D}{3\hbar}} \exp\left(-\frac{a}{\chi}\right). \]

(10)

Due to the rapidly decaying exponential where \(\chi \approx a\), it is clear that this process only extends to nearest neighbor hopping events.

### III. EXPERIMENTAL

All materials were grown on a quartz substrate in high vacuum \((1 \times 10^{-6}\) Torr\) at a deposition rate of between 0.4 and 0.6 nm/s. The total film thickness (typically between 200 and 600 nm) was larger than the largest optical path length \((1/\alpha_{\text{MIN}})\) determined by the wavelength range of the experiment. The quenching or blocking layer was then deposited on top of the organic film. The thickness of the quenching layer was varied between 5 and 10 nm to assure that the measurement was independent of this variable. Light was incident via the film surface (see Fig. 1: inset).

PL data were obtained in a PTI QuantaMaster spectrophotometer at incident and detection angles of 45° using unpolarized monochromatic light from a Xe lamp under flowing nitrogen at low incident intensities (<1 mW/cm²). Excitation spectra were collected for samples with quenching and blocking layers at fixed peak emission wavelengths. For materials with emission at \(\lambda > 500\) nm, a long pass filter was used to eliminate wavelength-doubled light. Absorption coefficients, transmission losses, and the ratio of the spectrally dependent reflectance of the quenching and blocking layers were measured using unpolarized light with a Perkin Elmer spectrophotometer. Film thicknesses and indices of refraction were obtained using a variable angle spectroscopic ellipsometer for films grown on Si substrates.

Lifetime measurements were preformed using a pulsed N₂ laser pump (wavelength \(\lambda = 337\) nm; pulse width ~0.8 ns) focused onto the sample under flowing nitrogen. A Hamamatsu C4334 streak camera was used to monitor the time-resolved emission decay. The lifetime data were deconvolved from the laser pulse width and then fit with a single exponential decay to extract the natural lifetime, except for PtOEP emission, where triplet-triplet annihilation\(^{23}\) was taken into consideration in analyzing the data. The crystallinity and stacking orientation of each sample were determined using a rotating anode Rigaku Cu Ka x-ray diffractometer (XRD). For crystalline films, the volume-averaged crystal size was extracted from XRD data using the Scherrer relationship.\(^{26}\)

### IV. RESULTS

Excitation spectra were collected at a fixed wavelength located near a peak in the emission. The peaks shown in Fig. 2 correspond to singlet excited states, except for PtOEP where the emission between \(\lambda = 625–725\) nm and 725–850 nm is due to triplets localized on a single molecule and a triplet dimer state, respectively.\(^{27}\)

Quenching and blocking layers were selected for each material based on the alignments of highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) energies to that of the material under test,\(^{28}\) as well as ab-
Both quenching layers for each material yielded nearly identical results in the quenching and blocking layers were considered in determining the overlap with CBP and NPD emission.

Figure 3 shows \( \alpha(\lambda) \) for all of the materials studied. Example excitation data corrected for transmission losses for SubPc and PtOEP are shown in Fig. 4. From such data, the experimental quenching ratio \( \eta \) is plotted versus \( \alpha' \) in Fig. 5.

XRD data for films of SubPc, PtOEP, DIP, and PTCDA are shown in Fig. 6. No x-ray peaks were observed for SubPc, NPD, or CBP, indicating that these films are amorphous. For PtOEP, four (001) diffraction orders are observed, along with two weak peaks possibly due to a small fraction of a secondary crystalline phase. Films of PTCDA exhibit the (102) diffraction peak at \( 2\theta=27.80^\circ \) \((d=0.32 \text{ nm})\), suggesting that the molecules lie flat on the substrate.\(^\text{1}\) Multiple orders of the DIP (001) diffraction peak \((d=1.67 \text{ nm})\) are associated with the upright molecular orientation of the \( \beta \) phase,\(^\text{10}\) Also, smaller peaks at \( 2\theta=6.09^\circ \) \((d=1.45 \text{ nm})\) and \( 20.86^\circ \) \((d=0.43 \text{ nm})\) correspond to the (001) peak of the \( \alpha \) phase and the (020) peak of the \( \beta \) phase, respectively,\(^\text{30}\) suggesting a small degree of polymorphism. For DIP grown on a thin crystal template layer of PTCDA, the diffraction peaks at \( 2\theta=20.86^\circ \) \((d=0.37 \text{ nm})\), and \( 25.06^\circ \) \((d=0.36 \text{ nm})\) are associated with (020), (120), and (121) planes of the \( \beta \) phase, respectively, indicating that the DIP molecular planes lie parallel to the substrate surface in this case.

