Exciton Diffusion Length and Charge Extraction Yield in Organic Bilayer Solar Cells

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Organic light emitting diodes (OLEDs), solar cells, and photosensitive detectors have proven their potential to outperform their inorganic counterparts regarding flexibility, light-weight, transparency, scalability, and fabrication costs as demonstrated by the successful commercialization of OLEDs. Hereby, all organic optoelectronic devices share a series of electrical and optical processes mediated by a Coulombically bound electron–hole pair called an exciton. Driven by concentration gradients, these electrically neutral quasiparticles cover an average distance $\ell_d$ within their lifetime of typically a few nanoseconds by means of Förster or Dexter energy transfer. The so defined exciton diffusion length is one of the critical material parameters determining the performance of organic optoelectronics. Organic photovoltaics and photosensitive devices with a blended photoactive layer\(^1\) benefit from a long $\ell_d$: As the absorber phase separation can be increased, charge recombination is reduced, resulting in an increased operating voltage.\(^2\) Meanwhile, photosensitive devices with a planar photoactive structure such as multilayer emitter layers to confine singlet excitons to the latter.\(^3\)

In amorphous or polycrystalline organic semiconductors, the diffusion length of singlet excitons is often 10 nm or less as a result of exciton trapping.\(^5,6\) However, reliability and comparability of $\ell_d$ measurements still remain an issue, even within one technique.\(^7\) For example, for the thermally stable and chemically inert small molecule zinc phthalocyanine (ZnPc), reported $\ell_d$ values range over one order of magnitude (see Table S1 in the Supporting Information). Many of these differences can be attributed to a discrepancy upon modeling of the photocurrent, as discussed further in Section SI.1 (Supporting Information). Therefore, this article provides a refined technique based on modeling photocurrent spectra of solar cells comprising the material of interest. Our method gives consistent results even for rigorously differing sample architectures and the obtained diffusion length agrees well with complementary measurements based on photoluminescence (PL) quenching.

In contrast to PL based techniques, electrical measurements also allow to study $\ell_d$ of nonfluorescent materials. A key advantage of our photovoltaic approach is the simultaneous quantitative access to both the exciton diffusion length and the yield of charge extraction. To account for potential losses during the splitting of excitons at the donor–acceptor (DA) interface the subsequent charge transit to the desired electrode, via recombination processes, we introduce a charge collection yield $\eta_c$. It mediates between exciton diffusion toward the DA interface, leading to a generation flux of charge transfer (CT) states $\phi_{\text{CT}}(\ell_d)$, and the extracted photocurrent density $j_{\text{photo}}$ via:

$$j_{\text{photo}} = \eta_c \phi_{\text{CT}}(\ell_d)$$

\(^1\) with $\varepsilon$ as elementary charge.\(^16\) The value of $\eta_c$ is often hard to determine, both in experiment and simulation (details in Section SI.2 in the Supporting Information). This uncertainty affects the accuracy of $\ell_d$ when determining it using Equation (1). On the other hand, for known exciton dynamics, steady-state or transient\(^1\) measurements of $j_{\text{photo}}$ seem a suitable choice to access $\eta_c$. In this study, however, we demonstrate access to $\ell_d$ and $\eta_c$ at the same time, based on easy and standardized methods, namely measurements of photovoltaic external quantum efficiencies (EQEs) and thin-film optics. For this purpose, we utilize a simultaneous variation of the layer thickness $x_0$ and the excitation wavelength $\lambda$ in conjunction with optical simulations.

In our exemplary study of ZnPC, we build pin-type bilayer solar cells with C$_{60}$ as efficient quencher for ZnPc excitons.\(^12\) This allows characterizing the material in an application oriented layer sequence, as often used in organic solar cells (alternative exciton quenchers for high bandgap absorbers are discussed in Section SI.3a in the Supporting Information).
A first set of solar cells comprises as electron transport layer (ETL) C_{60} n-doped with tetrakis(1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidinato)ditungsten(II) (W_{2}(hpp)_{4}) (chemical nomenclatures in the Experimental Section) and as hole transport layer (HTL) N4,N4'-bis(9,9-dimethyl-9H-fluoren-2-yl)-N4,N4'-diphenylbiphenyl-4,4'-diamine (BF-DPB) p-doped with C_{60}F_{36}. As shown in Figure 1 (top), we center the maximum of the optical field in the ZnPc layer for 680 nm, a wavelength close to which ZnPc has its peak absorption (details in Section SI.3b in the Supporting Information). For centering, we adjust the thickness of HTL and ETL for all ZnPc thicknesses x_{o} by means of numerical transfer-matrix-simulations.\[13\]

