

Build-up of Triplet Population in Operating TQ1:PC71BM Devices Does Not Limit Their Performance

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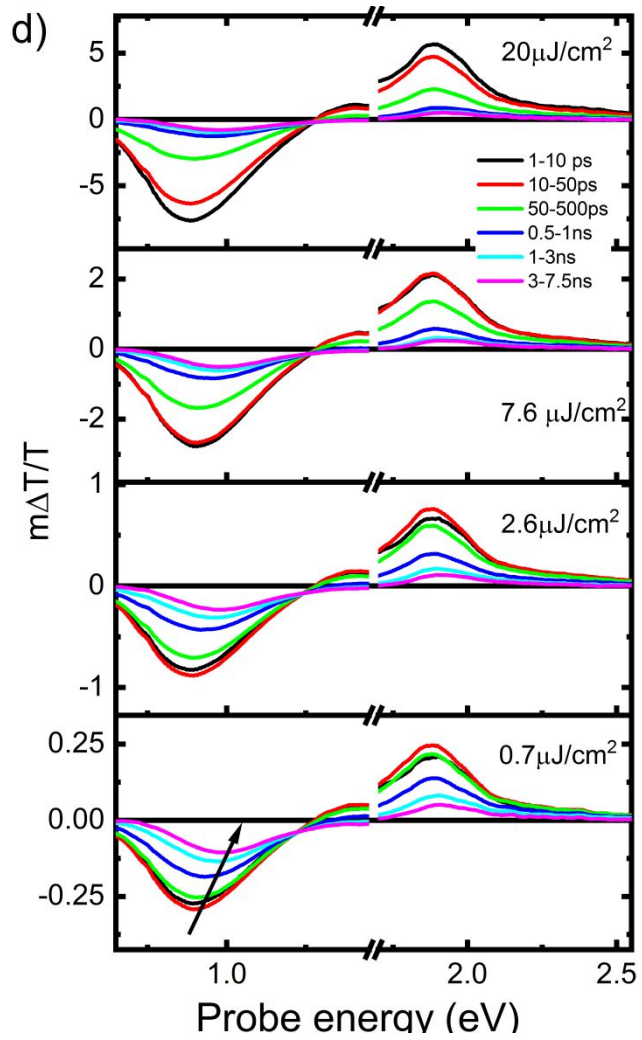
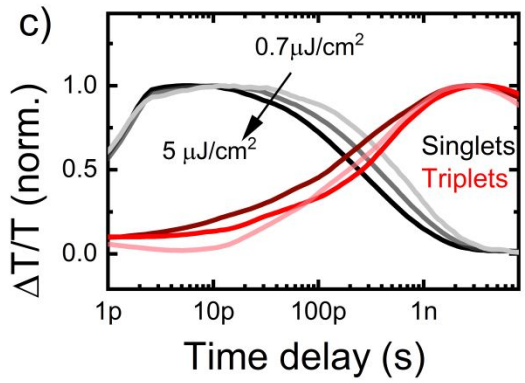
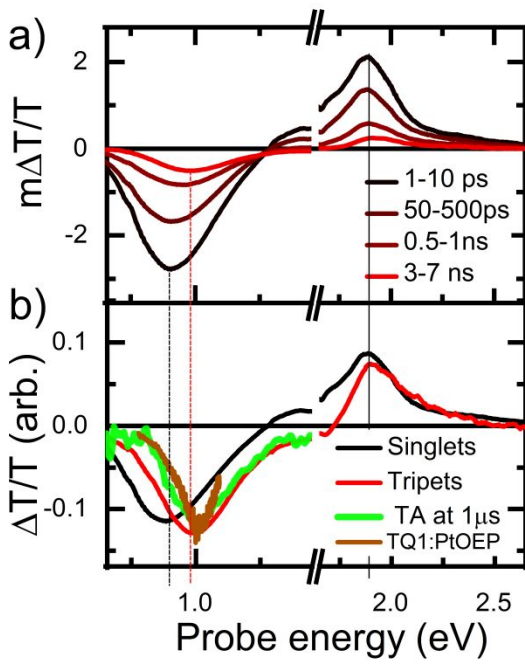
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S1. Additional transient spectroscopy data



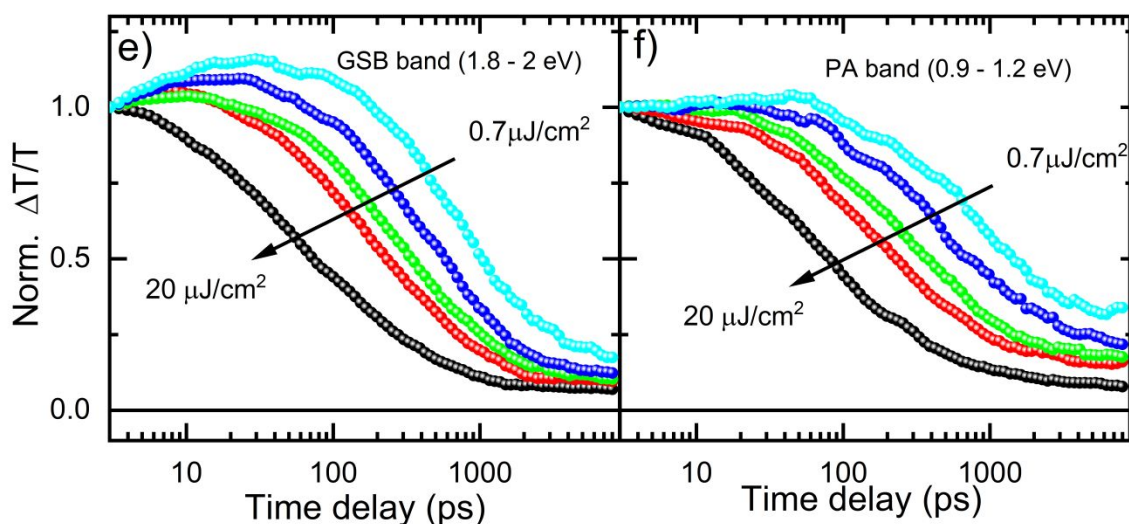


Figure S1. TA on pristine a TQ1 film. (a) ps-ns TA spectra of a pristine TQ1 film after photoexcitation at 600 nm with 7 $\mu\text{J}/\text{cm}^2$. (b) Spectra of singlet excitons (black line) and triplet excitons (red line) of pristine TQ1 obtained from MCR analysis and the TA spectrum of TQ1 film measured at 1 μs (green line) and of TQ1:PtOEP (95:5 wt%) film at 100 μs (brown line). The spectral region from 1.45 eV-1.65 eV is excluded due to artifacts from optical filters. (c) Normalized kinetics of singlet and triplet states in pristine TQ1 films at different fluences as obtained from MCR analysis. (d) Fluence dependent ps-ns TA spectra of pristine TQ1 film measured in vacuum for fluences indicated in the panels after excitation at 600 nm. (e) GSB band (1.8-2 eV) and (f) PA band (0.9-1.2 eV) at different fluences following 600 nm excitation.