![Figure 3](image3.png)  
**FIG. 3.** Measured (normal incidence) absorption coefficients \( \alpha \) as functions of wavelength for CBP (filled circle), NPD (hollow triangle), SubPc (filled square), PTCDA (hollow circle), PtOEP (hollow square), DIP standing up (light X), and DIP lying flat (black X). The absorption coefficient at \( \lambda=550 \text{ nm} \) for samples with DIP lying flat on the substrate is roughly three times larger than that for molecules oriented upright.

![Figure 4](image4.png)  
**FIG. 4.** PL excitation spectra for (a) SubPc at an emission wavelength of \( \lambda=630 \text{ nm} \) and (b) PtOEP at \( \lambda=790 \text{ nm} \) with (black line) and without (gray line) a quenching layer \( (C_{60}) \). For PtOEP, BCP is used as an exciton blocking layer. Excitation spectra were corrected for transmission losses and reflectance variations in the quenching and blocking layers. Absorption coefficients, adjusted for 45° incidence, are also included as dotted black lines for both materials.

![Figure 5](image5.png)  
**FIG. 5.** Quenching ratio \( \eta \) versus absorption coefficient \( \alpha' \) for (a) 600 nm DIP, (b) 450 nm PtOEP, (c) 400 nm PTCDA, (d) 300 nm SubPc, (e) 400 nm NPD, and (f) 400 nm CBP. Transmission losses and reflectance variations in the quenching and blocking layers were considered in determining \( \eta \) from the excitation scans. The quenching data were fit using Eq. (3) except for NPD and CBP where Förster energy transfer was considered. Black and gray circles in (b) represent PtOEP at emission wavelengths of \( \lambda=655 \text{ nm} \) and 790 nm corresponding to monomer and dimer excitons, respectively. The DIP films grown on quartz (gray circles) and (0.5 nm) PTCDA/quartz (black circles) show x-ray diffraction peaks corresponding to standing and flat lying molecular orientations, respectively.
observed at wavelengths where $\alpha'$ is largest, indicating that the quenching data in Fig. 5 can be used to obtain $L_D$ as discussed in Sec. II. The effect of nonradiative energy transfer to the quenching layer is negligible for most of the materials combinations studied since $R_Q \ll R_D$ with the exceptions of NPD and CBP. Accordingly, data from PtOEP, PTCDA, DIP, and SubPc were fit with a linear regression to Eq. (3), while data from CBP and NPD were iteratively fit with the use of Eqs. (1), (2), and (5). The linear relationship between $\eta$ and $\alpha'$ is shown in Fig. 5, suggesting the presence of only a single resolvable diffusion length (and hence a single excitonic species), independent of exciting wavelength. Indeed, our method is only capable of observing excitons with strong oscillator strengths in both absorption and emission and hence is not sensitive to the presence of, for example, nonradiative triplet or charge transfer (CT) states which also might be present.\textsuperscript{1} Diffusion lengths obtained from Fig. 5 are included in Table I, and a comparison with values calculated using Eq. (8) are provided in Table II. The corresponding diffusivities are found in Table III.

V. DISCUSSION

Using the emission data in Fig. 2, the Förster radius $R_Q$ for transfer between each material and its quenching layer are listed in Table I. These radii are calculated assuming randomly oriented rigid dipoles, a refractive index of the film evaluated at the wavelength corresponding to the peak of the absorption-emission spectral overlap, and a PL quantum efficiency of 2% for DIP and SubPc.\textsuperscript{22} Literature values of the PL quantum efficiency for NPD,\textsuperscript{32} CBP,\textsuperscript{22} PtOEP,\textsuperscript{33} and PTCDA (Ref. 34) were found to be 29%, 60%, 0.1%, and 0.9%, respectively.

The Förster self radius for a particular material $R_0$ was calculated using the data from Figs. 2 and 3 and the corresponding PL quantum efficiency. The angles $\phi_3$ were found to be $\phi_{102}=80^\circ$ for PTCDA and $\phi_{020}=70^\circ$ and $\phi_{001}=22^\circ$ for DIP molecules in the flat lying and upright stacking directions, respectively.\textsuperscript{35} The closest intermolecular spacing $a$ for the crystalline materials was extracted from data in Fig. 6 and for amorphous materials was estimated from the density as a volume-averaged radius. The resulting values of $\kappa$, $\alpha$, and $R_0$ are given in Table II.

