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Thermal Annealing Reduces Geminate Recombination in TQ1:N2200 All-Polymer Solar Cells

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A combination of steady-state and time-resolved spectroscopic measurements is used to investigate the photophysics of the all-polymer bulk heterojunction system TQ1:N2200. Upon thermal annealing a doubling of the external quantum efficiency and an improved fill factor (FF) is observed, resulting in an increase in the power conversion efficiency. Carrier extraction is similar for both blends, as demonstrated by time-resolved electric-field-induced second harmonic generation experiments in conjunction with transient photocurrent studies, spanning the ps-μs time range. Complementary transient absorption spectroscopy measurements reveal that the different quantum efficiencies originate from differences in charge carrier separation and recombination at the polymer-polymer interface: in as-spun samples ~35 % of the charges are bound in interfacial charge-transfer states and recombine geminately, while this pool is reduced to ~7 % in thermally-annealed sample, resulting in higher short-circuit currents. Time-delayed collection field experiments demonstrate a field-dependent charge generation process in as-spun samples, which reduces the FF. In contrast, field-dependence of charge generation is weak in annealed films. While both devices exhibit significant non-geminate recombination competing with charge extraction, causing low FFs, our results demonstrate that the donor/acceptor interface in all-polymer solar cells can be favourably altered to enhance charge separation, without compromising charge transport and extraction.

Introduction

Organic photovoltaics (OPV) is an emerging technology for renewable energy production, which offers unique device properties: flexibility, colour tunability, possibility of low production costs due to compatibility with solution-processing and printing, low carbon footprint in conjunction with short energy payback times, and importantly, non-toxicity of the

photoactive organic materials.¹⁻⁵ However, the power conversion efficiency (PCE) of single photoactive layer organic solar cells (OSCs) has only recently surpassed 11 % for conventional polymer:fullerene systems, now approaching efficiencies eventually allowing commercialization of this technology.⁶⁻⁹

In the past, improvements of the performance of OSCs have mainly been achieved by introducing new low-bandgap donor materials, which more efficiently harvest the red part of the solar spectrum and are typically combined with fullerenes as electron acceptors. In fact, fullerene C₆₀ and its derivatives are still widely used, although they are prone to (photo)degradation, expensive, have a large energy footprint, suffer from morphological instability as they undergo dimerization, and exhibit only weak absorption in the visible and near-infrared (NIR) spectral region.^{3, 10-14} Recently, novel small molecule non-fullerene acceptors (SMA), exhibiting stronger absorption, ideally complementary to the donor, have attracted a lot of attention as they yield solar cells with broader and increased light absorption and thus higher efficiency, now even outperforming fullerene-based devices.¹⁵ Complementary and enhanced absorption, control of energy

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ARTICLE

Journal Name

levels, and better molecular and morphological stability is also achieved with polymer acceptors in all-polymer solar cells that, as the non-fullerene small molecule acceptors, have attracted increasing attention in recent years, since they have achieved efficiencies approaching those obtained by fullerene-based devices.^{16–19}

However, while the PCE of all-polymer solar cells has now reached more than 9 %, it still lags behind the PCE of polymer/fullerene or polymer/SMA systems.^{16, 20} Often, all-polymer solar cells exhibit low short-circuit currents (J_{sc}) and low fill factors (FF), while they provide higher open-circuit voltages (V_{oc}) due to energetically higher-lying LUMOs (lowest occupied molecular orbitals) of the acceptor polymers compared to common fullerene derivatives. Consequently, the low PCE of all-polymer solar cells often originates from poor charge generation, potentially connected to the lower LUMO energy offsets, and limited carrier extraction due to fast geminate and non-geminate recombination losses.^{17, 21, 22}

In this study, we investigate and unravel the origin of performance differences in all-polymer solar cells composed of poly[2,3-bis(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (TQ1) as donor and a naphthalene-diimide (NDI) based polymer, namely poly[N,N'-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl-alt-2,20 bithiophene-5,50-diyl] (N2200) as acceptor. Specifically, we rationalize why thermal annealing of as-spun films at 100 °C for 15 minutes improves the PCE of TQ1:N2200 devices from 2 % to 3.15 %. Thermal annealing has previously been shown to improve the TQ1 backbone planarity and N2200 crystallinity, however, the precise effect on transient charge generation and recombination processes and how they are altered by thermal annealing remained unexplored.¹⁷ Here we demonstrate that although thermal annealing does not change charge extraction, it reduces geminate recombination, lowers the field-dependence of charge generation, and leads to higher fill factors in annealed devices. Nevertheless, the rate of non-geminate recombination is unaffected by annealing and remains high – non-geminate recombination constitutes a significant efficiency-limiting process even in annealed TQ1:N2200 devices.

Experimental

Sample preparation

The inverted structure solar cells were fabricated with the following device structure: glass/ITO/ ZnO (25 nm)/active layer (85 nm)/MoO₃ (8.5 nm)/Al (90 nm). The ITO glasses were cleaned by using detergent and TL-1 treatment: a mixture of water, ammonia (25%), and hydrogen peroxide (28%) (5 : 1 : 1 by volume) as detailed in reference 17.¹⁷ The ZnO layer and active layer were deposited in the glove-box filled with nitrogen. After the ZnO (nanoparticles dissolved in chloroform) was spin-coated on top of the cleaned ITO glass substrates were heated for 30 min at 150 °C. The active layers were spin-cast from chloroform solutions with a total concentration of 9 mg mL⁻¹ at a spin speed of 3000 rpm for 50 s to achieve a

thickness of 85 nm, and then annealed at 100 °C for 15 minutes. After annealing, MoO₃ and Al layers were deposited by thermal evaporation under a pressure less than 1×10^{-5} mbar. The effective area of the solar cells was 0.046 cm². The same devices were used for TREFISH, TPC, and J-V measurements. For TDCF measurements the preparation conditions of the devices were the same however, a smaller active area (1 mm²) was used to reduce the RC response of the device. TA measurements were performed on thin films prepared with the same conditions, which resulted in the same active layer thickness and comparable optical density.

