Chapter 2


Single-material organic solar cells have recently come to the research spotlight due to their simplicity, morphological robustness and high yield of exciton dissociation, which potentially enables high and stable power conversion efficiencies. In the most efficient devices, the exciton dissociation is believed to occur at the boundaries of domains with different molecular orientations. How exactly this is realized, remains an open question important to answer for future applications. Using α-sexithiophene as a model system, here it is shown that the single-event probability of the exciton dissociation at the boundaries of polycrystalline domains with different molecular orientation is extremely low (~0.5%) while the high efficiency of charge generation is gained via hundred-fold crossings of the domain boundaries due to long exciton diffusion length (~45 nm). In this capacity, the reported findings have direct implications on the understanding of the charge separation mechanism in neat films of organic semiconductors.

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2.1. Introduction

Single-material organic solar cells (OSCs) have a long history of almost half-century, with early simple devices based on tetracene\(^1\) and chlorophyll-a\(^2,3\). Since then, the power conversion efficiency has increased from 0.01% to impressive \(\sim 11\%\)\(^4-6\), owing to improved device architecture and better organic materials. Instead of donor and acceptor materials in the bulk heterojunction (BHJ) architecture\(^7\) of the most advanced OSCs\(^8-10\), a single organic material\(^11-15\) is used here as the photoactive layer. Single-material OSCs have recently begun to revitalize because of their conceptual simplicity\(^6,11\) and significantly improved stability\(^5,16,17\) but also as a playground for fundamental understanding of exciton dissociation and charge separation mechanisms\(^18,19\). In such devices, exciton dissociation has been reported to be facilitated by the formation of intermediate inter-molecular charge-transfer (CT) excitons\(^20,21\), at the homojunction of single \(p\)- and \(n\)-type doped organic semiconductors\(^22\), or at the interface of undoped domains with different molecular orientations and packing\(^23,24\). The latest approach has been thoroughly examined by Dong et al.\(^23\) who demonstrated efficient charge generation at the interfaces of polycrystalline alpha-sexithiophene (\(\alpha\)-6T) domains of standing and lying molecular orientations. As a result, inter-domain CT states are formed which mediate the charge generation, finally leading to an external quantum efficiency (\(EQE\)) of \(\sim 45\%\), a short-circuit current density of 3.6 mA cm\(^{-2}\), a high open-circuit voltage of 1.61 V, and a power conversion efficiency of 2.9%.

While the very mechanism of charge generation at the domain boundaries has been proven beyond any reasonable doubts, a central aspect of the exciton-to-charge conversion remains unaddressed: what is the probability of dissociation upon a single domain boundary crossing event? There are two conceivable scenarios: similarly to conventional BHJ OSCs, the probability is close to unity so that a single bounce against the interface suffices to dissociate the exciton into charges – which of course might occur at very different rates\(^25\). The important consequence is that the exciton diffusion length should be of the same order as the domain size — typically \(\sim 10\) nm\(^26-28\). Alternatively, the probability might be relatively low (say, < 1%) but the exciton passes many boundaries along its long diffusional path\(^29\), hereby increasing its accumulated chances to dissociate. The latter scenario may potentially offer an explanation for efficient exciton...
dissociation under conditions of a small interfacial driving force\textsuperscript{25,30} but it also calls for the exciton diffusion length which is well in excess of the domain size.

In this chapter, in fact the second scenario is realized in the case of neat \(\alpha\)-6T thin films is demonstrated. To investigate exciton diffusion and quenching at boundaries of \(\alpha\)-6T domains with different molecular orientations, a combination of precise sample fabrication, the photoluminescence (PL) quenching technique and kinetic Monte Carlo (KMC) simulations is used. It is shown that the probability of the single exciton dissociation event at the domain boundary is extremely low (~0.5%); however, the total share of thereby generated charges is substantial (more than 50% of the initial excitons) because excitons cross domain boundaries hundreds of times. In this case, a high overall dissociation probability is facilitated by the long exciton diffusion length of ~45 nm.