Figure S1b shows the two component spectra obtained from MCR-ALS analysis of the neat TQ1 film's TA data. The singlet exciton-induced absorption peaks at 0.88 eV, while the second component spectrum peaking at 0.99 eV is assigned to triplet exciton-induced absorption. The triplet exciton-induced absorption obtained from MCR analysis is in agreement with the TA spectrum measured at 1 μs (green line), indicating that on the microsecond timescale triplet states are still present in neat TQ1 films. We confirmed the triplet-induced absorption by TA measurements on TQ1 films doped with the triplet sensitizer platinum octaethylporphyrin, PtOEP (95:5 wt% TQ1:PtOEP). The component-associated kinetics of singlet excitons (black shade) and triplets (red shade) obtained from MCR-ALS analysis are shown in Figure S1c. The weakly fluence-dependent decay of singlets and concomitant rise of triplets indicates that in addition to ISC, some triplet formation occurs via singlet-singlet annihilation (SSA) at the excitation fluences used in our TA experiments (0.7, 2.5, and 5 $\mu\text{J}/\text{cm}^2$). Kinetic plots extracted from the photo-induced absorption band (PA) and ground state bleach (GSB) region of the experimentally

measured TA data can be found in Figures S1e and S1f. To further support our assignment of this band to triplets in neat TQ1 films, we also measured ps-ns TA in air. TA measurements in air have previously been used to distinguish between triplet states and charges in organic semiconductors and dyes as only triplet states are quenched by oxygen.^{1, 2} Indeed, the decay of the signal of the TQ1 film measured in air is faster than the decay measured in vacuum (see Figure S2). This supports our assignment to triplet states in neat TQ1, which are generated via intersystem crossing and are sensitive to quenching by oxygen.

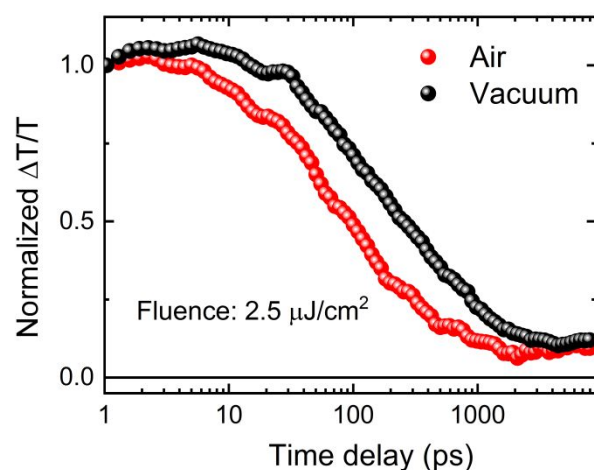


Figure S2. Quenching of the triplet signal in air in a pristine TQ1 film. ps – ns kinetics of a TQ1 film integrated over the PA region (0.95 eV-1.2 eV) in air (red symbols) show a faster decay compared to the kinetics of TQ1 film measured under dynamic vacuum conditions (black symbols), indicating triplet formation in the neat TQ1 films.

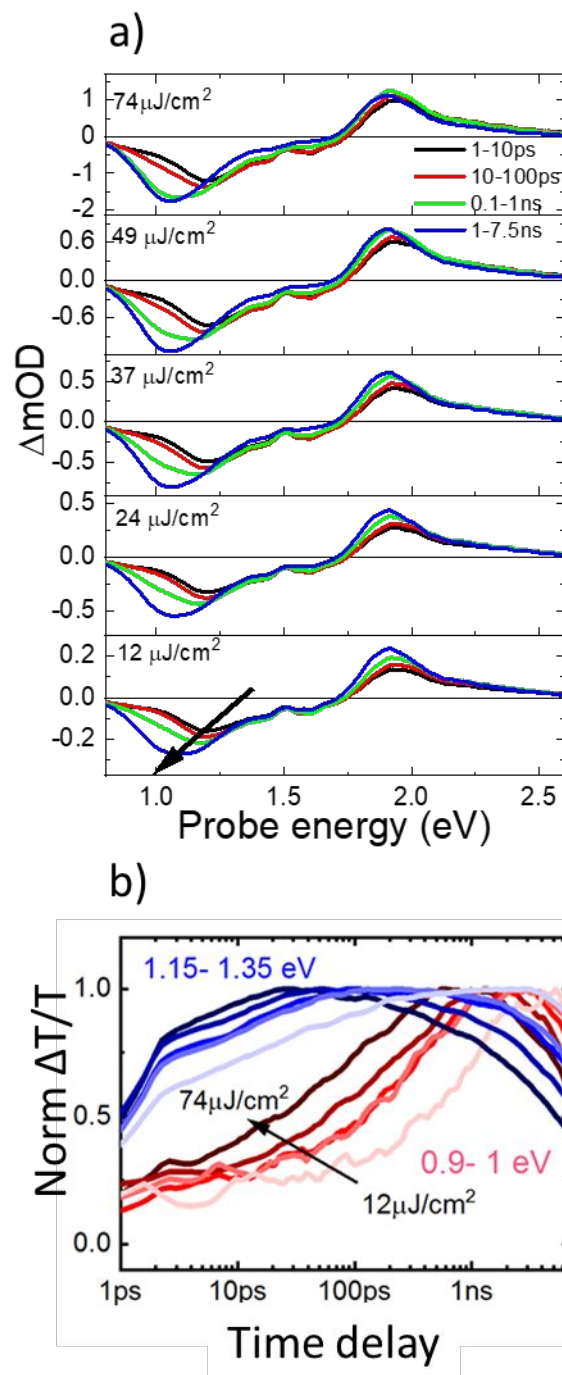


Figure S3. ps-ns TA spectroscopy of a TQ1:PC₇₁BM blend thin film at different excitation fluences. Excitation at 500 nm. **(a)** Spectra of selected delay times. Note the clear and progressive red-shift of the PA band between 1.0 – 1.25 eV and PB (1.8-2.1 eV) band. The absolute shift in the spectra is shown in Figure S7. **(b)** Normalized fluence-dependent evolution of the low energy (mostly triplets) and high energy (mostly charges) photoinduced absorption features.

