Quasi-steady-state measurement of exciton diffusion lengths in organic semiconductors

Drew B. Riley, Oskar J. Sandberg, Wei Li, Paul Meredith, and Ardalan Armin

Sustainable Advanced Materials Programme (Sêr SAM), Department of Physics, Swansea University, Singleton Park, Swansea SA2 8PP, United Kingdom

ABSTRACT

Exciton diffusion plays a decisive role in determining the recent rise in charge-generation yield (CGY) and power-conversion efficiency brought about by non-fullerene acceptor (NFA) solar cells. In this presentation a technique, named pulsed-PLQY, is introduced to measure the exciton diffusion length in organic semiconductors through exciton-exciton annihilation (EEA) without the need for temporal measurements. Pulsed-PLQY is validated by comparing to established EEA techniques using both simulated and experimental results. It is found that Pulsed-PLQY conserves the validity of established EEA techniques while the implementation is faster, easier, significantly simplifies the equipment required, and is less sensitive to experimental conditions than traditional EEA techniques. Utilising pulsed-PLQY, it is found that NFA’s have increased diffusion lengths, compared to fullerene acceptors, and that this increase is driven by increases in diffusivity.

Keywords: organic semiconductors, organic solar cells, diffusion length, exciton-exciton annihilation

1. INTRODUCTION

Organic solar cells (OSCs), created by blending a donor and acceptor molecule and depositing to create a bulk heterojunction solar cell, are a promising solar harvesting technology for many new applications such as indoor and stand-alone power. These materials have a number of advantageous features such as low embodied energy processing, earth abundant constituent materials, suitability for flexible form factor, and tunable optoelectronic properties. Due to the low dielectric constants of organic semiconductors the primary exciton species upon photon absorption are bound electron-hole pairs known as excitons. The generation of free carriers requires excitons to diffuse to the interface between the donor and acceptor phases of the BHJ and create a charge-transfer (CT) state by transferring an electron (hole) from the donor (acceptor) to the the acceptor (donor) phase. The transfer of an electron (hole) from the donor (acceptor) to the acceptor (donor) molecule in these cells is typically considered to be driven by an energetic offset between the lowest unoccupied (highest occupied) molecular orbital, LUMO (HOMO), levels of the two materials, known as type I (II) charge generation.

The recent advent of non-fullerene acceptor (NFA) based OSCs have propelled power conversion efficiencies consistently above 15% and as high as 18.2%. Low offset NFA solar cells have minimal offset between the HOMO levels of the donor and acceptor molecule. Despite this, low-offset NFA systems show dramatic increases in short-circuit current and high charge generation yield, compared to the fullerene predecessors. It has been conjectured that the lack of driving force in NFA’s is compensated for by an increase in exciton lifetime or diffusivity, amalgamated into diffusion length, increasing the attempt frequency of CT-state formation.

Time resolved photoluminescence (TRPL) exciton-exciton annihilation (EEA) experiments are a robust technique for measuring exciton diffusion lengths in organic semiconductors. In this technique the exciton annihilation coefficient is measured by linearizing TRPL data at high excitation fluences, allowing for the calculation of the low density diffusion length, assuming a value for the average distance over which annihilation occurs, known as the capture radius. Recent studies have found that the $d_{100}$ lamellar spacing measured by grazing-incidence wide-angle X-ray scattering (GIWAX) to be a close estimate of the exciton capture radius.

In this work the limits of EEA experiments are explored by evaluating the density dependence of the diffusion length extracted from TRPL-linearization using a Mote-Carlo hopping model. Then an alternative quasi-steady-state
state EEA approach, named pulsed-PLQY, is proposed and demonstrated via the same simulations. TRPL linearization and pulsed-PLQY are then performed on the well studied system P3HT and the results compared. Overall, it is found that pulsed-PLQY has a larger operational window, is less sensitive to excitation fluence, is faster, easier, and requires less specialized equipment. Finally, pulsed-PLQY is used to measure the diffusion length as well as the annihilation and diffusion coefficients of technologically relevant NFA organic semiconductors. It is found that diffusion lengths in NFA organic semiconductors are longer than the fullerene acceptors and that this difference is driven by an increase in diffusivity.