\section*{2.2. Results and Discussion}

Samples of \(\alpha\)-6T thin films were fabricated by thermal evaporation in vacuum onto quartz substrates (see Section 2.4.1). The films with standing, lying and mixed molecular orientations (Figure 2.1a–c) were obtained by varying the deposition conditions and using 2 nm of Copper Iodide (CuI) as a templating interlayer between the substrate and the \(\alpha\)-6T layer. In the mixed-orientation \(\alpha\)-6T films, standing and lying molecular orientations co-exist in domains with typical sizes of 10–20 nm as were previously characterized by x-ray scattering\textsuperscript{23,31,32}. The difference in absorption spectra also confirmed the molecular orientation of \(\alpha\)-6T thin films (Figure S2 of ESI). Figure 2.1d,e (open dots) shows PL transients of 40-nm thick films with two regular (standing and lying) molecular orientations; similar decay trace\textsuperscript{1} with a characteristic time of ~600 ps are measured. In contrast to the standing and lying films, PL in the mixed film decays noticeably faster, at ~400 ps (Figure 2.1f; open dots). A similar acceleration has been previously attributed\textsuperscript{23} to exciton quenching at the boundaries between polycrystalline domains with different molecular orientations.

\textsuperscript{1} Note that the faster PL decay of lying \(\alpha\)-6T reported by Dong et al.\textsuperscript{23} is most probably related to the used film thickness of 60 nm under which the lying molecular orientation for the lying film is not preserved, in line with results of Section S11 of ESI.
Figure 2.1. Sketches of molecular stacking (a–c) and time-resolved PL transients (d–f) of the standing (a, d), lying (b, e) and mixed orientation (c, f) α-6T (open dots) and α-6T/C<sub>60</sub> heterojunction (filled dots) films under 400 nm excitation. The excitons and their diffusional paths are depicted as red circles and black curve arrows, respectively. The red and blue dots represent electron and hole charge carriers, respectively. The thickness of all neat α-6T films and α-6T in the heterojunction film with mixed orientation is 40 nm; the thickness of α-6T in the heterojunction films with standing and lying α-6T orientations is 20 nm. The transients were obtained by integrating the PL maps measured by a streak-camera (see Figure S4 of ESI) in the 520–700 nm spectral range. The thick lines show the results of kinetic Monte Carlo simulations convoluted with the Gaussian apparatus function with standard deviation of ≅6 ps. C<sub>60</sub> stands for a 30-nm thick quenching layer. CuI served as the optically-transparent, 2 nm thick templating layer, used to obtain a lying α-6T orientation. All samples were encapsulated to avoid degradation in air; the data for samples without encapsulation are given in Figure S8 of ESI.

To get hold of the quenching efficiency at the domain boundaries, samples of the standing and lying molecular orientations were fabricated with a thickness of 20 nm, i.e. on the order of the domain size in the mixed orientation film<sup>23,31,32</sup>, and covered at the top with a 30-nm layer of C<sub>60</sub>. The latter is a strong electron acceptor that quenches the excitons with a high (close to 100%) efficiency<sup>33</sup>. Evidently (Figure 2.1d,e; filled dots), the PL from both these samples decays much faster (at ~100 ps time) than the PL from the sample of the mixed orientation, at ~400 ps (Figure 2.1f; open dots). If the probability of the domain boundary quenching had been close to unity, the PL of the mixed-orientation sample would have decayed similarly or even faster than in the standing and lying α-6T/C<sub>60</sub> samples because the domain size (estimated as 10–20 nm<sup>23,31,32</sup>) is smaller
than the α-6T thickness. The fact that this is not the case incontrovertibly proves that the quenching probability at a single standing/lying α-6T domain boundary is much lower than unity.

A plausible concern in the argumentation above is whether the excitons in the mixed film maintain their diffusivity similar to that in the standing or lying film. Otherwise an exciton might be trapped as e.g. a CT exciton at the domain boundary still retaining its PL, and dissociates into charges at a time scale of 100’s ps. To rule out this possibility, the 40-nm thick mixed film is covered with the C₆₀ quenching layer, which resulted in a substantial acceleration of the PL transient with a decay time of ~150 ps (Figure 2.1f; filled dots and Section S13 of ESI). If the excitons had ceased to retain mobility due to trapping at the domain boundaries (or even within a single domain), there would have been very little acceleration of the PL decay because the excitons would have not been able to reach the quenching layer at the top. In contrast, the much faster PL decay was experimentally observed, revealing that excitons in the mixed films retain their mobility to travel through domain boundaries. The exciton–exciton annihilation experiments in the mixed film (see Figure S14 of ESI) further support the above conclusion.