UV-Vis absorption spectra

UV-vis absorption spectra were measured with a Perkin Elmer Lambda 900 UV-Vis-NIR absorption spectrometer.

J-V curve and EQE spectra

J-V curves were recorded with a Keithley 2400 Source Meter under AM 1.5G illumination (100 mW cm⁻²), generated by a solar simulator with a 180 Watt xenon arc lamp as the light source (Model SS50A, Photo Emission Tech., Inc.). Light intensity was set to 1 sun intensity using a standard silicon photodiode calibrated at the Energy Research Centre of the Netherlands (ECN). EQE spectra were recorded with a home-built setup using a Newport Merlin lock-in amplifier. Devices were illuminated with chopped monochromatic light through the transparent ITO electrode. Measured EQE spectra were scaled so that the estimated short-circuit current density from the EQE measurement matched the short-circuit current density of the corresponding JV curve.

TREFISH

Charge carrier extraction investigation by means of TREFISH (time-resolved electric-field-induced second harmonic generation) technique were carried out by means of experimental setup based on Ti-Sapphire femtosecond laser (Quantronix Integra C, 1 kHz, 810 nm, 130 fs). The samples were excited biphotonically by the fundamental laser radiation. Voltage to the samples was applied by reverse bias pulses of 10 μ s duration, synchronized with the laser pulses. A fraction of the same laser pulse was used as the probe for the second harmonic generation (at 405 nm) efficiency in the investigated layer. Mechanical optical delay stage was used to change the delay time between excitation and probe pulses. The electric field strength was evaluated as being proportional to the square root of the second harmonic intensity. Decrease of the electric field $\Delta E(t)$ caused by drifting photogenerated charge carriers was equal to $\Delta E(t) \approx e n(t) \langle l(t) \rangle / \epsilon \epsilon_0$, where e is the elementary charge, $n(t)$ is the charge carrier concentration, and $\langle l(t) \rangle$ is the average drift length of generated charge carriers along the electric field direction. The charge extracted from the sample was obtained from the electric field dynamics as $q = \Delta E(t) d C_{sam}$, where d is the film thickness and C_{sam} is the sample capacitance. The integral-mode photocurrent transients were measured simultaneously using the same pump pulses and recording the voltage on a 10 k Ω load resistor connected in series with the solar cell using a 500 MHz bandwidth Agilent Technologies oscilloscope DSO5054A.

Transient absorption (TA) spectroscopy

Transient absorption (TA) spectroscopy was carried out using a home-built pump-probe setup. Two different configurations of the setup were used for either short delay, namely 100 fs to 8 ns experiments, or long delay, namely 1 ns to 100 μ s delays, as described below:

probe from -400 ps to 8 ns. For measuring TA whole visible range, we used 1300 nm (signal) of TOPAS 2 to produce white-light super continuum from 350 to 1100 nm.

For the 1 ns to 100 μ s delay (long delay) TA measurement, the same probe white-light supercontinuum as for the 100 fs to 8 ns delays. But the excitation light (pump pulse) was provided by an actively Q-switched Nd:YVO₄ laser (InnoLAS piccolo AOT)

Figure 1- (a) Chemical structures of TQ1 and N2200 polymers. (b) Absorption coefficients of neat (dotted lines) and blended (solid lines) materials. (c) Current-voltage characteristics of photovoltaic devices based on as-spun TQ1:N2200 (black) and annealed TQ1:N2200 (red). (d) EQE spectra of the photovoltaic devices based on the materials shown in panel (a). The blue solid line indicates the EQE ratio between annealed and as-spun devices.

The output of titanium:sapphire amplifier (Coherent LEGEND DUO, 4.5 mJ, 3 kHz, 100 fs) was split into three beams (2 mJ, 1 mJ, and 1.5 mJ). Two of them were used to separately pump two optical parametric amplifiers (OPA) (Light Conversion TOPAS Prime). The TOPAS 1 generates tunable pump pulses, while the TOPAS 2 generates signal (1300 nm) and idler (2000 nm) only. A fraction of the output signal of titanium:sapphire amplifier was focused into a c-cut 3 mm thick sapphire window, thereby generating a white-light supercontinuum from 500 to 1600 nm. For short delay TA measurements, we used the TOPAS 1 for producing pump pulses while the probe pathway length to the sample was kept constant at approximately 5 meters between the output of the TOPAS 1 and the sample. The pump pathway length was varied between 5.12 and 2.6 m with a broadband retroreflector mounted on automated mechanical delay stage (Newport linear stage IMS600CCHA controlled by a Newport XPS motion controller), thereby generating delays between pump and

frequency-doubled to provide pulses at 532 nm. The laser was triggered by an electronic delay generator (Stanford Research Systems DG535), itself triggered by the TTL sync from the Legend DUO, allowing control of the delay between pump and probe with a jitter of roughly 100 ps.