2. THEORETICAL BACKGROUND

Singlet-singlet exciton annihilation can occur when two excitons interact with each other, typically assumed to be on neighbouring molecules. The result of this interaction is an exciton with excess energy, which quickly relaxes to the lowest excited-state, and one non-radiative decay event to the ground state. The rate equation for the density of excitons ($\rho$) in an organic semiconductor is determined by the sum of this second order non-radiative decay and the first order natural decay

$$\frac{d\rho(t)}{dt} = -\frac{\rho(t)}{\tau} - \gamma \rho^2(t)$$

(1)

where $t$ is the time, $\tau$ is the natural (low-density) lifetime for singlet excitons, and $\gamma$ is the exciton-exciton annihilation coefficient. When the process of annihilation is diffusion-limited $\gamma$ can be related to the diffusion constant ($D$) in the film as

$$\gamma = 4\pi D R_0$$

(2)

where $R_0$ is the exciton capture radius. The solution to Eq. 1 is

$$\rho(t) = \frac{\rho_0 \exp(-t/\tau)}{1 + \gamma \rho_0 \tau \left[ 1 - \exp(-t/\tau) \right]}$$

(3)

where $\rho_0$ is the initial exciton density (at $t = 0$). Eq. 3 can be linearized as

$$\frac{1}{\rho(t)} = \left[ \frac{1}{\rho_0} + \gamma \tau \right] \exp(t/\tau) - \gamma \tau$$

(4)

allowing for $\gamma$ to be obtained from either slope or intercept of a $1/\rho$ vs $\exp(t/\tau)$ plot, assuming $\tau$ is known. Finally, the annihilation coefficient can be related to the low-density diffusion length ($L_D$), through Eq. 2, noting that

$$L_D = \sqrt{2nD\tau}$$

(5)

where $n$ is the dimensionality of the diffusion, although some researchers choose to drop the factor of 2 for convenience. Extracting $\gamma$ from the slope or intercept of Eq. 4 in combination with Eqs. 2 and 5 allows for the calculation of the low density diffusion length. In contrast to this method one can analyse the dynamics expressed by equation 1 in a steady-state manner. The total number of excitons that decay naturally in accordance with Eq. 1 is $\rho = \int_0^\infty \rho(t)/\tau dt$. While the photoluminescence quantum efficiency can be expressed as $\eta_{PL} = \rho_0 \eta_{PL,0}/\rho_0$, where $\eta_{PL,0}$ is the low density photoluminescence quantum efficiency. From Eq. 3 the photoluminescence quantum efficiency is then obtained as:

$$\eta_{PL} = \eta_{PL,0} \frac{\ln \left[ 1 + \rho_0 \gamma \tau \right]}{\rho_0 \gamma \tau}$$

(6)

Therefore, by measuring $\eta_{PL}/\eta_{PL,0}$ as a function of $\rho_0$ one can fit to obtain the product of $\gamma \tau$ and either: (i) calculate the diffusion length directly using Eqs. 2 and 5 without the need for any temporal measurements, or (ii) measure the natural lifetime to calculate $\gamma$ (or $D$).
3. RESULTS AND DISCUSSION

Prior to performing TRPL linearization and pulsed-PLQY the limits of each method were explored using a Monte-Carlo Hopping model including linear (natural) decay and exciton-exciton annihilation, assumed to occur between nearest neighbour pairs.\(^{28}\) The simulations were limited to nearest neighbour interactions in order to capture only the relevant physics and to allow for each experimental technique to be evaluated under conditions where the systems parameters, such as diffusion length, are known and can be compared to extracted values. Further, limiting annihilation to nearest neighbour pairs allows for the calculation of \(\gamma\) and \(L_D\) since \(R_0\) is known exactly. To this end the exciton dynamics were simulated over a wide range of densities and the resulting simulated photoluminescence was analysed with both TRPL-linearization and pulsed-PLQY. This analysis allows for the identification of operational windows, defined as the range of densities over which each analysis of the simulated kinetics reproduces the input diffusion length. The lattice spacing (dx), temporal step size, and natural lifetime used were 0.775 nm, 1 ps, and 300 ps respectively, corresponding to a diffusion coefficient of \(10^{-3} \text{ cm}^2/\text{s}\) and an input 3D diffusion length \((L_{D,inpt})\) of 13.4 nm. Figure 1 shows the results of these analyses.