The quenching probability of excitons at the domain boundary more qualitatively can be estimated in the following simple way. First, the diffusion length \( L_D \) in the standing and lying films can be estimated as \( L_D = d_q \sqrt{T/\tau_q} \), where \( d_q = 20 \) nm is the thickness of the α-6T layer in the α-6T/C₆₀ heterojunction sample, \( T \) is the exciton lifetime \( (T \cong 600 \) ps as estimated from the PL trace of the 40-nm layer of standing or lying α-6T in Figure 2.1), and \( \tau_q \) is the decay time of PL from the α-6T/C₆₀ layer \( (\cong 100 \) ps). Therefore, \( L_D \cong 50 \) nm which is in line with the earlier-reported value. Next, the hopping time between α-6T molecules can now be calculated as \( \tau_h = (\delta^2/L_D^2)T \), where \( \delta \cong 0.87 \) nm is the (average) intermolecular distance (calculated as the cubic root from the elementary cell volume of \( 0.495 \times 0.6 \times 2.24 \) nm³), Reference 35 and Figure S17 of ESI), so that \( \tau_h \cong 0.18 \) ps. The number of boundary crossings is calculated as \( N = L/d \), where \( L = (\delta/\tau_h)T_m \) is the exciton travelling distance (i.e. the sum of the lengths of all segments over which an exciton has travelled), \( d \cong 10 \) nm is the domain size, and \( T_m \cong 400 \) ps is the diffusion time as obtained from PL decay of the mixed film. Note that the travelling distance \( L = 1900 \) nm is not to be confused with an exciton diffusion length \( L_D \cong 50 \) nm, i.e. the distance between initial and final exciton positions. For instance, if
the exciton travels back and forth in between two points, the diffusion length is short, but the travelling distance is long. Substituting the numerical values, $N \approx 190$ is obtained. Assuming the total probability of cumulative exciton dissociation as 70% (i.e. approximately the internal quantum efficiency, $IQE$, which is the measured $EQE$ of 45% divided by absorption by the photoactive layer of ~0.65), the probability of a single exciton dissociation event amounts to $p = 1 - 0.7^{L_D/N} \approx 0.2\%$. This probability of exciton dissociation at the single crossing of the domain boundary is arguably very low which is compensated by multiple domain boundary crossings because of a long travelling distance (i.e. a long $L_D$) so that the excitons crosses domain boundaries many times.

The probability of exciton dissociation at a domain boundary can be obtained more accurately from KMC simulations by fitting the KMC simulated transients to the experimental PL transients. First, parameters of exciton diffusion into different directions, i.e. for standing and lying molecular packings were obtained (see greater details in Section S16 of ESI). Figure 2.2a shows a scheme of the KMC simulation for standing and lying α-6T films. In brief, PL transients were calculated in the KMC simulations with the following input parameters: exciton lifetime $\tau_0$, site-to-site hopping time $\tau_{hop}$, and quenching probability at the α-6T/substrate interface $P_{substrate}$. The simulated transients for all samples with different film thicknesses were calculated to best-fit (as judged by a visual inspection) the respective experimental PL transients (Figure 2.1d,e and Figure S18c,d of ESI). After that, the optimised $\tau_0$, $\tau_{hop}$ and $P_{substrate}$ (see Table S10 of ESI) were used as the fixed input for the KMC simulation of the mixed α-6T films, with quenching probability at the domain boundaries $P_{domain}$ as the only varied parameter.

Table 2.1 summarizes the exciton diffusion coefficients and lengths. The diffusional coefficients into the $a$- and $b$-axis dimensions are quite similar. This is explained by a balance between the distance along the molecular stacking and the exciton hopping rate which depends on the dipole–dipole coupling (see Section S15 of ESI). Similar results have also been previously reported for zinc phthalocyanine and rubrene. The hopping time in the $c$-axis dimension of the crystallographic unit cell could not have been directly obtained from experimental data. However, as the coupling energy between two adjacent molecules is similar in both $b$-axis and $c$-axis dimensions (see Section S15 of ESI), diffusion coefficients in both dimensions ($D^c \approx D^b$) were set to be similar. The three-
dimensional diffusion length of 40–50 nm is in good agreement with the previous estimation using the simple model. Such long diffusion length is partially attributed to extremely low energetic disorder (< 4 meV) which excluded exciton cooling due to relaxation to lower energetic states\(^{37,42}\).