In Fig. 4, the maximum differences in excitation spectra between the samples with the blocking or quenching layers is

![Image](https://example.com/image.png)

**TABLE I.** Calculated quenching layer Förster radii ($R_Q$) and diffusion lengths ($L_D$) for singlet ($S$) and triplet ($T$) excitons of crystalline (C.) and amorphous (Amorph.) films.

<table>
<thead>
<tr>
<th>Material</th>
<th>Exciton</th>
<th>Crystallinity (Orientation)</th>
<th>Quenching/Blocking Layers</th>
<th>$R_Q$ with $C_{60}$ (nm)</th>
<th>$L_D$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPD</td>
<td>S</td>
<td>Amorph.</td>
<td>$C_{60}$/BCP</td>
<td>2.4</td>
<td>5.1 ($\pm 1.0$)\textsuperscript{*}</td>
</tr>
<tr>
<td>CBP</td>
<td>S</td>
<td>Amorph.</td>
<td>$C_{60}$ (or NTCDAG)/Bare</td>
<td>2.7</td>
<td>16.8 ($\pm 0.8$)\textsuperscript{a}</td>
</tr>
<tr>
<td>SubPc</td>
<td>S</td>
<td>Amorph.</td>
<td>$C_{60}$/Bare</td>
<td>1.1</td>
<td>8.0 ($\pm 0.3$)</td>
</tr>
<tr>
<td>PTCDA</td>
<td>S</td>
<td>C.-55 nm (flat)</td>
<td>$C_{60}$ (or NPD)/NTCDAG</td>
<td>0.9</td>
<td>10.4 ($\pm 1.0$)</td>
</tr>
<tr>
<td>DIP</td>
<td>S</td>
<td>C.-150 nm (upright)</td>
<td>$C_{60}$/Bare</td>
<td>1.2</td>
<td>16.5 ($\pm 0.4$)</td>
</tr>
<tr>
<td>DIP</td>
<td>S</td>
<td>C.-30 nm (flat)</td>
<td>$C_{60}$/Bare</td>
<td>1.2</td>
<td>21.8 ($\pm 0.6$)</td>
</tr>
<tr>
<td>PtOEP</td>
<td>T-Mon.</td>
<td>C.-150 nm (upright)</td>
<td>$C_{60}$/Bare</td>
<td>0.6</td>
<td>18.0 ($\pm 0.6$)</td>
</tr>
<tr>
<td>PtOEP</td>
<td>T-Dim.</td>
<td>C.-150 nm (upright)</td>
<td>$C_{60}$/BCP</td>
<td>0.6</td>
<td>13.1 ($\pm 0.5$)</td>
</tr>
</tbody>
</table>

\textsuperscript{*}Corrected for energy transfer to the quenching layer.

A. Singlet exciton diffusion

Amorphous SubPc has been used as a donor material in high open circuit voltage OPVs.\textsuperscript{36} The optimal SubPc thickness for such OPV cells was found to be 13.5 nm, suggesting a relatively short diffusion length, which is consistent with $L_D=8.0 \pm 0.3$ nm measured using data in Fig. 5. Similarly, NPD—a commonly used hole transporting layer in OLEDs—has also been used as a donor in OPVs\textsuperscript{37} with an optimal layer thickness of only 10 nm. In this case, we obtain $L_D=5.1 \pm 1$ nm which is comparable to $L_D=4.9$ nm inferred from thickness dependent OLED performance.\textsuperscript{38} For CBP, an emissive-layer host used in OLEDs, we find $L_D=16.8 \pm 0.8$ nm, clearly the largest diffusion length of the amorphous materials studied here. From Eq. (8), it is evident that the large PL quantum efficiency implies a large diffusion length.

Perhaps the most extensively studied crystalline organic electronic is the compound PTCDA.\textsuperscript{3} The diffusion length of polycrystalline films was first reported by Bulović and Forrest\textsuperscript{9} using the method of Ref. 5 to obtain $L_D=225$ nm, 88 nm, and 79 nm at the exciting wavelengths of 590 nm, 500 nm, and 400 nm, respectively. The long wavelength excitation has been identified as a CT state, whereas the shorter
TABLE II. Average hopping distance ($a$), index of refraction ($n$), dipole orientation factors ($\kappa$), Förster self radii ($R_0$), and calculated ($L_D$ calc.) and measured diffusion lengths ($L_D$ meas.).