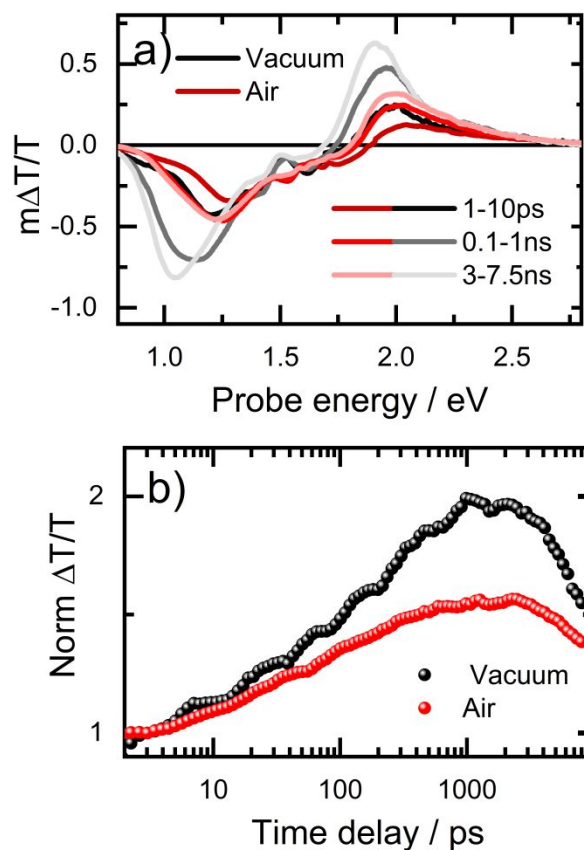


Figure S4. Quenching of the ps – ns triplet signal in air in a TQ1:PC₇₁BM blend films. (a) ps - ns TA spectra of TQ1:PC₇₁BM in vacuum (black lines) and in air (red lines). The red shift and growth of the PA band are significantly reduced in air, pointing to the presence of triplet states. The GSB band still showed a rise in air, indicating that the rise is due to exciton diffusion from PC₇₁BM to the interface followed by hole transfer to the polymer; the similar magnitude of the GSB redshift in air is consistent with essentially unchanged carrier relaxation. (b) Normalized (at 1 ps) PA (0.95-1.3 eV) kinetics for vacuum (black symbols) and air (red symbols) TA measurements.

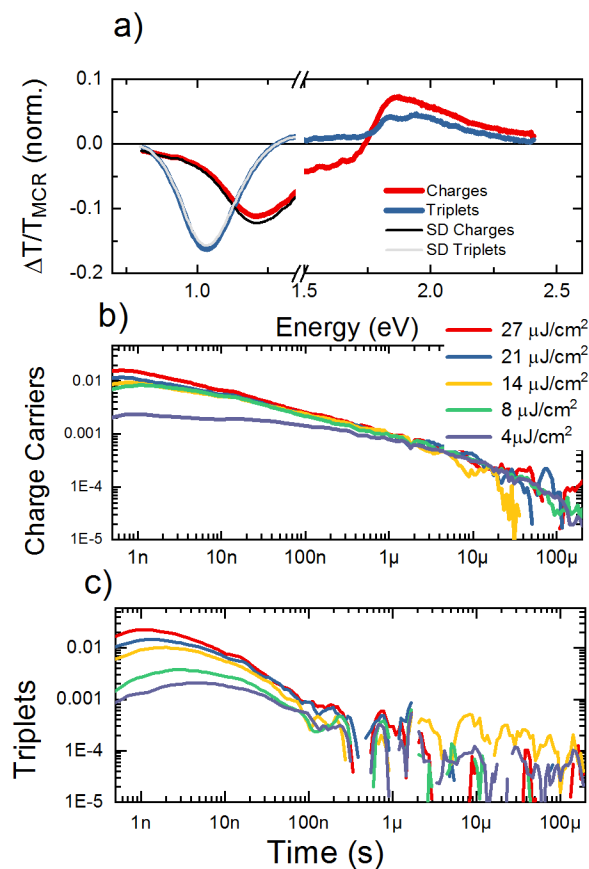


Figure S5. MCR decomposition of the ns - μs TA experiments on TQ1:PC₇₁BM blends in vacuum. (a) Component spectra; by convention the spectral shape are normalized in surface area. Spectra obtained from the MCR decomposition of the ps – ns (SD for short delay) data are shown for comparison. **(b)** Time-dependent charge induced signal amplitude for the different fluences, **(c)** Time dependent triplet induced signal for the different fluences. For each time delay and fluence, the charge-induced (resp. triplet-induced) signal can be obtained by multiplying the signal amplitude (Figure. S7b, resp. S7c) by its spectral shape (Figure S7a)