Pump and probe beams were focused on the sample with the aid of proper optics, which was kept under a dynamic vacuum of $<10^{-5}$ mbar. The transmitted fraction of the white light was guided to a custom-made prism spectrograph (Entwicklungsbüro Stresing) where it was dispersed by a prism onto a 512 pixel NMOS linear image sensor (HAMAMATSU S8381-512). The probe pulse repetition rate was 3 kHz, while the excitation pulses were mechanically chopped to 1.5 kHz (100 fs to 8 ns delays) or directly generated at 1.5 kHz frequency (1 ns to 100 μ s delays), while the detector array was read out at 3 kHz. Adjacent diode readings corresponding to the transmission of the sample after excitation and in the absence of an excitation pulse were used to calculate $\Delta T/T$.

ARTICLE

Journal Name

Measurements were averaged over several thousand shots to obtain a good signal-to-noise ratio. The chirp induced by the transmissive optics was corrected with a home-built Matlab code. The delay at which pump and probe arrive simultaneously on the sample (i.e. zero time) was determined from the point of maximum positive slope of the TA signal rise for each wavelength.

TDCF

The home-built TDCF (time delayed collection field) setup uses the second harmonic (532 nm) of an actively Q-switched sub-nm Nd:YVO₄ laser (Innolas piccolo AOT) operating at 5 kHz as excitation. To minimize the RC response time, a small device area of 1 mm² is used. The samples were measured under dynamic vacuum conditions to avoid any degradation. A Keysight S1160A functional generator was used to provide the pre-bias and extraction bias, while a Keysight four channel digital oscilloscope was used to measure the current response of the device.

Results and discussion

Absorption and device performance

Figure 1a shows the chemical structures of the donor polymer TQ1 and acceptor polymer N2200. Recently, Xia et al. reported that annealing increases the PCE by a factor of roughly 1.5 in TQ1:N2200 (2:1 wt %) solar cells.¹⁷ Light-intensity dependent J_{SC} and V_{OC} measurements indicated that in annealed samples first order recombination processes, e.g. trap-assisted and geminate recombination, are reduced, as we will confirm below by time-resolved measurements. The higher J_{SC} and V_{OC} after annealing reflect an increase in the efficiency of one or more of the elementary steps of photocurrent generation: 1) photon absorption, 2) exciton diffusion and charge transfer at the donor-acceptor (D/A) interface, 3) charge separation, and 4) charge extraction at the respective electrodes. Together, they define the external quantum efficiency (EQE): $EQE = \varphi_{abs} \times \varphi_{diss} \times \varphi_{sep} \times \varphi_{extr}$, in which φ_{abs} is the efficiency of photon absorption, φ_{diss} is the exciton dissociation efficiency, φ_{sep} is the efficiency of charge pair separation, and φ_{extr} is the efficiency of charge extraction. However, typically several efficiency-limiting processes occur concurrently in organic solar cells: 1) exciton recombination to the ground state, 2) incomplete charge separation at the interface followed by geminate recombination, 3) charge carrier trapping followed by trap-assisted recombination, and 4) non-geminate recombination of charge carriers prior to their extraction, possibly also forming triplet states.²³⁻²⁶ In the following, we monitor these processes at all relevant time scales by a combination of optical and electro-optical spectroscopy techniques: transient absorption (TA) spectroscopy, time-delayed collection field (TDCF) experiments, and a combination of ultrafast charge extraction measurements

using time-resolved electric-field-induced second harmonic generation (TREFISH) and transient photocurrent (TPC) spanning the ps to several μ s temporal range.^{27, 28}

TREFISH and transient photocurrent experiments

We investigated the charge extraction and recombination dynamics in complete OPV devices by time-resolved electric-field-induced second harmonic generation (TREFISH) combined with transient photocurrent (TPC) measurements.²⁷ We have previously shown that the TREFISH technique allows monitoring the charge extraction dynamics in complete OPV devices at all relevant time scales, i.e. from the first hopping events to full extraction.^{14, 19} Briefly, the motion of photogenerated charges partially screens the electric field induced by the applied bias, resulting in an electric field change ΔE . The temporal evolution of $\Delta E(t)$ is detected optically by recording the dynamics of the second harmonic intensity $I_{2H}(t) \propto \Delta E^2(t)$, which can be converted to the number of charges collected at the electrodes.^{14, 19} The TREFISH measurement is complemented by a simultaneous (using the same pump pulse) recording of the (integrated) photocurrent transient on an oscilloscope. Thus, all relevant time scales for charge extraction and recombination (ps to μ s) are probed in a single measurement. Detailed experimental descriptions can be found elsewhere.^{13, 19, 27}

Figure 2a shows the transient extraction of charges. The traces

Figure 2- Time-resolved charge extraction. (a) Comparison of the charge extraction kinetics normalized to the amount of extracted charge at high reverse bias, see Figure S1 for the non-normalized kinetics. (b) Comparison between normalized charge extraction kinetics in as-spun (red) and annealed (grey scale) TQ1:N2200 blends at the indicated applied bias reveals that charge extraction in both blends is quite similar. The inset shows a zoomed-in portion of the initial charge separation kinetics at $U = -1V$.

were normalized to the total amount of extracted charge at high reverse bias ($U = -5V$) to estimate the Internal Quantum Efficiency (IQE) (non-normalized traces are shown in Figure S1). Since at high reverse bias ($U = -5V$) the non-geminate recombination of free charges should be largely suppressed, the normalized amount of extracted charge in Figure 2a, i.e. at the longest time delay, is a direct measure of the IQE at $U = -1V$ (the lowest reverse bias we were able to measure for TQ1:N2200 successfully). For the case of TQ1:N2200 devices we observed a significant increase in the IQE at $U = -1V$ upon annealing: IQE ($-1V$) = 63 % for the annealed and IQE ($-1V$) = 42 % for the as-spun device. In fact, the IQE($-1V$) ratio between the samples is in good agreement with the EQE ratio at short-circuit conditions (≈ 1.45 in Figure 1d). Given the field-dependence of photocurrent generation measured by steady-state IV measurements in Figure 1c and knowing IQE($-1V$), we can also estimate the expected IQE at 0V. The ratio of steady-state current-density at 0V to that at $-1V$ in Figure 1c is ~ 0.83 for the as-spun sample and ~ 0.58 for the annealed sample. IQE (0V) can be estimated by multiplying these values by IQE ($-1V$), leading to IQE (0V) = 36 % and 58 % for the as-spun and thermally-annealed samples, respectively, in good agreement with transfer matrix model calculations giving IQE (0V) = 36 % and 50 %, respectively.