**Figure 2.2.** Schematics of the KMC simulations for standing/lying (a) and mixed-orientation (b) \(\alpha\)-6T films. The input parameters in panel a are exciton lifetime \(\tau_0\) (with the initial guess obtained from experimental PL transients), site-to-site hopping time \(\tau_{\text{hop}}\) and quenching probability at the \(\alpha\)-6T/substrate interface \(P_{\text{substrate}}\). The only varied parameter in panel b is quenching probability at the domain boundaries \(P_{\text{domain}}\). The input parameters are refined via several iterations of the KMC algorithm.

**Table 2.1.** Summary of the exciton diffusion coefficients \(D = \delta^2/(2\tau_{\text{hop}})\) (where \(\delta\) is the hopping distance) in the \(a\)- (\(D^a\)) and \(b\)- (\(D^b\)) axis dimensions, and average diffusion lengths \(\langle L_D \rangle\) in one (1D) and three (3D) dimensions, for different molecular orientations. The average diffusion lengths were obtained from histograms of the exciton displacement (Section S16 of ESI).

<table>
<thead>
<tr>
<th>Molecular orientation</th>
<th>(D) (nm(^2) ps(^{-1}))</th>
<th>1D (\langle L_D \rangle) (nm)</th>
<th>3D (\langle L_D \rangle) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standing</td>
<td>(D^a = 2 \pm 0.2)</td>
<td>28 (\pm 2)</td>
<td>48.5</td>
</tr>
<tr>
<td>Lying</td>
<td>(D^b = 1.4 \pm 0.4)</td>
<td>23 (\pm 2)</td>
<td>40</td>
</tr>
<tr>
<td>Mixed</td>
<td>(D = 1.6^i)</td>
<td>–</td>
<td>35 (\pm 5^ii)</td>
</tr>
</tbody>
</table>

\(^i\) Mean value of diffusion coefficients into three dimensions.

\(^ii\) The value is lower than that for the standing and lying molecular orientations because the exciton lifetime is reduced due to exciton dissociation at the domain boundaries.
Next, the mixed α-6T films as alternative cubic domains of lying and standing molecular orientations with the size of 10–20 nm, based on reported x-ray diffraction data\textsuperscript{23,31,32}, were modelled. When crossing boundaries of the domains, excitons are quenched with a probability $P_{\text{domain}}$, which becomes the only fitting parameter (Figure 2.2b). From the best fitting (Figure 2.1d–f and Figure S12 of ESI), $P_{\text{domain}}$ was determined as 0.6% and 0.3% for 20 and 10 nm domain sizes, respectively, and the average number of the domain boundary crossings amounts to ~60 and ~130, respectively (see Figure S22b of ESI). Note that the parameters obtained from KMC simulations are reasonably close to those from a simple estimate above, thereby lending support to either approach. Figure 2.3 shows the shares of excitons producing PL and quenched at the domain boundaries and at the α-6T/substrate interface as a function of the α-6T thickness. As the α-6T thickness increases, the share of excitons quenched at the domain boundaries increases up to ~50% for 70 nm thickness while the share of excitons quenched at the α-6T/substrate interface rapidly decreases. At the same time, the share of excitons produced PL, increases from ~15% to ~35%. Therefore, a substantial share of excitons dissociates into charges at the domain boundaries despite of the low single-event probability. This is consistent with a maximum $IQE$ of 70% (as estimated earlier from EQE of 45% and active layer absorption of 0.65, Reference 23), if exciton losses at the α-6T/substrate interface (~15% in Figure 2.3) in real devices are assumed to be negligible.