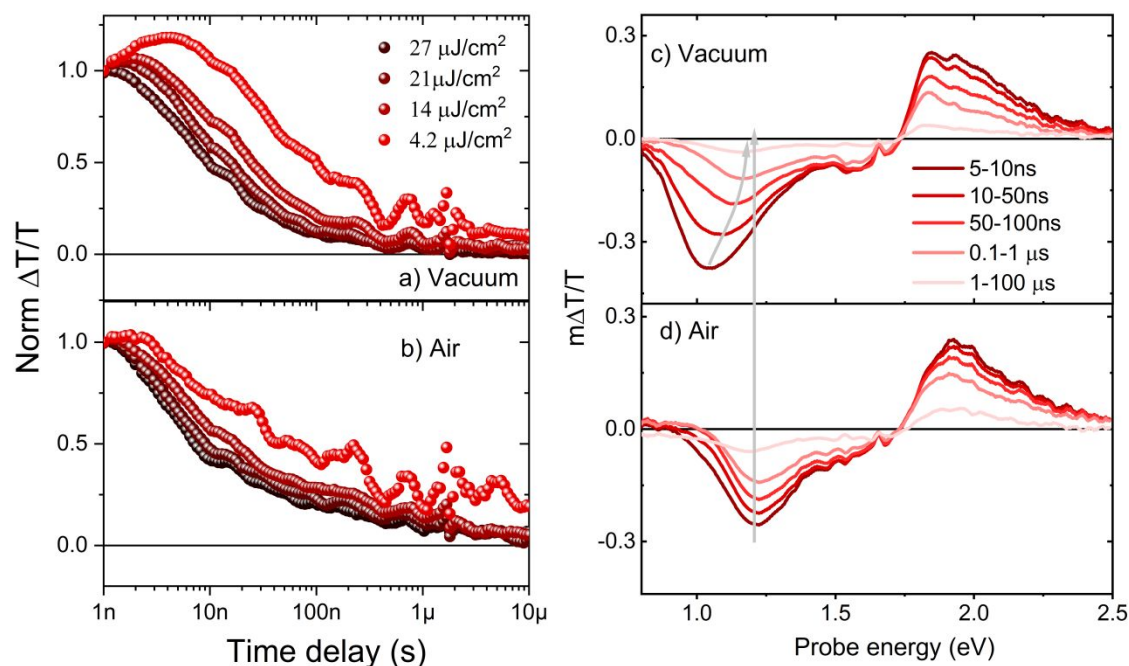


Figure S6. Quenching of the ns – μs triplet signal in air in a TQ1:PC₇₁BM blend films. (a) ns- μs TA kinetics of photo-induced absorption region of TQ1:PC₇₁BM at different fluences under vacuum and (b) in air as indicated in the panels. (c) ns- μs TA spectra of TQ1:PC₇₁BM under vacuum and (d) in air at 4.5 $\mu\text{J}/\text{cm}^2$ with 532 nm excitation pulses. The spectrum measured in air shows a lower $\Delta T/T$ values and reduction in the spectral blue shift, indicating that triplets were quenched by oxygen.

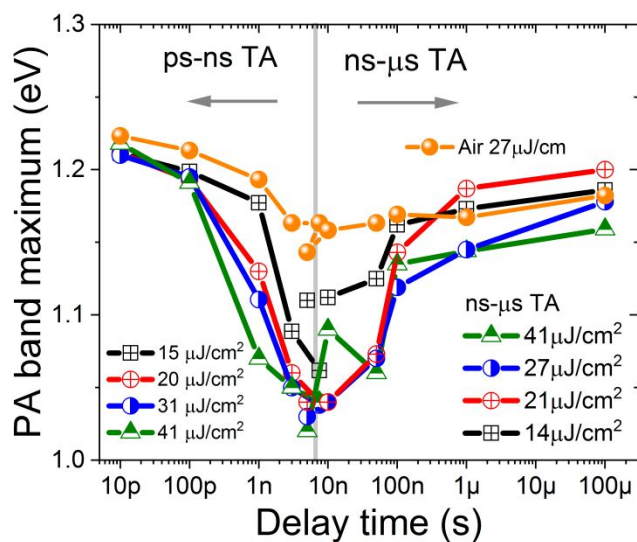


Figure S7. Spectral shift of the photoinduced absorption maxima (PA_{max}) band of TQ1:PC₇₁BM. Measured under vacuum for a wide dynamic range from 2 ps to 200 μs at different fluences as indicated in the legend.

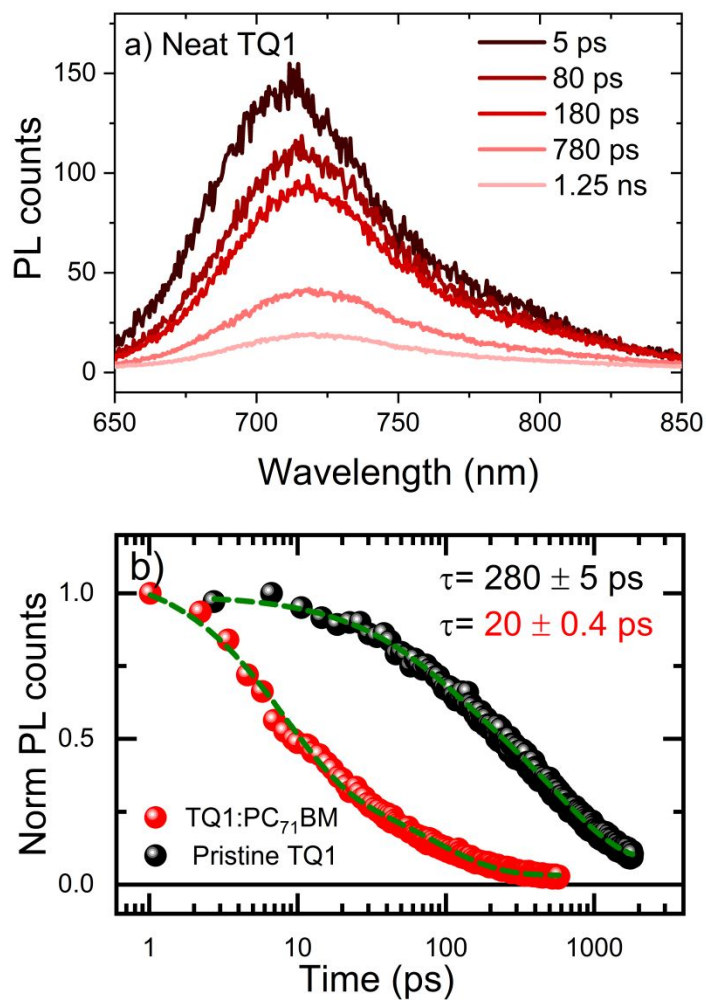


Figure S8. Time-resolved photoluminescence. (a) Time-resolved photoluminescence (TRPL) spectra of pristine TQ1 after exciting at 530 nm. (b) TRPL kinetics traces of pristine TQ1 (black symbols) and of TQ1:PC₇₁BM (red symbols) with respective (green dotted line) exponential fits. Details of TRPL experiments can be found elsewhere.³

S2. Estimation of the excited state absorption cross sections

We used the Lambert-Beer law to calculate the absorption cross-section of all excited states in TQ1:PC₇₁BM,

	$\frac{\Delta T}{T} = \sigma(\lambda) \times c(t) \times d$		(S1)
	$\sigma(\lambda) = \frac{\Delta T}{T} / (c(t) \times d)$		(S2)

where, $\sigma(\lambda)$ is the wavelength-dependent absorption cross-section, $c(t)$ is the time-dependent concentration of the excited state, and d is the thickness of the sample

S2.1. Singlet excited state absorption cross-section calculated from TA experiments on pristine TQ1 films

The absorption coefficient (α) of neat TQ1 films at 600 nm was obtained from UV-Vis absorbance measurements (Figure 1b).