Figure 1 (a) shows the TRPL-linearization of the simulated photoluminescence for a selection of initial densities, the black dashed lines indicate fits to Eq. 4. \(\gamma\) was extracted from both the slope and intercept of the fits and used to calculate the diffusion length using Eqs. 2 and 5. In contrast to this, Figure 1 (b) shows the same simulated data analysed in a steady-state manner. Here the photoluminescence quantum efficiency is taken as the ratio of the number of excitons decaying naturally to the total number of excitons in the simulation. The blue circles indicate the normalized photoluminescence quantum efficiency as a function of initial exciton density, the black line indicates these data fit to Eq. 6. Figure 1 (c) summarizes this data by showing the diffusion length calculated from the slope (green circles) and intercept (red circles) of the TRPL-linearization as a function of the initial excitation density and from the fitting of Eq. 6 to the PLQY data as a function of the upper limit to the fitting (blue circles).

The diffusion lengths extracted from TRPL-linearization reproduce \(L_{D,inpt}\) at high \(\rho_0\), where the second-order non-radiative decay dominates Eq. 1. However, the diffusion length (or \(\gamma\)) extracted from the slope increasingly overestimates the input diffusion length with decreasing \(\rho_0\). Similar reduction in extracted annihilation coefficient (as measured by high density TRPL experiments) with increasing excitation density has been observed by other researchers in previous studies on organic semiconducting polymers.\(^{18}\) The apparent dependence of \(\gamma\) on \(\rho_0\) limits the range over which the true value of \(\gamma\) (and hence \(L_D\)) can be extracted. In the case of extraction from the slope, which depends inversely on \(\rho_0\), the extracted value converges to the expected low-density diffusion length only when \(\gamma \tau \gg 1/\rho_0\). Therefore, the operational window for extraction from the slope starts at high excitation densities, as indicated by the green shading in Figure 1 (c). On the other hand, according to Eq. 4, the intercept does not depend on \(\rho_0\). This is reflected in the larger operational window for the diffusion length extracted from the intercept (red shaded region in Figure 1 (c)). However, in the limit where \(\rho_0 \gamma \tau \ll 1\) Eq. 3 is reduced to a single exponential decay and one cannot expect to extract any second-order information, reflected in the increasing overestimation of the diffusion length with decreasing \(\rho_0\). The diffusion lengths extracted from pulsed-PLQY reproduce the input diffusion length for a wider range of initial densities, reflected in the larger operational window (blue shaded region in Figure 2). Importantly, the confidence in the extracted value from pulsed-PLQY increases with increasing initial densities. Whereas, in the case of TRPL-linearization, depending on the choice of initial densities, the confidence in the extracted value may decrease.

Actualization of TRPL-linearization requires careful analysis of the range of excitation densities used, as well as a femptosecond laser source to inject (and subsequently let evolve) the initial exciton density, accurate measure of the natural lifetime, and specialized equipment capable of measuring the quenching kinetics described by Eq. 1, which occur on the order of picoseconds in organic semiconductors.\(^{16,19-23,25}\) Furthermore, as described above, the operational window for determining the diffusion length (or \(\gamma\)) of these materials occurs at high excitation density where the quenching is fastest requiring increasing resolution to resolve. Besides which, not all organic semiconductors are stable at high excitation densities and may undergo photo- or thermal-oxidation at sufficiently high excitation fluences. In contrast to this, implementation of pulsed-PLQY requires the same femptosecond source as TRPL-linearization, however; the light-collection can be accomplished with non-specialized equipment operating at a quasi steady-state. Further, the exciton diffusion length can be calculated directly from the
product $\gamma \tau$ without the need for any temporal measurements, and $\gamma$ (or $D$) can be determined without the need for a high resolution TRPL apparatus.