**Figure 2.3.** Shares of excitons producing PL (red), dissociated at domain boundaries (green) and quenched at the α-6T/substrate interface (blue) for various α-6T thicknesses as obtained from KMC simulations. The size of domains is 20 nm.
Finally, a commentary on the low values of the single exciton dissociation probability despite a considerable offset of $\sim$0.4 eV$^{23,43}$ between the positions of the frontier orbitals of domains with different molecular orientations is included. The optical gaps at both sides of the interface are equal as PL spectra do not depend on the particular molecular orientation (see Figure S6 of ESI). Furthermore, no redshifted CT absorption/PL band$^{44}$ related to inter-domain CT excitons could be detected in mixed orientation $\alpha$-6T films, indicating that the energy difference between intra- and inter-domain excitons is negligibly small. Therefore, creation of the inter-domain CT excitons$^{23}$ (the first step towards exciton dissociation) competes with inter-domain exciton hopping due to dipole–dipole coupling. The latter wins so that most of the excitons continue diffusing even after having crossed the domain boundary as has been established experimentally (see Section S13 of ESI). Therefore, the envisioned approaches towards improving the efficiency of overall exciton dissociation in single-material OSCs, should focus on the increase of either the number of boundaries crossings or the dissociation probability at a single-event crossing. The former approach requires OSC materials with long $L_D$ together with minimizing exciton losses at the interfaces. The latter approach calls for an efficient intermediate CT state for charge generation, which might result in voltage losses.

2.3. Conclusions

In conclusion, the exciton diffusion and dissociation at the domain boundaries in $\alpha$-6T films with different molecular orientations were investigated. An extremely low probability of the single exciton dissociation event at a single domain boundary ($\sim$0.5%) was obtained. However, as excitons cross domain boundaries hundreds of times due to their long diffusion length, the total share of thereby generated charges is substantial (more than 50% of the initial excitons). This finding directly contributes to the understanding of exciton dissociation in single-material OSCs but might also be applicable to non-fullerene based OSCs with small driving force$^{25,30,45}$. This also highlights the importance of a long exciton diffusion length the requirement of which becomes more challenging for solution-processed organic materials as contrasted to well-ordered evaporated materials considered herein.
2.4. Samples and Methods

2.4.1. Sample Preparation

The samples fabricated herein, are similar to those used in Reference 23; the same techniques and approaches were used. In brief, thin films of α-6T (Lumtec Corp.) were thermally evaporated in a vacuum system with a base pressure of $10^{-8}$ mbar onto quartz substrates. The evaporation rate was tracked by using quartz crystal microbalances connected with a thickness monitor. The deposition rates were $0.1 - 0.3 \text{ Å}/\text{s}$ for α-6T and $\sim 0.3 \text{ Å}/\text{s}$ for C$_{60}$. Based on the studies by Taima et al.$^{46}$ and Moser et al.$^{47}$, the films of lying and standing molecular orientations were prepared as follows. For lying films, α-6T was deposited on a 2 nm CuI (abcr Gute Chemie) interlayer with a deposition rate of 0.1 Å/s at room temperature. Standing α-6T films were prepared by growing α-6T directly on quartz at 100 °C during the deposition. An intermediate case of mixed-orientation α-6T films was fabricated by the deposition of α-6T on an unheated quartz substrate (~24 °C). The α-6T films were also deposited on other substrates such as glass or indium tin oxide (ITO); they show similar PL decay times to those on the quartz substrate (see Section S10 of ESI).

For absorption measurements, several films with the thickness between 10 nm and 70 nm for each α-6T orientation were prepared. For time-resolved PL measurements, α-6T films with the thickness of 20, 40 and 70 nm were prepared for each α-6T orientation (see the sample list in Table S1 of ESI). In the lying α-6T film, maintaining the right molecular orientation becomes impossible beyond 40 nm (see Section S11 of ESI) which limits the sample variety. To obtain heterojunction films, a 30-nm C$_{60}$ layer was deposited on top of α-6T on a half of the substrate area without heating the substrate during the deposition. This ensures that the thickness and molecular orientation of α-6T are always identical for both neat α-6T and heterojunction films. The molecular orientation of α-6T stays constant upon the deposition of C$_{60}$, as confirmed by x-ray reflectivity and grazing incidence x-ray diffraction.$^{48}$ After deposition, all samples were encapsulated with an epoxy-glued glass cover in the glovebox under nitrogen environment with very low oxygen and moisture contents ($< 1 \text{ ppm}$). Without encapsulation, the samples quickly (in matter of hours) degrade due to environmental factors such as oxygen and/or moisture (see Section S8 of ESI).
2.4.2. Thin-Film Characterization