<table>
<thead>
<tr>
<th>Material</th>
<th>$a$ (nm)</th>
<th>$n$</th>
<th>$\kappa$</th>
<th>$R_0$ (nm)</th>
<th>$L_D$ calc. (nm)</th>
<th>$L_D$ meas. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPD</td>
<td>0.58</td>
<td>2.0</td>
<td>0.69</td>
<td>1.9</td>
<td>8 (±2)</td>
<td>5.1</td>
</tr>
<tr>
<td>CBP</td>
<td>0.53</td>
<td>1.9</td>
<td>0.69</td>
<td>1.5</td>
<td>6 (±2)</td>
<td>8.0</td>
</tr>
<tr>
<td>SubPc</td>
<td>0.51</td>
<td>3.1</td>
<td>0.69</td>
<td>1.0</td>
<td>5 (±1)</td>
<td>16.5</td>
</tr>
<tr>
<td>Dip (upright)</td>
<td>0.83</td>
<td>1.7</td>
<td>1.55</td>
<td>2.0</td>
<td>10 (±2)</td>
<td>21.8</td>
</tr>
<tr>
<td>Dip (flat)</td>
<td>0.43</td>
<td>1.6</td>
<td>0.65</td>
<td>1.7</td>
<td>11 (±3)</td>
<td>10.4</td>
</tr>
<tr>
<td>PTCDA</td>
<td>0.32</td>
<td>2.3</td>
<td>0.92</td>
<td>1.4</td>
<td>0.4 (±0.5)</td>
<td>18.0/13.1</td>
</tr>
<tr>
<td>POEP</td>
<td>1.14</td>
<td>1.8</td>
<td>1.0</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1Evaluated at the wavelength of maximum spectral overlap between the absorption and emission.
2Transition dipole moment vector for crystalline films calculated using MATERIAL STUDIO v4.1.
3From Eq. (8) in text.
4Volume average radius as inferred from the thin film density.
5From XRD data.
6From Ref. 45.
7 Tritrplet absorption coefficients were measured with thick films (~450 nm). The triplet absorption peak was at 715 nm with a maximum absorption coefficient of ~2 x 10^4 cm^-1.

wavelength species was attributed to a singlet Frenkel exciton. The diffusion length was also found to be 9 nm as measured by singlet-singlet annihilation experiments, while $L_D$ = 15 nm was reported using TD-PLQ experiments. In this work, we find $L_D$ = 10.4 ± 1.0 nm for singlets in polycrystalline (55 nm crystalline grain size) PTCDA lying with its (102) axis oriented perpendicular to the substrate plane. This is in agreement with reports in Ref. 39. The value reported in Ref. 40 is possibly an overestimation of the diffusion length since nonradiative Förster energy transfer from PTCDA to the quenching layer was not taken into account. These differences may also, in part, be due to differences in crystalline order between samples which can have a significant effect in determining this parameter. As noted above, the low oscillator strength of CT excitons makes it difficult to measure their diffusion lengths by our technique.

Another perylene derivative (DIP) has been widely investigated due to its ability to grow in a tightly packed monoclinic lattice with the potential for high charge mobility and long exciton diffusion lengths. Recently, the diffusion length of this material was reported to be 80–100 nm by Kurrle and Pflaum using the method of Gosh and Feng. In contrast, we find a singlet exciton diffusion length of $L_D$ = 16.5 ± 0.4 nm. As with PTCDA, difficulties in applying the method of Ref. 5 can significantly overestimate the diffusion length and may incorrectly identify the existence of multiple exciton species, problems that are largely avoided using SR-PLQ.

The change in crystal orientation of DIP grown with and without a predeposited crystalline templating layer of PTCDA, as inferred from the XRD data in Figs. 6(b) and 6(c), is similar to that reported previously. It is found that the absorption coefficient of the DIP film with the (020) axis oriented normal to substrate increases by nearly threefold (see Fig. 3) over that of the upright (001) orientation, while also resulting in an increase in the diffusion length to $L_D$ = 21.8 ± 0.8 nm. Similar anisotropy has been observed for single crystalline anthracene, where the diffusion length along its $c$ axis was found to be smaller than along $a$ and $b$ axes.

We compare the calculated singlet diffusion lengths based on Förster transfer to measurements in Table II. We find good agreement between the two values, particularly, for the amorphous materials. This implies that while long range transfer can occur through the Förster process, it is predominantly nearest neighbor interactions with a very high transfer rate that dominate the energy migration process. Equation (8) also implies that the directions of closest molecular spacing in crystalline films will likely have the largest diffusion length, which is consistent with our observations for DIP and for anthracene. From Eq. (8), we also see that the natural lifetime does not impact the singlet diffusion length when Förster transfer is the dominant mechanism. Lastly, an increase in fluorescence yield should result in an increase in diffusion length due to increases in the radiative decay rate.