To validate these simulations TRPL-linearization and pulsed-PLQY were carried out on a P3HT thin film and the results compared. Figure 2 shows these results. Figure 2 (a) shows the linearized high density TRPL data. The data for each density was fit to Eq. 4 and $\gamma$ was extracted from the intercept, as that was shown to be the more accurate measure. The 1D diffusion length was calculated from $\gamma$ using Eqs. 2 and 5, assuming a value of $R_0$ equal to the $d_{100}$ spacing measured by GIWAX.\textsuperscript{29} These results are shown as the red circles in Figure 2 (c). Figure 2 (b) shows the relative photoluminescence quantum yield as a function of initial excitation density. To measure $\eta_{PL}$, the photoluminescence was collimated and focused into an imaging spectrograph. $\eta_{PL}$ was calculated by dividing the peak spectral intensity by the associated excitation density, this is shown by the blue circles in Figure 2 (b). To exemplify the simplicity of the measurement a second set of data was collected where the imaging spectrograph was replaced with a silicone diode and the voltage response was measured using a lock-in technique. The voltage response divided by the excitation density was used to calculate the relative $\eta_{PL}$. Although the use of a silicon photodiode does not provide spectral information, the relative $\eta_{PL}$, and therefore $\gamma \tau$ (or $L_D$), can be measured with a further reduction in equipment specialization. To ensure that the samples were not damaged by the high excitation fluences, the experiment was performed forwards (low-to-high density) and reverse (high-to-low density) subsequently. The $\eta_{PL}$ data collected with the spectrograph are fit to Eq. 6, shown by the black dashed line, and the extracted product of $\gamma \tau$ is used, with the $d_{100}$ spacing as an estimate of $R_0$, to calculate the diffusion length via Eqs. 2 and 5.

The results of the experiments on P3HT are summarized in Figure 2 (c) which shows the 1D diffusion length extracted from TRPL-linearization as a function of initial density and pulsed-PLQY as a function of upper limit to the fitting. As predicted by the simulations the diffusion length extracted from TRPL-linearization

![Figure 1. Simulated exciton dynamics. a) Linearized TRPL results for selected initial densities, black dashed lines indicate fits to Eq. 4. b) Relative PLQY as a function of density, black dashed line indicates fit to Eq. 6. c) Diffusion length extracted from the slope (green circles) and intercept (red circles) of Eq. 4 for each excitation density, and the simulated PLQY data as a function to the upper limit of the fitting to Eq. 6. (blue circles)](image-url)
Figure 2. P3HT thin film data. a) TRPL-linearization, black dashed lines indicate fits to Eq. 4, and b) pulsed-PLQY data taken by spectrograph (blue circles) and lock-in (orange squares) methods, black dashed line indicate fit to Eq. 6. c) Diffusion length measured from the intercept of the TRPL-linearization data as a function of the excitation density (red circles) and pulsed-PLQY as a function of the upper limit to the fit of Eq. 6 (blue circles). Black dashed line indicates calculated 1 dimensional $L_D$.

(red circles) decreases to a constant value with increasing initial density. The diffusion length measured by pulsed-PLQY (blue circles) converges to a constant value with increasing upper fitting limit. These results verify the simulations and demonstrate that pulsed-PLQY is a viable and accurate alternative measurement technique for measuring diffusion lengths without the need for any temporal measurements, or the annihilation coefficient without the need for high resolution TRPL equipment.