We further investigated whether the difference in quantum efficiency between the as-spun and thermally-annealed TQ1:N2200 devices is only due to charge carrier recombination or also due to charge transport losses. By normalising the charge extraction kinetics in Figure 2a to the total amount of extracted charge at long time delays, i.e. at complete extraction, we can eliminate the influence of charge carrier generation and recombination and mainly investigate the rate of charge carrier extraction (Figure 2b). Surprisingly, we find that the normalized charge extraction kinetics in the as-spun and the annealed TQ1:N2200 devices are rather similar (Figure 2b), which indicates similar transient mobilities in both samples. This is in contrast to our earlier steady-state mobility measurements using space-charge limited currents (SCLC).¹⁷ The difference originates from the fact that the SCLC technique cannot capture non-equilibrium charge transport processes, rendering it not meaningful in this case. In contrast, the TREFISH/TPC technique spans the full temporal range relevant for charge extraction, and clearly shows that photogenerated carrier mobilities are in fact similar in both samples (see ref. 19 for a more detailed explanation). Hence, the difference in the EQE in Figure 1d must stem from a difference in the generation and / or charge carrier recombination and cannot be due to differences in long-range charge transport.

We hypothesize at this stage that the morphological changes occurring upon annealing mainly affect the efficiency of short-range charge separation. In other words, annealing reduces losses to geminate recombination.¹⁷ We hypothesize further that this originates from improved TQ1 backbone planarity and improved N2200 crystallinity obtained upon thermal annealing.¹⁷ In addition, conductive AFM imaging suggested improved percolation pathways in the TQ1 network following

thermal annealing.¹⁷ Since TREFISH/TPC measurements indicate similar bulk charge transport properties, it appears that the improved TQ1 interconnectivity facilitates mostly short-range charge separation, thereby reducing geminate recombination. Note that in this case morphological changes reduce only geminate recombination without significantly affecting other photo physical processes. As the TREFISH / TPC experiments yield only indirect insights into the recombination processes, we further rely on a more suitable technique to investigate the difference in the carrier recombination kinetics by the use of transient absorption spectroscopy.

Transient absorption spectroscopy

Transient absorption (TA) spectroscopy has become an important tool to monitor the population dynamics of excitons and charge carriers in photovoltaic devices such as organic solar cells.^{20, 29-33} This technique is capable of covering the dynamic range in which charge generation, geminate and non-geminate recombination processes occur, starting at sub-100 fs and extending beyond microseconds.^{34, 35} The specific setup used in our experiments covers a wide temporal (fs to μ s) and spectral range (350 nm to 1600 nm), and we used advanced data analysis techniques such as multivariate curve resolution to deconvolute the complex TA spectra composed of several states (components) and to obtain the component-associated spectra and dynamics.²³

Picosecond-nanosecond TA spectroscopy. Figure 3a-d shows ps-ns transient absorption spectra at different delay times (left panel) and spectrally-integrated dynamics (right panel, integrated over 1.75 -2.25 eV) of the ground state bleach (GSB) of annealed TQ1:N2200 and as-spun TQ1:N2200 films. The same blends yielded PCEs of 3.15 % and 2 % in OPV devices, respectively (Figure 1c). The TA spectra of the annealed blend showed a GSB at high probe photon energies and photoinduced absorption at low probe photon energies. The singlet exciton-induced absorption of TQ1, which in this blend peaks around 1.0 eV, was entirely quenched within the first 10 ps after photoexcitation, indicating fast generation of charges and only a minor component of diffusion-limited exciton dissociation (see Figure S2). At later times, charges can readily be identified by the emergence of charge-induced absorption, as previously reported for many other material systems, for instance P3HT:PCBM and Si-PCPDTBT:PCBM.^{30, 36}

The spectrally-integrated kinetics of the GSB of annealed TQ1:N2200 are shown in Figure 3b for different excitation fluences. At the lowest fluence ($0.8 \mu J / cm^2$) used in our measurements more than 80 % of the GSB signal remained after recombination on the (sub-)nanosecond timescale.^{24, 30, 34, 37} For a more detailed analysis of the PA band kinetics we refer to Figure S2. The fast sub-10 ps generation of charges and high fraction of long-lived separated charge carriers is in line with the higher device performance of the thermally-annealed to be intensity-dependent, indicating that separated charges underwent non-geminate TQ1:N2200 films compared to the as-spun samples, as we discuss in more detail below.

Figure 3- Picosecond-nanosecond TA spectra of (a) annealed TQ1:N2200 blends and (c) as spun TQ1:N2200 blends respectively. Picosecond-nanosecond kinetics of the photoinduced bleach of (b) annealed TQ1:N2200 and of (d) as spun TQ1:N2200 at different fluences. For the kinetics of PA bands, see Figure S2.