As shown in Figure 2, the measured EQE maximizes for a ZnPc thickness x_{o} between 15 and 18 nm, increasing with \lambda. This already indicates \ell_d to be much smaller than the absorption length which for ZnPc is above 100 nm. For modeling the...
measured photocurrent data as function of \(x_p\) and \(\lambda\), we consider the general exciton diffusion equation:

\[
\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} + G(x,t) - k_{PL}(t) \cdot n - k_{FRET}(x) \cdot n - \alpha \cdot n^2
\]

(2)

where \(n\) denotes the density distribution of singlet excitons at position \(x\) in the absorber film (here ZnPc), \(D\) the diffusion coefficient, and \(G(x,t)\) the time dependent exciton generation profile. The radiative decay rate in absence of quencher sites is \(k_{PL}\), whereas \(k_{FRET}\) denotes the rate of Förster resonance energy transfer (FRET) in presence of a neighboring material with equal or smaller optical gap. \(\alpha\) quantifies the rate for exciton–exciton annihilation.

Exciting the samples under steady-state conditions and low intensities (translating to exciton densities far below the annihilation threshold\(^\text{[14]}\) of \(10^{18}\ \text{cm}^{-3}\)) permits to apply Equation (2) with the following simplifications: \(\partial n/\partial t = 0\), \(k_{PL} = \tau_{-1} = D/\alpha \cdot 2\), \(\alpha = 0\) with \(\tau_{-1}\) as intrinsic exciton lifetime. Considering only low light photons (\(\lambda > 635\ \text{nm}\), see Section S1.3b in the Supporting Information) allows to draw exclusive conclusions about the exciton dynamics in ZnPc, due to its smaller optical bandgap (1.5 eV) in comparison to C\(_60\) (1.8 eV). Furthermore, embedding ZnPc into media \(m\) of a greater optical gap, \(\beta\)-BF-DPB with 3.0 eV and C\(_{60}\) allows neglecting FRET dynamics and thus circumvents additional PL studies to determine the Förster radius\(^\text{[15]}\). \(k_{FRET}\text{ZnPc}:m = 0\). Moreover, within the framework of interference based thin-film-optics,\(^\text{[15]}\) we find the spatial distribution of the optical field, and thus the exciton generation, to be approximately parabolic \(G_{x}(x) = a_{1}x^{2} + b_{1}x + c_{1}\) within a single layer (details in Section S1.4 in the Supporting Information). As boundary conditions for our simplified diffusion equation,

\[
a_{1}x^{2} + b_{1}x + c_{1} = D \left( \frac{1}{\ell_{d}} - \frac{\partial^2}{\partial x^2} \right) n
\]

(3)

we choose ZnPc excitons reaching the HTL to be reflected \((\partial n/\partial x) (x = \text{ZnPc-HTL}) = 0\), details in Section S1.5 in the Supporting Information) and those reaching C\(_{60}\) to decay immediately into CT states\(^\text{[16]}\) \((n(x = \text{ZnPc:C}_{60}) = 0)\text{.}\)

We obtain an analytical expression for the photocurrent as a function of \(I_{p}\) and \(\eta_{p}\), derived as Equation (S11) in Section S1.6 (Supporting Information). We apply it to simultaneously fit all EQE spectra (solid lines) under variation of \(\lambda\) and \(x_{p}\), as representatively depicted in Figure 2 for four wavelengths of the analyzed interval between 635 and 800 nm (exclusive ZnPc absorption). For this purpose, \(\eta_{p}\) is assumed to be independent of \(\lambda\), as wavelength independent internal quantum efficiencies have been experimentally demonstrated for both polymer and small molecule systems.\(^\text{[12,17]}\) We exclude thin ZnPc layers up to a threshold thickness of \(x_{p} = 11\ \text{nm}\) from the fitting routine due to layer roughness\(^\text{[18]}\) and DA interdiffusion\(^\text{[8,19]}\) (details in Section S1.6b in the Supporting Information). For thicker absorber layers, we model the charge extraction to be spatially uniform, as no significant concentration of recombination centers is present in the bulk of the neat absorber.\(^\text{[20,22]}\)