Inserting the value of the absorption coefficient ($\alpha_{600 \text{ nm}} = 7.5 \times 10^4 \text{ cm}^{-1}$), and the thickness of the sample ($d = 85 \text{ nm}$) into $A = 1 - 10^{-\alpha \cdot d}$ yields a 77 % of incident photons absorbed and generating singlet excitons. We consider that in the pure material, each absorbed photon is initially converted into a singlet exciton. The initial density of excitons is thus simply obtained by dividing the absorbed fluence by the sample thickness (85 nm) and the single photon energy ($3.31 \times 10^{-19} \text{ J}$ for 600 nm photons). Those initial concentrations are reported in Table S1.

Table S1: Estimated singlet and triplet exciton density from absorbed photons for different fluences.

Incident fluence	Initial singlet density	Fraction of the photo bleach remaining between 5 and 7 ns	Corresponding triplet density
0.71 $\mu\text{J}.\text{cm}^{-2}$	$1.9 \times 10^{17} \text{ cm}^{-3}$	17.4%	$3.4 \times 10^{16} \text{ cm}^{-3}$
2.6 $\mu\text{J}.\text{cm}^{-2}$	$7.1 \times 10^{17} \text{ cm}^{-3}$	12.7%	$9 \times 10^{16} \text{ cm}^{-3}$
5 $\mu\text{J}.\text{cm}^{-2}$	$1.4 \times 10^{17} \text{ cm}^{-3}$	11.1%*	$1.5 \times 10^{17} \text{ cm}^{-3}$
7.6 $\mu\text{J}.\text{cm}^{-2}$	$2.08 \times 10^{17} \text{ cm}^{-3}$	9.96%*	$2.1 \times 10^{17} \text{ cm}^{-3}$
20 $\mu\text{J}.\text{cm}^{-2}$	$5.5 \times 10^{17} \text{ cm}^{-3}$	7.32%*	$4 \times 10^{17} \text{ cm}^{-3}$

* As can be seen in Figure S1, the exciton-induced signal seems to increase up to the tens of ps timescale, corresponding to the loss of polarization anisotropy between the pump and the probe, we thus take as a reference exciton spectrum the spectrum averaged between 15 and 30 ps for the two lowest fluences (for higher fluences, 2nd order reactions such as exciton-exciton annihilation have already set in before the end of this relaxation meaning that the maximal singlet signal can not be precisely determined).

Dividing those maximal TA spectra by the initial singlet densities and the sample thickness yields the exciton cross section spectrum represented in Figure S9a (the average cross section and standard deviation can be seen in Figure S9d).

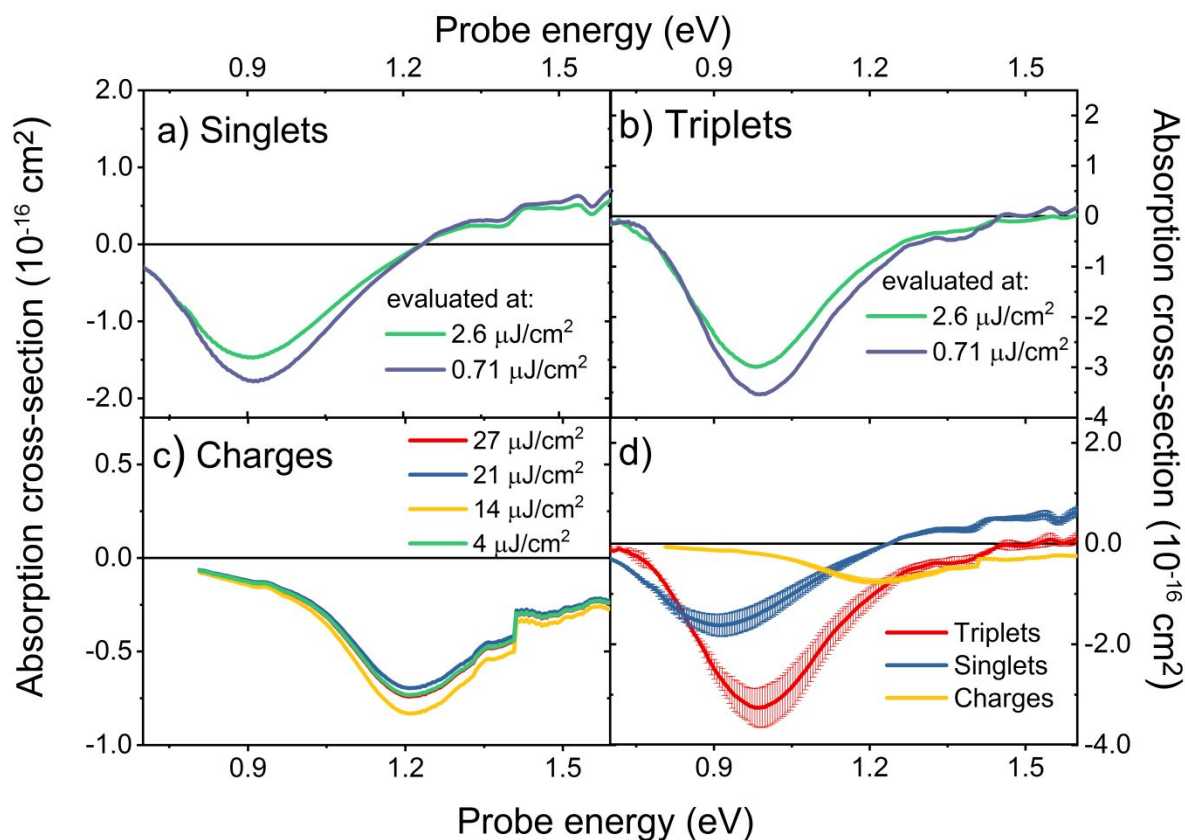


Figure S9. Absorption cross section spectra of the individual excited species. (a) singlets, (b) triplets, (c) charges, (d) compared cross sections (with standard deviation).

S2.2. Triplet exciton cross-section calculated from TA experiments on pristine TQ1

We assume that in pristine TQ1, the excited states remaining between 5 and 7 ns are triplets, as the singlet almost entirely extinguish within 300 ps (as seen from the extinction of the photoluminescence, see time-resolved photo-luminescence (TRPL) in Figure S8. A rough estimation of the triplets cross section is obtained by assuming that singlets and triplets share the same cross section in the photobleach region (here we considered the most clear region: 1.8 – 2 eV). Under this approximation, the triplet density at 5-7 ns (when only triplets subside) is equal to the initial singlet density times the ratio of the triplet induced photobleach at 5-7 ns divided by the

maximum singlet induced photobleach (obtained at 15 - 30 ps): $T(5 - 7 \text{ ns}) = PB(5 - 7 \text{ ns}) / PB(15 - 30 \text{ ps}) * S(15 - 30 \text{ ps})$. Table 1 summarizes the fraction of the maximal photobleach that remains in the timescale where only triplets are expected as well as the corresponding triplet densities extracted, assuming identical triplet and singlet cross sections in that spectral range. The corresponding triplet cross section spectra in the rest of the spectral range are shown in Figure S9b.