On the timescale of several picoseconds, the as-spun and thermally-annealed TQ1:N2200 films exhibited a reduction of the PA signal intensity below 1 eV and a rise of the PA signal intensity in the region between 1.2-1.5 eV (Figure 3c and S2, ESI). We assign the PA around 1 eV to exciton-induced absorption based on the similarity to the PA of a neat TQ1 film (see Figure S3a) and the PA between 1.2-1.5 eV to charge-induced absorption, indicating the conversion of a fraction of TQ1 polymer excitons to charge carriers by diffusion-limited exciton dissociation. However, a qualitative comparison of the dynamics of the photoinduced absorption (PA) (see Figure S2) of the two samples did not reveal any obvious differences in the dynamics of the exciton-to-charge conversion.

Comparing the GSB dynamics of the as-spun sample to that of the annealed sample, c.f. Figure 3b and d, a faster GSB signal decay past 100 ps was observed in the as-spun sample compared to that of the annealed sample, reducing the GSB signal to about ~50 %. Additionally, the as-spun sample exhibited virtually fluence-independent decay dynamics at the two lowest fluences, indicating that geminate recombination dominates and depopulates the pool of charge carriers. We note that these bound charges are unlikely to contribute to photocurrent, as they do not separate entirely and recombine quickly. This points to the reason for the lower EQE in the as-spun TQ1:N2200 devices compared to thermally-annealed devices: less efficient charge generation and / or increased geminate recombination losses occur in the as-spun sample.

Finally, we note that, unlike for the neat polymer films, we observe no evidence of triplet formation in these blends (see

ESI Figure S2-S4 for TA spectra and kinetics of neat TQ1 and N2200 films). It appears the fast charge generation in these blends kinetically outweighs triplet formation by intersystem crossing, but also population of the triplet state by geminate or non-geminate recombination was not observed, unlike recently reported for several other polymer:fullerene blends.^{23, 26, 30, 32, 38-41} However, we cannot entirely rule out triplet formation, although experimentally we did not observe it in this material system (TQ1:N2200). In fact, in TQ1:N2200 the lowest energy triplet level should be localized on the acceptor polymer N2200. However, we did not observe a clear photoinduced absorption of the triplet state in neat N2200 films (figures S3 and S5 in the ESI), only a long-lived ground state bleach.

Nanosecond-microsecond TA on blend films. We now examine the (nanosecond-microsecond) ns-μs dynamics. Here, we can safely exclude any contribution from singlet excitons to the spectra and dynamics, as charge transfer occurred on the sub-ns time scale. Figure 4 shows experimentally determined ns-μs TA spectra (left panel) and kinetics (right panel) of the same blends as used for the ps-ns experiments. The TA spectra of thermally-annealed TQ1:N2200 films (Figure 4a) show that a large fraction of the charge carrier population is still present after 100 ns under these excitation conditions. The PA kinetics exhibit a clear non-geminate (i.e. fluence-dependent) recombination component (Figure 4b).

We quantified the fraction of charges undergoing non-geminate and geminate recombination and extracted the non-geminate recombination coefficient by using a two-pool

Figure 4- Nanosecond-microsecond TA spectra of **(a)** thermally-annealed TQ1:N2200 and **(c)** as-spun TQ1:N2200 blends. Corresponding PA kinetic traces of thermally-annealed TQ1:N2200 and as-spun TQ1:N2200, respectively, with two pool model fits (black dashed lines) shown in **(b)** and **(d)** at different fluences.

model, previously introduced by Howard et al., and thereafter also applied to several other polymer:fullerene blends.^{30, 34} Here, the fit was performed as a global fit across all measured fluences with shared fitting parameters. The two-pool model is based on concomitant intensity-independent geminate recombination and intensity-dependent non-geminate recombination channels without conversion of charges between the two pools. Assuming that there is no difference between the cross section of CT states and spatially-separated charges, as typically observed for polymer:fullerene blends, the dynamics of the entire charge carrier population can be fitted with Equation 1:³⁴

$$n(t) =$$

$$(N_0(1-f)[\exp(-k_{CT \rightarrow GS}t)] + [\lambda\gamma t + (fN_0)^{-\lambda}]^{-1})/N_0 \quad (1)$$

Here, $k_{CT \rightarrow GS}$ is the monomolecular (geminate) rate constant, $\lambda+1$ and γ are the non-geminate recombination order and coefficient respectively, and f is the fraction of the initial population that decays non-geminately (equivalent to fraction of separated charges). N_0 is the initial charge carrier concentration calculated from the number of absorbed photons, which was allowed to vary within small boundaries during the fitting to account for experimental errors, while $n(t)$ is the carrier population undergoing recombination. Further details of this model can be found elsewhere.³⁴

As shown in Figure 4, the fit of the charge carrier-induced recombination dynamics describes the experimentally-

determined dynamics over the range of fluences measured here reasonably well, and it demonstrates that ~93 % of the photogenerated carriers in the annealed film are spatially-separated and thus could potentially be extracted from the solar cell. On the other hand, in the first nanoseconds we observed a fluence-independent geminate recombination process, which consumed ~7 % of the total charge carrier population present directly after excitation, followed by a pronounced fluence-dependent nano- to microsecond non-geminate recombination process of spatially-separated charges. An effective bimolecular recombination coefficient of $1.2 \times 10^{-12} \text{ cm}^3/\text{s}$ was calculated from the fit parameters using a carrier concentration of $5 \times 10^{15} \text{ cm}^{-3}$ approximately equivalent to 1 sun illumination conditions. We note that the recombination coefficient is in the range of values reported earlier for other polymer:fullerene blends, including TQ1:PC₇₁BM.^{12, 34, 36} More details of the calculation of the non-geminate recombination coefficient can be found elsewhere.³⁴ An overview of all fitting parameters is shown in Table 1. The fraction of spatially-separated charge carriers, denoted as f , is close to unity in the annealed blend, which explains to some extent the overall higher short-circuit current of the thermally annealed blend in OPV devices. The initial carrier densities N_0 of each fluence obtained from fits are shown in table S1 in the ESI.