Following this procedure unfolds an exciton diffusion length in ZnPc of \(\ell_{d} \approx (10.0 \pm 0.8)\ \text{nm}\) and a collection yield of \(\eta_{c} = (58 \pm 6)\%\). Note that a successful EQE fit features a peak position \(x_{p}\) coinciding with the experimental data (Figure 2). As the optical field is constructed to be approximately constant in ZnPc, \(x_{p}\) is found in proximity to the diffusion length. However, for smaller \(\ell_{d}\), it would be desirable to achieve a peak position \(x_{p}\) much greater than the diffusion length to still overcome the thickness threshold for uniform charge extraction \((x_{p} > x_{c})\).

For this purpose, we introduce a pronounced slope in the optical field in the absorber, rising with distance to the quenching interface. It aims to extend the exciton diffusion toward this interface, at the cost of overall exciton density. A second set of solar cells (Figure 1 bottom) is prepared showing such a field gradient in absence of thicknesses variations of both transport layers. It also differs with respect to its electronic polarity through inverse layer stacking and its transport layers. Here, \(4,7\)-diphenyl-1,10-phenanthroline (Bphen) is used as ETL and as HTL \(N,N,N',N'\text{-tetrakis(4-methoxyphenyl)}\)-benzidine (MeO-TPD) (optical gap of 2.9 eV) p-doped with 2,2\(^{-}\)(perfluoronaphthalene-2,6-diyldenedimalononitrile) (F\(_{2}\)TCNQ). Comparing to set 1, we observe a pronounced shift of the EQE peak position to \(x_{p} \approx 25\ \text{nm}\) (see Figure S3 in Section S1.7 in the Supporting Information). Taking the respective field distribution into account and assuming complete exciton reflection at the interface between ZnPc and intrinsic MeO-TPD, we obtain \(\ell_{d} = (10.2 \pm 0.8)\ \text{nm}\) in ZnPc and a collection yield of \(\eta_{c} = (58 \pm 6)\%\) which confirms the previous results within the measurement uncertainty.

The agreement of the fitted values proves the modeling approach to be independent of the considered device geometry and underlines the thickness of maximum photocurrent \(x_{p}\) typically not be identical with \(\ell_{d}\). Furthermore, the result implies equal efficient charge extraction for the transport layers of sets 1 and 2, as expected. For both device architectures, CT states at the DA interface formed upon successful exciton diffusion are inefficiently harvested as extracted photocurrent. This can be attributed to incomplete CT dissociation and has been observed in ZnPc–C\(_{60}\) cells before by Rand et al. \(^\text{[23]}\) The authors attributed this finding to an unfavorable orientation of the ZnPc molecules with regard to the interface with C\(_{60}\). Beyond, the measurements recorded in such an exciton diffusion study can be used to evaluate the potential of a corresponding blended absorber system as discussed in Section S1.8 (Supporting Information).

To obtain an independent confirmation of the outlined method, an alternative method to determine \(\ell_{d}\) based on the transient decay of PL is performed.\(^\text{[8,24]}\) A sequence of ZnPc thin-films with varying layer thickness is prepared on quartz glass substrates in the absence and presence of 50 nm C\(_{60}\), as shown in Figure 3 (top). The ZnPc–C\(_{60}\) interface acts as a complete quencher\(^\text{[22]}\) and reduces the effective exciton lifetime. Meanwhile, ZnPc excitons at the interface with quartz glass or vacuum are expected to reflect, with vacuum being known as an imperfectly reflecting medium.\(^\text{[25]}\) For a conjoint analysis (details in Section S1.9 in the Supporting Information) of both thin-film sets, a remarkably good agreement is obtained between all measured and modeled PL decays (Figure 3 bottom). The diffusion length \(\ell_{d} = (9.6 \pm 0.8)\ \text{nm}\) is obtained using a Förster radius of \((1.4 \pm 0.4)\ \text{nm}\), and agrees well with the value obtained via spectral modeling, presented earlier. As the interface between ZnPc and vacuum is modeled
Two rigorously differing solar cell architectures were studied in conjunction with subsequent charge extraction as photoactive system, this procedure yields an exciton diffusion length $\ell_d$ in ZnPc of $(10.1 \pm 0.9) \text{ nm}$ and $\eta_c = (58 \pm 6)\%$. Two rigorously differing solar cell architectures were studied and give consistent results. The value of $\ell_d$ is furthermore in excellent agreement with time resolved measurements of phosphorescence quenching resulting in a diffusion length $\ell_d$ of $(9.6 \pm 0.8) \text{ nm}$, which underlines the reliability of the newly proposed method.