S2.3. Charge carrier absorption cross-section calculated from TA experiments on TQ1:PC₇₁BM

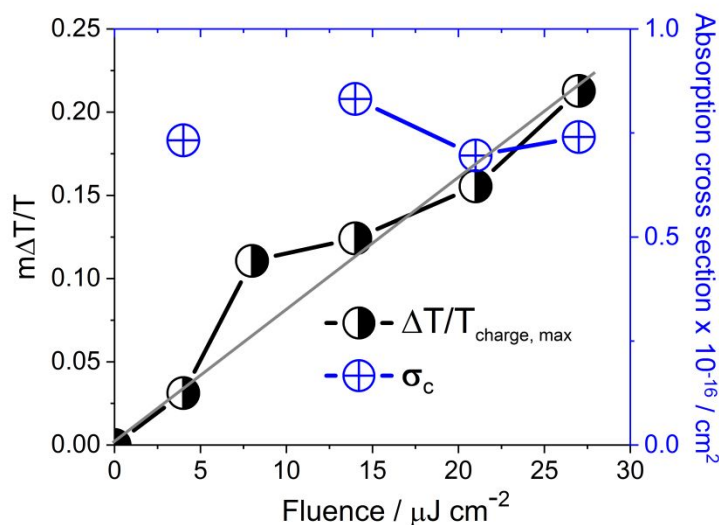


Figure S10. Absence of non-linear losses in the fluence-dependent charge induced PA signal in the 0.6 – 1 ns time range. Maximum $\Delta T/T$ value for charge carriers signal (black symbols) obtained from MCR analysis for TQ1:PC₇₁BM blend. Estimated absorption cross section for charge carriers (blue crossed circle), at the maximum of absorption.

The charge carrier absorption cross section was estimated by dividing the maximal (obtained between 0.6 and 1 ns) charge induced spectra as extracted via MCR from the ns- μs TA data (see spectral shape in Figure S5a and signal amplitude in Figure S5b) by the density of absorbed pump photons (33% of absorbed photons at 532 nm on a 85 nm TQ1:PC₇₁BM film) and the film thickness.

Considering the initial density as equal to absorbed photon density is an optimistic estimate that we justify by the high IQE (82% at 532 nm, see Figure 1) measured on devices. We also stress that the main loss mechanisms have not set in yet at the time delays where the maximal signal is obtained (0.6 - 1 ns): the linear growth of the signal with fluence (see Figure S10) indicates the absence of non-geminate recombination while geminate recombination has a time constant of 2.8 ns (see table 1). The only loss channel left is thus exciton losses before charge transfer, which we neglect based on the very efficient exciton harvesting (exciton lifetime in the ps range in the blend) and the high IQE (82% at 532 nm, including geminate recombination losses which can occur in the IQE measurement but have not occurred yet at the delay time of below 1 ns used here, indeed, as seen in Table 1, we find a geminate recombination time constant of 2.8 ns). Note that the maximal error involved by doing so would be $1 - \text{IQE} = 18\%$ for an excitation wavelength of 532 nm, but the actual error –if any- is probably much lower as IQE losses include geminate recombination (18 % of the charges at open circuit, see Table 1, but possibly less at short circuit in case of field-assisted polaron pairs dissociation).

As shown in Figure S10, the initial charge induced signal as extracted from MCR grows linearly, with one outlier: the $8 \mu\text{J}/\text{cm}^2$ experiment which is thus disregarded for all the evaluation process (especially for the 2-pool fit, and the triplet rate equation determination). The calculated absorption cross-section spectra for the 4 remaining fluences, are shown in Figure S9c. As can be seen the 4 fluences show consistent absorption cross section with a rather weak deviation.

S2.4. Maximum charge and triplet state densities

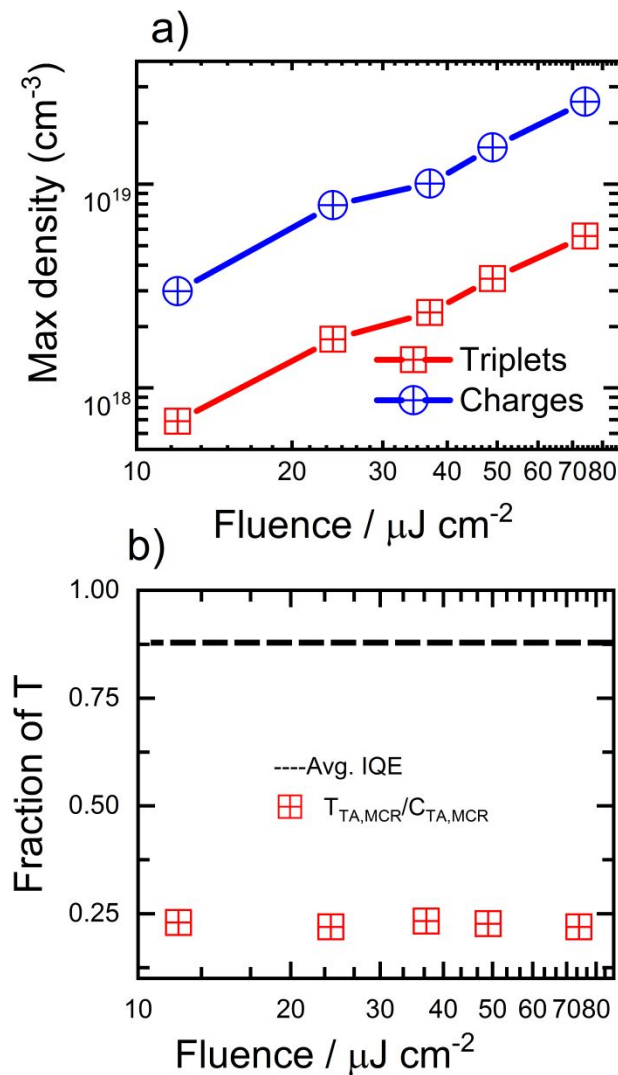


Figure S11. Relative charge and triplet max densities. Panel (a) shows the density of charge carriers (blue) and triplet excitons (red) obtained from MCR kinetics (Figure 2) at signal maxima, whereas panel (b) shows the ratio of the maximal triplet density to the maximal charge density, in transient experiments.