Figure 4c depicts the ns-μs TA spectra of as-spun TQ1:N2200 blends. Unlike the annealed TQ1:N2200 sample, the PA band is very broad and quickly decays on a sub-ns timescale. The

ARTICLE

Journal Name

increased width of the charge carrier-induced absorption band is an indication of a larger energetic disorder compared to the annealed films, possibly originating from a more amorphous morphology of the as-spun sample.¹⁷

The kinetic traces of the PA bands of the as-cast film are largely fluence-independent as shown in Figure 4d. Even at the lowest fluence, more than 60 % of the charges are lost within 100 ns. The two-pool model fit to the data yields an effective bimolecular recombination coefficient of $0.3 \times 10^{-12} \text{ cm}^3/\text{s}$ and suggests that $\sim 65\%$ of the photogenerated charges are spatially separated on the nanosecond timescale. The effective bimolecular recombination coefficients of annealed and as-spun TQ1:N2200 are on the same order which is consistent with the long-rang charge carrier kinetics being similar in both blends as concluded from the TREFISH experiments shown above (figure 2).

Figure 5- Bimolecular recombination coefficient ($\beta_{TA} = \gamma \times n^{\lambda-1}$) estimated from the two-pool fit of the charge carrier recombination dynamics for both annealed (red line) and for as-spun devices (black line) plotted against the charge carrier density n . The red dot and black square indicate the β_{TDCF} values obtained from fits of the TDCF data for annealed and as-spun samples, respectively.

Figure 5 shows carrier density-dependent bimolecular recombination rates for both annealed and as-spun samples calculated from the results of the two-pool model and compares them to those obtained from TDCF measurements. We note that for both samples, the non-geminate recombination coefficients obtained from TA and TDCF differ quite substantially (see also Table 1). This mismatch is largely due to the n -dependence of β : indeed in TA, non-geminate recombination is empirically found to exhibit an order of $\lambda+1>2$, the equivalent β_{TA} is thus calculated as $\beta_{TA} = \gamma \cdot n^{\lambda-1}$ (by equalizing the recombination rates: $\beta_{TA} \cdot n^2 = \gamma \cdot n^{\lambda+1}$). The value presented in table 1 corresponds to the value of β_{TA} for a charge density of $5 \times 10^{15} \text{ cm}^{-3}$, corresponding to a device under solar operation. For the same fluence used in TDCF ($6 \mu\text{J}/\text{cm}^2$) we obtain β_{TA} of 4.2 and $2.7 \times 10^{-12} \text{ cm}^3$ for annealed and as-spun samples, respectively. Additionally β_{TDCF} is an upper limit for

recombination, because it is obtained by fitting the evolution of the number Q_{col} of charges extracted when applying the collection field (V_{col}) as a function of the time delay t_d between the laser pulse and the application of V_{col} . Implicitly, this means that all charges Q_{pre} escaping the device before t_d are considered recombined, thus overestimating charge recombination. While Q_{pre} is kept as low as possible by applying a prebias voltage close to V_{OC} , the remaining current, when integrated over larger delays, leads to the leakage of a rather large density of charges (see figure S7) before the application of V_{col} . Considering that those charges have recombined thus leads to an overestimation of the recombination coefficient. Similarly, in spite of the collection field, some charges may remain trapped in the device during the TDCF experiment and thus are considered recombined, while they are detected in TA. We hypothesize this is responsible for the larger mismatch between β_{TA} and β_{TDCF} observed in the as-spun film, where disorder is expected to result in a larger density of trap states.

The Langevin recombination coefficient $\beta_{Langevin}$ decreases with mobility from $2 \times 10^{-9} \text{ cm}^3/\text{s}$ to $4 \times 10^{-11} \text{ cm}^3/\text{s}$ (TREFISH + TPC, see figure S8) leading to reduction factors ($\zeta = \beta_{TA}/\beta_{Langevin}$) between ~ 0.01 and 0.001 . This is in the range of reduction factors expected for organic bulk heterojunctions.^{42, 43} ζ becomes 0.1 if considering mobilities of relaxed charges as obtained from SCLC measurements (compared to the bimolecular recombination coefficient obtained from TA at $1 \mu\text{s}$ ($\beta_{TA, @1\mu s}$), see figure S8-b). However, we note that this latter mobility value may not be relevant as most of the extraction occurs in a device prior to full charge relaxation.^{14, 19} We also note that a recent review from Collins et al. reported reduction factors ranging from 0.3 – 0.007 for a series of organic solar cells.⁴⁴

At the same time, the EQE of the corresponding OPV devices are very different. In fact, the ratio of spatially-separated charges in the annealed and as-spun films ($0.93/0.65 = 1.44$) is in good agreement with the EQE ratio of the corresponding OPV devices (see Figure 1d), implying that the IQE ratio is similar, as the absorption does not significantly change upon annealing.¹⁷ This also implies that both devices are similarly affected by non-geminate recombination losses, that is, losses during extraction are comparable. Furthermore, since charge extraction measurements have shown similar charge extraction rates for both annealed and as-spun devices, the increased fraction of geminate recombination in as-spun TQ1:N2200 devices largely accounts for the lower J_{sc} and EQE compared to thermally-annealed TQ1:N2200 devices. We hypothesize that the improved TQ1 backbone planarity and improved N2200 crystallinity following thermal annealing changes the energetic landscape and interfacial interaction of the materials, thereby leading to reduced geminate recombination in the annealed blend.