B. Triplet exciton diffusion

Recently, POEP has gained interest for use in OPVs, where fast intersystem crossing to the long lived (~110 μs) triplet state has been proposed to result in a concomitant increase in the exciton diffusion length. However, POEP-C60 bilayer cells have been shown to have an optimal POEP thickness of only 30 nm, suggesting that the diffusion length of triplets may be comparable to singlets in these films.

TABLE III. Measured natural lifetime ($\tau$) and calculated diffusivities ($D$) from experimental diffusion lengths in Table I.

<table>
<thead>
<tr>
<th>Material</th>
<th>Exciton</th>
<th>$\tau$ (ns)</th>
<th>$D$ (10^-4 cm^2/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPD</td>
<td>S</td>
<td>3.5</td>
<td>0.7 (±0.2)</td>
</tr>
<tr>
<td>CBP</td>
<td>S</td>
<td>0.7</td>
<td>40 (±12)</td>
</tr>
<tr>
<td>SubPc</td>
<td>S</td>
<td>≤1</td>
<td>6.4</td>
</tr>
<tr>
<td>PTCDA</td>
<td>S</td>
<td>3.2 (±0.7)</td>
<td>3.4 (±0.9)</td>
</tr>
<tr>
<td>Dip (upright)</td>
<td>S</td>
<td>1.8 (±0.5)</td>
<td>15 (±4)</td>
</tr>
<tr>
<td>Dip (flat)</td>
<td>S</td>
<td>1.8 (±0.5)</td>
<td>26 (±7)</td>
</tr>
<tr>
<td>POEP</td>
<td>T-Mon.</td>
<td>800 (±50)</td>
<td>0.041 (±0.003)</td>
</tr>
<tr>
<td>POEP</td>
<td>T-Dimer</td>
<td>2800 (±300)</td>
<td>0.00061 (±0.0001)</td>
</tr>
</tbody>
</table>

8From Ref. 32.
fluorescent materials. Indeed, we measure \( L_D = 13.1 \pm 0.5 \) and \( 18.0 \pm 0.6 \) nm for the PtOEP triplet dimer \(^{27,45} \) (at \( \lambda = 790 \) nm) and monomer (\( \lambda = 655 \) nm) excitons, respectively. A similarly short diffusion length has been measured for the phosphor, platinum(II)-tetraphenyltetrazoporphyin (PtTPBP), where \( L_D = 5.7 \pm 0.5 \) nm for amorphous films.\(^{46} \)

To understand the differences between \( L_D \) for the monomer and dimer excited states, we measured their natural lifetimes of 0.8 \( \mu s \) and 28 \( \mu s \), respectively. This reduction in lifetime is expected, since trapping at the lower energy dimer populates the monomer state. Given the much longer lifetimes of triplets as compared with singlets, their comparable values for \( L_D \) suggest much lower diffusivities. For example, for PtOEP, we infer \( D = 4.0 \times 10^{-6} \) cm\(^2\)/s and 6.2 \( \times 10^{-8} \) cm\(^2\)/s for the monomer and dimer triplets, respectively (see Table II). The presence of dimer states reduces \( D \), and therefore the absence of such states within crystalline films could result in a longer \( L_D \). From Eq. (10), we expect the triplet diffusivity to be particularly sensitive to crystalline order as a result of the exponential dependence of the transfer rate on the molecular separation distance. This can qualitatively be seen between the longer \( L_D \) measured for crystalline films of PtOEP compared to amorphous films of PtTPBP.

VI. CONCLUSIONS

We have shown that SR-PLQ is useful for measuring the exciton diffusion lengths of a wide range of amorphous and crystalline organic thin films. We find that the stacking habit and the existence of dimer states strongly affect the exciton diffusion length in polycrystalline vacuum-deposited films. Surprisingly, the diffusion lengths of both triplet and singlet states are offset by their lower diffusivities that result from the short range Dexter energy transfer process. This is in contrast to singlet diffusion by long range Förster transfer.

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\(^{16}\)R. C. Powell and Z. G. Soos, J. Lumin. 11, 1 (1975).
\(^{20}\)\( D = a \sin(\theta_1/n_1) \sin(\theta_2/n_2) \) is the index of refraction for the quenching layer, and \( n_2 \) is the index for the organic layer.
\(^{22}\)\( \rho_0 = \frac{1}{1.1} \text{nm}^{-2} \) for \( C_0 \text{g} \) close packing.
\(^{26}\)A. L. Patterson, Phys. Rev. 56, 978 (1939).
\(^{31}\)Roughly approximated by comparison with materials of known \( \Phi_F \).
\(^{35}\)Angles were calculated using MATERIAL STUDIO V4.1.