Experimental Section

Preparation of Solar Cells: Substrates with prestructured indium tin oxide (90 nm, 32 $\Omega$ sq$^{-1}$), Thin Film Devices, USA) were purchased as bottom electrode. All organic and metal layers were deposited via thermal evaporation in ultrahigh vacuum (K. J. Lesker, UK) with a base pressure of around $10^{-4} \text{ mbar}$. Quartz crystal microbalances were used to monitor the deposition rates (for organics, 0.3–0.4 Å s$^{-1}$) and thus to control layer thicknesses and doping ratios. Set 1 followed the nip-type layer sequence ($40 \text{ nm} - x/2$) of C$_{60}$ n-doped with 3 wt% W$_2$(hpp)$_x$, 20 nm of intrinsic C$_{60}$, $x_0$ of ZnPc (supplier: TCI Europe N.V., Belgium), (82 nm-$x/2$) of BF-DPB p-doped with 10 wt% C$_{60}$F$_{36}$, and 100 nm of aluminum (Al) as reflecting top electrode (photocative area of 6.4 mm$^2$). Set 2 followed the pin-type sequence $1 \text{ nm}$ of dopant F$_2$-TCNNQ, 20 nm of MeO-TPD p-doped with 2 wt% F$_2$-TCNNQ, 5 nm of intrinsic MeO-TPD, $x_0$ of ZnPc, 20 nm of C$_{60}$, 6 nm of BPhen, and 100 nm of Al. Besides the n-dopant W$_2$(hpp)$_x$, all organic materials were purified at least once by vacuum gradient sublimation. After deposition, both sets were sealed under nitrogen with a cover glass and a humidity getter via a UV-hardened epoxy glue.

Analysis of Solar Cells: For measuring the EQE, xenon light (Oriel Xe Arc-Lamp Apex Illuminator, Newport, US) was filtered to 5 nm spectral width with a monochromator (Cornerstone 260 1/4 m Monochromator, Newport, US). Excitation light chopped at 215 Hz excited the sample on a mask area of 2.8 mm$^2$. $J_{phot}$ was detected via a lock-in amplifier (Signal Recovery SR 7265, National Instruments, US). A calibrated silicon diode (ST337, Hamamatsu, Japan) monitored the excitation intensity. A compact charge–coupled device spectrometer (USB4000, Ocean Optics, US) read out the relative excitation spectrum. The optical constants were determined via transmission and reflection (UV-3100 Spectrometer, Shimadzu, Japan) of thin films with varying layer thickness and subsequent optical modeling.

Preparation of PL Quenching Samples: The same evaporation system was used to deposit thin films of ZnPc and optionally C$_{60}$ onto quartz substrates. Storing and analysis of the sample were performed under vacuum.

Analysis of PL Quenching Samples: Samples were excited with 100 fs pulses at 400 nm from a frequency doubled Ti:sapphire laser. The subsequent decay of the PL was detected between 810 and 830 nm with a time resolution of a few ps via a streak camera (CS860, Hamamatsu, Japan) in synchroscan mode with the laser at 80 MHz.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
Acknowledgements

The authors thank the German BMBF for funding within the scope of the projects InnoProfile 2.2 (03IP1602X) and MEDOS (03EK3503A) as well as the European Commission within the scope of the Career Integration Grant (FP7, MSCA, 630864). The authors also thank Caroline Walde and Andreas Wendel from IAPP for sample preparation as well as Dr. Mauro Furno and Sim4tec for providing the software for optical transfer matrix calculations. I.D.W.S. and M.T.S. acknowledge support from the European Research Council (grant number 321305) and from EPSRC (grant number EP/L017008/1). I.D.W.S. also acknowledges a Royal Society Wolfson Research Merit Award. K.L. is a fellow of the Canadian Institute for Advanced Research (CIFAR). The research data supporting this publication can be accessed at http://dx.doi.org/10.17630/af263bfb-620c-40a8-9929-86658e5187d3.

Received: August 19, 2016
Revised: December 16, 2016
Published online: February 1, 2017

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