The product of $\gamma \tau$ found from pulsed-PLQY was $(7.2 \pm 0.2) \times 10^{-19}$ cm$^3$, leading to a 1D diffusion length of $8 \pm 1$ nm, comparable to literature values (using the same value for $R_0$). Using the natural lifetime, found to be $330 \pm 10$ ps, a value of $\gamma = (2.15 \pm 0.08) \times 10^{-9}$ cm$^3$/s was found for the annihilation coefficient, slightly lower than previous values extracted from TRPL-linearization. However, as exemplified by the simulations, a slightly lower value of $\gamma$ is expected from pulsed-PLQY than from TRPL-linearization. Finally, the diffusion coefficient was calculated from $\gamma$, and $R_0$ according to Eq. 2 and found to be $(1.0 \pm 0.3) \times 10^{-3}$ cm$^2$/s, in agreement with previous values from quenching experiments.

After pulsed-PLQY was established it was used to evaluate $\gamma \tau$ and the subsequent 1D and 3D diffusion lengths in a collection of organic semiconductors, including several technologically relevant NFAs used in state-of-the-art organic solar cells. Further, the natural lifetime was measured, at low excitation density, to evaluate the annihilation and diffusion coefficients. These results are summarized in Table 1. The NFAs (such as ITIC, IT4F, Y6, and BTP-eC9) were found to have much longer diffusion lengths than the benchmark fullerene acceptor PC$_{60}$BM. Subsequent measurement of the natural lifetime shows that the increase in diffusion length is driven by increased diffusivity. Increases in diffusivity increase the diffusion length, allow for excitons to travel to the interface more easily. Additionally, increased diffusion coefficients allow interfacial excitons to attempt to form CT states multiple times. Both these affects increase the probability of CT-state formation regardless of HOMO
Table 1. Material parameters extracted from the pulsed-PLQY fittings (γτ and LD), low-density TRPL fittings (τ), and subsequently calculated (γ and D) for various organic semiconductors. R₀ is assumed to be the d₁₀₀ spacing taken from the provided references, the error in R₀ is assumed half the value given by the d₁₀₀ spacing. |PC₆₀|BM estimate for R₀ is taken as 1 nm as GIWAX d₁₀₀ does not give intermolecular distance in this case.

| Material          | γτ(×10⁻¹⁸) (cm³) | R₀ (nm) | LD (nm) | LDp (nm) | τ (ps) | γ(×10⁻⁹) | D(×10⁻⁴) (cm²/s) |
|-------------------|------------------|---------|---------|----------|--------|-----------|------------------|
| PM6               | 0.088±0.002      | 2.1⁸    | 2.6±0.3 | 4.5±0.3  | 64     | 1.4±0.2   | 5±1              |
| P3HT-Regi random  | 0.134±0.02       | 1.0³¹   | 5±1     | 8±1      | 175    | 0.76±0.05 | 6±3              |
| PTB7-Th           | 0.144±0.004      | 2.4³¹   | 3.1±0.3 | 5.4±0.3  | 123    | 1.17±0.09 | 3.9±0.9         |
| PCDTBT            | 0.329±0.005      | 1.6³²   | 5.7±0.9 | 9.9±0.9  | 203    | 1.62±0.08 | 8±2              |
| P3HT-BM           | 0.52±0.01        | 1.0¹    | 9±2     | 23±3     | 777    | 0.65±0.02 | 5±2              |
| ITIC (NFA)        | 1.23±0.03        | 1.6³³   | 11±2    | 19±2     | 120    | 10.3±0.9  | 50±10            |
| IT4F (NFA)        | 2.54±0.07        | 1.8³⁴   | 15±2    | 26±2     | 205    | 12.4±0.7  | 60±10            |
| Y6 (NFA)          | 8.5±0.2          | 1.5⁸    | 30±5    | 51±5     | 799    | 10.6±0.3  | 60±10            |
| BTP-eC9 (NFA)     | 10.6±0.3         | 1.6⁹    | 33±5    | 56±5     | 389    | 27±1      | 140±40           |

In conclusion, pulsed-PLQY was introduced as an alternative approach to established exciton-exciton annihilation techniques. A Monte-Carlo hopping model was used to validate the experimental technique and the subsequent results on P3HT agree with the models predictions. Pulsed-PLQY was then used to determine the diffusion lengths of various organic semiconductors and the results show a dramatic increase in diffusion length in NFA materials, primarily driven by increased diffusivity. These results support the assertion that increases in diffusion constant contribute to the charge generation efficiency in low-offset NFA based organic solar cells. Pulsed-PLQY will contribute to the field of organic photovoltaics specifically, and organic optoelectronics more broadly, by providing an alternative technique to measure the diffusion length in organic semiconductors without the need for temporal measurements, or to measure annihilation coefficients without the need for a high resolution TRPL apparatus.