**Steady-State Absorption.** Optical transmission and reflection spectra of \( \alpha \)-6T thin-films with a thickness between 10 nm and 70 nm were recorded with an UV/Vis/NIR spectrophotometer (SolidSpec-3700, Shimadzu) using an integrating sphere. From the transmission \( T \) and reflection \( R \) spectra, extinction coefficient \( \kappa \) and refractive index \( n \) were computed using internal software based on a transfer matrix method. The absorption coefficients \( \alpha \) of the \( \alpha \)-6T films were calculated from extinction coefficients using the following equation:

\[
\alpha = \frac{4\pi\kappa}{\lambda} \quad \text{(Eq. 2.1)}
\]

**Time-Resolved Photoluminescence Measurements.** Time-resolved PL spectroscopy measurements were carried out using a Hamamatsu C5680 streak camera equipped with a Ti:sapphire laser (Mira 900, Coherent). The excitation wavelength at 400 nm was obtained by second harmonic generation of the laser output at 800 nm with a 76-MHz repetition rate. The apparatus function of the setup was \(~6\) ps (the standard deviation of a Gaussian apparatus function). In all experiments, \( \alpha \)-6T film samples were measured at room temperature (~20 °C) with normal incidence of the excitation beam to the plane of the film. The excitation laser beam illuminated the substrate side of the samples first and the PL signal was also collected from the same side in the normal incidence geometry. A long-pass dichroic mirror with the cut-off wavelength at 420 nm was used to remove the stray light of the excitation beam to the monochromator entrance slit. PL of samples as a function of the wavelength and delay time (PL map) was measured at sufficiently low excitation intensities to avoid exciton–exciton annihilation and/or photodegradation (see Section S9 of ESI).

2.4.3. Kinetic Monte Carlo Simulations

KMC simulations were based on a stochastic random walk model. The \( \alpha \)-6T film was approximated as a three-dimensional \( (X, Y, Z) \) grid, consisting of periodic cubic unit cells. For the simulation of the mixed films, the alternated cubic domains of identical sizes of “lying” and “standing” molecular orientations were introduced. As the mean PL energy for neat \( \alpha \)-6T films with various molecular orientations remains constant in time (see Figure S15 of ESI), energetic disorder\(^{37,42}\) is weak and therefore is not included in KMC simulations.
When the simulation run started, excitons were created in the grid with a probability proportional to the intensity of the optical electric field in the layer, which was obtained from transfer matrix calculations (see Section S16.4 of ESI). The excitons might either randomly hop to one of the six closest neighbouring sites within a certain hopping time, or decay according to the exciton lifetime $\tau_0$. Excitons were reflected back to the grid from the interface facing the air. Excitons are quenched (i). with a probability $P_{\text{substrate}}$ when reaching the $\alpha$-6T interface facing the substrate, (ii). with a 100% probability when they reached the top C$_{60}$ layer (if any), or (iii). with a probability $P_{\text{domain}}$ when they cross the domain boundary. If the exciton decayed or was quenched, it was removed from the grid. The simulation run continued until the last surviving exciton.

By tracking the total number of excitons present in the grid at the given time, the KMC simulated PL transients were calculated for all samples to fit the experimental PL transients. Finally, when all experimental PL transients were fitted, exciton diffusion parameters such as exciton hopping time, exciton lifetime, $P_{\text{substrate}}$ and $P_{\text{domain}}$ were extracted (see Table S10 of ESI). More details on KMC simulations are given in Section S16 of ESI.

2.5. Author Contributions

N.V.H. and M.S.P. conceived the idea of this study. V.C.N., L.B. and N.V.H. prepared the samples. N.V.H. performed all experiments, kinetic Monte Carlo simulations and data processing. The project was supervised by K.V. and M.S.P.; N.V.H. and M.S.P. wrote the manuscript with the contribution from all authors.

2.6. References

6. Pierini, F. *et al.* Single-Material Organic Solar Cells Based on Electrospun Fullerene-