Table 1- Fit parameters obtained from the two-pool model fit describing the ns- μs charge carrier recombination dynamics in annealed and as-spun TQ1:N2200 blends. Here f is the fraction of free charge carriers, k_{CT-GS} is the geminate recombination

rate, $\lambda+1$ is the non-geminate recombination order, γ is the non-geminate decay rate, and β is the effective bimolecular recombination coefficient for annealed and as-spun blends calculated for a carrier density of $5 \times 10^{15} \text{ cm}^{-3}$. β_{TDCF} is the bimolecular recombination coefficient obtained from TDCF measurements for a fluence of $6 \mu\text{J}/\text{cm}^2$.

Sample/ Parameter	TQ1:N2200 (annealed)	TQ1:N2200 (as-spun)
f	$\sim 0.93 \pm 0.01$	$\sim 0.65 \pm 0.01$
$(1-f) \times 10^2$ (%)	~ 7	~ 35
$k_{\text{CT-GS}} (\text{s}^{-1})$	$4.1 \pm 0.3 \times 10^8$	$4 \pm 0.2 \times 10^8$
$\lambda+1$	2.36 ± 0.002	2.53 ± 0.002
$\gamma ((\text{cm}^3)^{-1} \text{s}^{-1})$	$3.2 \pm 0.1 \times 10^{-18}$	$1.2 \pm 0.03 \times 10^{-21}$
$\beta_{\text{TA}} (\text{cm}^3/\text{s})$	1.2×10^{-12}	0.3×10^{-12}
$\beta_{\text{TDCF}} (\text{cm}^3/\text{s})$	1.7×10^{-11}	7.5×10^{-11}

The free charge carrier yield f of 93 % of the thermally-annealed sample implies that charges readily separate in this blend and that the internal quantum efficiency (IQE) could theoretically exceed 90 %. However, this is not observed experimentally. The IQE of the thermally-annealed and as-spun samples are 52 % and 36 %, respectively, as determined from the experimentally-measured J_{SC} compared to the maximum theoretically possible J_{SC} calculated from the blends' absorption in a device structure using transfer matrix modeling. The difference between these values implies that a considerable fraction of spatially-separated charges are lost by other recombination processes, supposedly non-geminate recombination, during charge extraction. Subtracting the experimentally-measured IQE and the geminate losses determined by TA from a maximum possible IQE of 100 % demonstrates that as much as 41 % of the photogenerated charges recombine non-geminately in the thermally-annealed blend, whereas in the as-spun sample 29 % of charges undergo non-geminate recombination. Note that, since IQE and TA measurements were performed at different conditions (TA corresponds to V_{oc} , whereas IQE to short-circuit conditions), the above values are an upper limit of non-geminate recombination. Below we perform time-delayed collection field (TDCF) experiments to estimate these losses also at maximum power point (MPP) conditions.

Time delayed collection field (TDCF) experiments

We performed time-delayed collection field (TDCF) experiments, as this technique is able to distinguish between field-dependent charge generation and non-geminate recombination of free charges, which can both lower the FF in OPV devices under bias conditions directly relevant for device operation.^{45, 46} Details of the TDCF experiment are shown in Figure S6 in the ESI. The total extracted charge, Q_{tot} , as a function of the applied prebias (probing the field dependence of the charge generation process) during photoexcitation after a delay of 10 ns between prebias and collection field is shown in Figure 6 a, b.

We deliberately chose a low excitation fluence, at which non-geminate recombination losses during the time between photogeneration and extraction can be neglected. Under these conditions, Q_{tot} is a direct measure of the amount of free charge generated by the excitation laser pulse as a function of the applied prebias. An important difference was observed between the as-spun and annealed samples: charge generation is field-dependent in the as-spun sample, while it is not in the annealed one. Consequently, the field-dependent geminate recombination losses are considerably higher in the as-spun sample. In contrast, the thermally-annealed device exhibits virtually no field-dependence of charge generation and lower geminate recombination losses, leading to a higher

Figure 6- Total amount of charge (Q_{tot}) extracted from the device as a function of applied prebias during photoexcitation and JV-curves of: (a) thermally-annealed TQ1:N2200 devices and (b) as-spun TQ1:N2200 devices. The shaded region indicates the amount of field-dependent geminate recombination with respect to a negative bias of -1V, as indicated by the solid horizontal line. The arrows indicate the fraction of nongeminate recombination, which leads to further reduction of the device fill factor.

device fill factor. These results also support the time-resolved charge extraction experiments, indicating that the annealed films generated more charges compared to the as-spun devices (Figure S7). The TDCF experiments clearly demonstrate that the lower fill factor of as-spun TQ1:N2200 devices is a result of a more pronounced field dependence of charge generation. However, overall the moderate fill factor of both

ARTICLE

Journal Name

TQ1:N2200 devices appears to be caused to a large extent by non-geminate recombination of free charges competing efficiently with charge extraction as further discussed below.