APPENDIX A. EXPERIMENTAL

Time Resolved Photoluminescence: The thin films were held in a cryostat (Linkam LTS420) under a constant flow of nitrogen gas to prevent photo-oxidation, and an initial density of excitons \( ρ₀ = P_{\text{abs}}/πω²f_x E_{\text{ph}} d \), \( P_{\text{abs}} \)-absorbed laser power, \( f_x \)-repetrate and \( ω \)-spotsize of the laser \( E_{\text{ph}} \)-incident photon energy, \( d \)-film thickness) is injected by an ultrafast laser source (Pharos PHM02-2H-3H). The resulting photoluminescence is collimated, filtered to remove scattered pump light, and focused into the streak camera (Hamamatsu C14831).

Pulsed-PLQY: Here the focusing lens is removed from the laser path in order to make a uniform (in-plane) distribution of excitons and the streak camera is replaced with an imaging spectrograph (Hamamatsu C14631-03), or a photo-diode (Thorlabs SM1PD1A) connected to a lock-in amplifier (Stanford Research Systems SR860), with the pump laser chopped at the reference frequency.

Film thickness: The film thickness was measured from ellipsometry data (J.A. Woollam M-2000 Spectroscopic Ellipsometer).

APPENDIX B. MONTE-CARLO MODEL

With the aim of modelling the dynamics within an organic semiconductor a 3D Monte-Carlo hopping model was invoked. First a lattice of sufficient volume \( V \) to accommodate the input density was created with spacing between each point \( dx \). The lattice is randomly populated with \( N \) excitons (where \( N = ρ₀ V \)). Once the lattice has been initialized the simulation is evolved in time with a temporal step-size \( dt \), defining the diffusion coefficient as \( D = dx²/6dt \). To simulate a thin film deposited on glass periodic boundary conditions on the \( x \) and \( y \) axis.
and reflecting boundary conditions on the z axis were implemented. Further, the size of the z dimension was held at 50 nm.

Once the lattice is generated there are three routes for each exciton at any given time step. The first is annihilation, where any exciton within one lattice spacing of another will decay non-radiatively via exciton-exciton annihilation, such that $R_0$ in Eq. 2 equals $dx$. The second route is an exciton hopping to an adjacent lattice site along the major axes. The choice of site to hop to is given by the Gillespie algorithm with equal probability for movement in each direction but limited to nearest neighbour pairs, and a maximum hopping rate given by the inverse of the temporal step size. The amount of time the exciton occupies this new site (the dwell-time, $\tau_{\text{Dwell}}$) is given by the total hopping rate away from the site ($\Gamma_i$) as $\tau_{\text{Dwell}} = T/\Gamma_i$, where $T$ is a pseudo-random number generated from an exponential distribution with unit expectation value and unit variance. The final pathway for an exciton to evolve is natural decay. The probability of natural decay is given by the input natural lifetime ($\tau$) as $dt/\tau$. Therefore, after each dwell time a pseudo-random number on a unit interval is generated, an exciton decays naturally when this is smaller than the decay probability.

Once the system has sufficiently evolved the effective diffusion length can be found from the Euclidean distance travelled by each exciton ($L_i$)

$$L_{D,\text{eff}} = \sqrt{\frac{\sum_{i=1}^{N} (L_i)^2}{N}}$$

which will converge to the input diffusion length ($L_{D,\text{input}} = \sqrt{6D\tau}$) in the low-density limit.

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