S3. Effective bimolecular recombination coefficient

Empirically the non-geminate recombination of separated charges is found to follow an apparent order $\lambda+1$ higher than two:

	$\frac{dn}{dt} = - \gamma n^{\lambda+1}$		(S3)
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Which can also be written as a bimolecular recombination with a *n-dependent* recombination coefficient $k_{2,TA}$:

	$\frac{dn}{dt} = - k_{2,TA} n^2$		(S4)
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With $k_{2,TA} = \gamma n^{\lambda-1}$

Several theories currently exist to explain this dependence such as field dependent mobility, immobilization (trapping) of a part of the charges,⁴ non-uniform distribution of the charges through the layer thickness,⁵ or equilibrium between separated charges and interfacial CT-state.⁶

S4. Time Delayed Collection Field (TDCF) decay

The evolution of the density of extracted charges was fitted for each time delay using the approached proposed by Kniepert et al. that enables to not consider the charges extracted before applying the collection field as having recombined:⁷

$\Delta Q_{col} = Q_{col}(t_d + \Delta t) - Q_{col}(t_d) = - \Delta Q_{pre} - \frac{k_2}{eAd} [Q_{coll}^2(t_d) + 2Q_{coll}(t_d)Q_{bg}] \Delta t$	
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With Q_{col} the photogenerated charge collected during the application of the collection field (extraction voltage of -4V applied during 20 μ s starting at a delay t_d following the pulsed photoexcitation (532 nm, 700 ps laser pulses)); Q_{pre} the photogenerated charge collected between the excitation laser pulse and the extraction voltage pulse, while a prebias voltage of 0.82V ($\approx V_{OC}$ on that specific device) is applied; e the elementary charge, A and d the device surface area and active layer thickness, respectively ($= 1 \text{ mm}^2$ and 85 nm, respectively), Δt the time interval between the two successive delays and Q_{bg} the background charge (typically due to imperfectly cancelled injection).

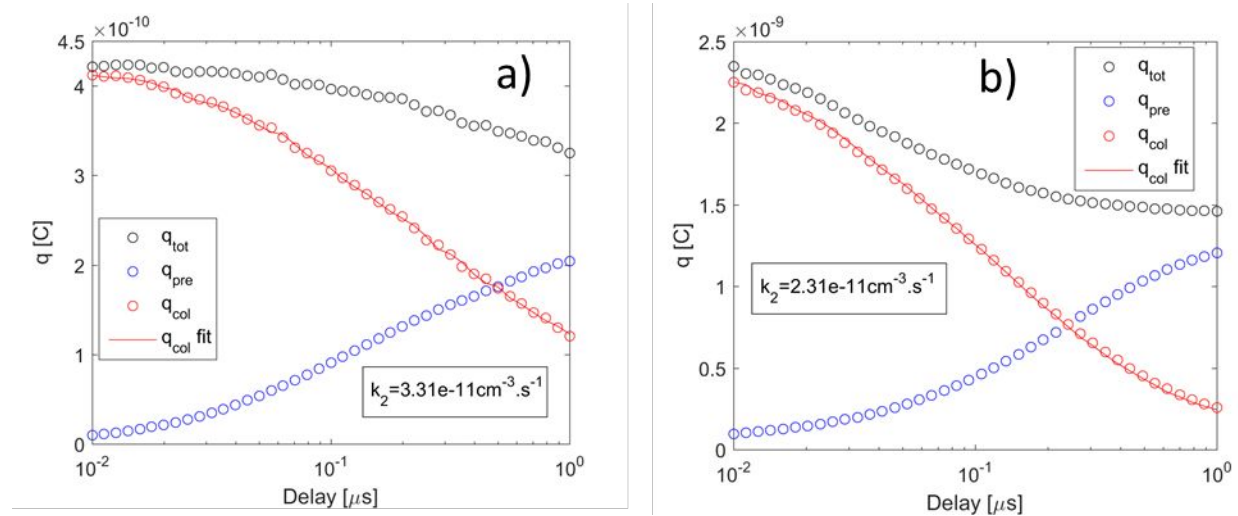


Figure S12. Electrical measurement of the bimolecular recombination rate. Fit of the decay of the extracted charge in a time delayed collection field experiment under an excitation density of 0.2 $\mu\text{J}/\text{cm}^2/\text{pulse}$ (a) and 3.6 $\mu\text{J}/\text{cm}^2/\text{pulse}$ (b) (532 nm, ~ 700 ps laser pulses) as function of the delay of application of the extraction field.

Applying this equation to all the delays enables to extract the bimolecular recombination coefficient k_2 (labelled $k_{2, TDCF}$ in the text). As can be seen in Figure S12 the use of a single k_2 value for all the time delays already enables an excellent fit of the experimental decay.

However, in our case we did not have access to Q_{bg} and thus chose to neglect it. In other words, we did not consider the recombination of photogenerated charges with background/injected ones. As will be shown when imputing $k_{2,TDCF}$ to the Setfos device simulation, neglecting the Q_{bg} may be a too rough approximation as it leads to an overestimate of k_2 as the recombining charge is underestimated (Q_{col} only instead of Q_{col} and Q_{bg}).⁸ This is confirmed by the fact that the fit for a higher excitation fluence (Figure S12b) gives a lower recombination coefficient k_2 (as the density of photogenerated charges is higher, the relative weight of background charges is lower). However as will be seen, $k_{2,TDCF}$ already provides a good starting point to give a first estimate of the charge density through the device, which is necessary to determine the relevant value of the n -dependent $k_{2,TA}$.