Impact on device performance

Table 2 presents an overview of the theoretically possible and experimentally determined J_{SC} values, the internal quantum efficiencies obtained from the ratio of J_{SC} values and TREFISH experiments, as well as the recombination losses determined by TA and TDCF experiments. Here, we determined the yield of free charges generated after photoexcitation of each blend from ns- μ s TA experiments, demonstrating that under Voc conditions 93 % of excitons are converted into free charges shortly after photoexcitation in the annealed sample, while this fraction is reduced to 65 % in the as-spun sample. Note that TA is measured under Voc condition. To obtain the IQE at J_{SC} conditions, we calculated the difference in charge density at Voc and J_{SC} conditions from the TDCF data and corrected it by $Q_{TA} \times (Q_{J_{SC},TDCF} / Q_{Voc,TDCF})$. The estimated upper limit for the IQE is 94 % for the annealed device and 69 % for the as-spun device, indicating the weak field dependence does only have a small impact on the amount of free carriers generated. These values can be considered as a ceiling for the IQE, corresponding to the situation that all free photogenerated carriers are extracted from the device. However, the experimentally determined IQE values (at short circuit) are significantly lower, at 50-58 % for the annealed and 36 % for the as-spun sample, respectively. This implies that non-geminate recombination contributes to the photocurrent loss in both devices, however, to a much larger extent in the annealed than in the as-spun film, possibly due to the larger carrier density in the annealed device. Furthermore, the free charge generation exhibits a stronger field-dependence in the as-spun device, which readily explains its lower fill factor.

TDCF experiments allowed us to further unravel the recombination losses at conditions relevant to operating devices, i.e. at short circuit (0V) and at maximum power point (MPP). Here, we estimated the additional non-geminate losses with respect to those occurring at -1V, our reference point in TDCF experiments. We find from TDCF experiments that under operating conditions non-geminate recombination increased by an additional 12 % and 40 % in the annealed sample at short circuit (0V) and at maximum power point (MPP) conditions compared to -1V, respectively. Furthermore, in the annealed sample the contribution from geminate recombination (GR) was negligible. The total additional recombination losses for the as-spun sample were 21 % at 0V with NGR = 17 % and GR = 4 % (as estimated from TDCF with respect to -1V), while at the MPP the total losses increased to 52 % with NGR = 44 % and GR = 8 % with respect to -1V. Hence, we observed an increase in non-geminate recombination between short circuit conditions (0V) and the maximum power point (MPP) of 28 % for the annealed sample and 27 % for the as-cast sample, respectively. Clearly, non-geminate recombination losses govern to a large extent the fill

factor of both devices – a pronounced competition between non-geminate recombination and charge extraction exists in this material system.

Table 2- Maximum obtainable photocurrent $J_{SC,max}$ for annealed and as-spun TQ1:N2200 devices obtained from TMM modelling, experimentally-measured short-circuit current $J_{SC,meas}$, internal quantum efficiency (IQE_{JSC}) predicted from the ratio of $J_{SC,meas} / J_{SC,max}$ and IQE_{TREFISH} as calculated from TREFISH experiments. $J_{photo} / \text{mAcm}^{-2}$ @ MPP is the photocurrent at the maximum power point (MPP). Fraction of non-geminate recombination NGR_{TA} and geminate recombination GR_{TA} determined from TA experiments for open circuit conditions, and increase in non-geminate recombination $\Delta\text{NGR}_{TDCF}/\%$ (MPP-0V) and geminate recombination $\Delta\text{GR}_{TDCF}/\%$ (MPP-0V) between MPP and short circuit (0V).

Sample/ Parameter	TQ1:N2200 (annealed)	TQ1:N2200 (as-spun)
$J_{SC,max} / \text{mAcm}^{-2}$	14.5	13.8
$J_{SC,meas} / \text{mAcm}^{-2}$ @ 0V	7.7	5
$J_{photo} / \text{mAcm}^{-2}$ @ MPP	3.1	2.1
IQE _{JSC} / % @ 0V	52	36
IQE _{TREFISH} / % @ 0V	58	36
GR _{TA} / % @ Voc	7	35
NGR _{TA} / % @ Voc	93	65
$\Delta\text{NGR}_{TDCF} / \%$ (MPP-0V)	28	27
$\Delta\text{GR}_{TDCF} / \%$ (MPP-0V)	-	4

Conclusions

Using a combination of TREFISH, transient photocurrent measurements, transient absorption and time-delayed collection field experiments, we uncovered the origin of larger photocurrents, higher fill factors, and concomitantly better device performance observed upon thermal annealing in TQ1:N2200 all-polymer bulk heterojunction organic solar cells. In addition to the improved TQ1 backbone planarity and improved N2200 crystallinity demonstrated in earlier work¹⁷, our data suggests that the interaction of the two polymers at the polymer-polymer interface changes upon thermal annealing. These morphological changes aid the separation of charges at, or in close vicinity of the donor-acceptor interface, as indicated by a weaker field dependence of charge generation, and reduce the fraction of bound interfacial charge-transfer states that geminately recombine, without significantly altering the long-range charge extraction. Ultimately, the increased dissociation efficiency results in higher quantum efficiencies and thus photocurrents, while the weakened field dependence of generation leads to increased fill factors. While charge separation improves upon thermal annealing, fast non-geminate recombination remains a significant bottleneck for device performance even in the thermally-annealed device, as it competes strongly with carrier extraction, thereby limiting the device fill factor. Future material development and device optimization strategies need

to address this issue by designing materials with higher charge carrier mobilities at all relevant time scales,¹³ in turn allowing faster extraction of charges, while kinetically outcompeting recombination.

Author contributions

S.K. performed TA experiments and data analysis. V.P. performed TREFISH measurements and A.M. analyzed the TREFISH data. Z.K. performed TDCF measurements and data analysis. Y.X. fabricated solar cells / thin films used in this study. O.I., V.G., and M.K. supervised the steady-state and electrical characterization. M.W. designed and set up the TDCF experiment. J.I.K. and J.G. helped with TA experiments and data analysis. S.K. and F.L. conceived and designed this study. All authors contributed to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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ARTICLE

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Annealing of TQ1:N2200 photovoltaic blends reduces geminate charge recombination, without compromising charge extraction, leading to higher photocurrents and device efficiency.