S5. Triplet formation and decay models and corresponding fits

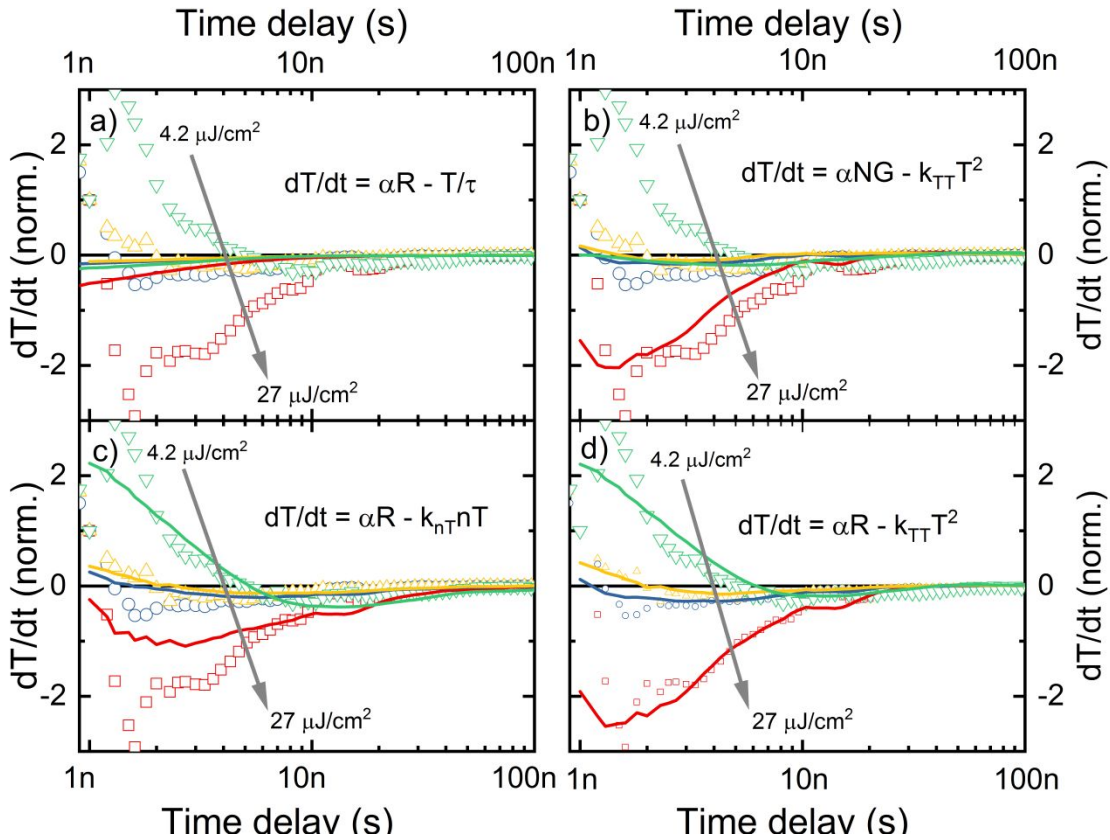


Figure S13. Fits of the variation of the triplet density for different models. The fitting rate equations are indicated in the subfigure with T the triplet density, R the overall charge recombination rate, NG the non-geminate charge recombination rate, n the charge density. Fit parameters: α the triplet formation efficiency upon recombination, k_{TT} the coefficient of the triplet triplet annihilation rate, k_{nT} the coefficient of the charge triplet annihilation rate (+ dT/dt the initial derivative of the triplet density = normalization factor). Note we used normalized derivatives so that the highest fluences are not overweighted in the fits (normalized to their value at 1 ns).

S6. Setfos simulations

S6.1. Optical simulation

The whole device (Glass/ITO(109 nm)/PEDOT:PSS(25 nm)/TQ1:PC71BM(85 nm)/Ca (5nm)/Al(80 nm)) was optically modelled to determine the amount of light that could be absorbed in the active layer. The complex refractive index ($n_r + ik$) of the active layer was determined by ellipsometry, while the indexes for the other layers were already available in the Setfos optical indexes library. Note that the asymptotic value of refractive index (n_r) for high wavelength (low frequency) was used to estimate the relative dielectric constant of the material as $\epsilon_r = n_r^2 = 3.44$ which corresponds to neglecting the change of that index due to the (weak) absorption in the infrared and microwave regions.

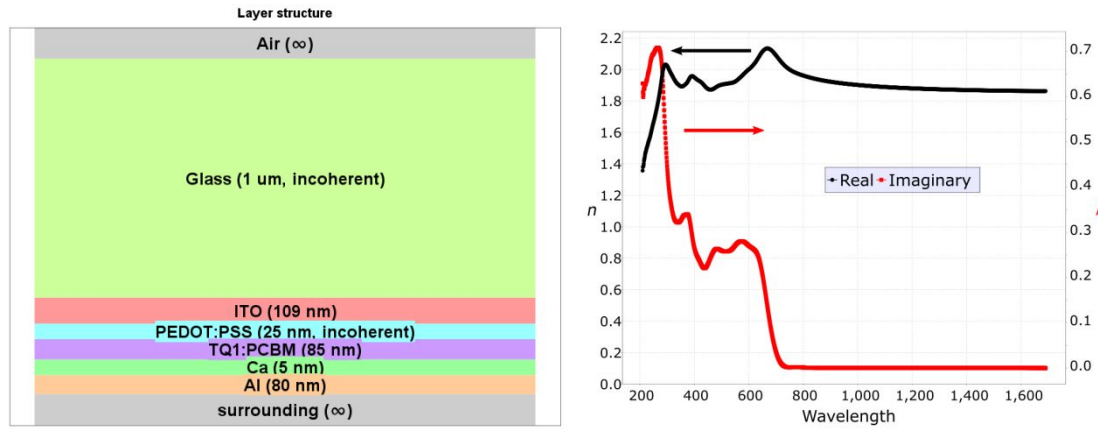


Figure S14. Optical simulation of the device. (a) Optical layers. (b) Refractive indexes used for the TQ1:PC₇₁BM layer.

S6.2. Energy levels

The metal (resp. PEDOT:PSS)/Active layer interface are considered as building an ohmic contact resulting in the pinning of the Fermi levels to the LUMO of the active layer's electron acceptor (Ca) and HOMO of the active layer's electron donor (PEDOT:PSS). Those energy were thus given to the electrodes.

Moreover, charge generation in organic semiconductor's heterojunction involves some energy losses which are still too improperly understood to be implemented in the model, such as the CT-state energy. As a result, those losses have to be accounted for by empirically lowering the $\text{HOMO}_{\text{Donor}}\text{-LUMO}_{\text{Acceptor}}$ gap given to the model until matching the experimental V_{OC} . We chose to do that by adjusting the value of the $\text{HOMO}_{\text{Donor}}$ (and the pinned Fermi level of PEDOT:PSS). Interestingly, the same effect can be obtained by adjusting the effective density of state of the active layer. Practically, it appears that – in the range of occupation fraction of the bands relevant to photovoltaic applications – increasing the effective density of states by one order of magnitude is fully equivalent to increasing bandgap the $\text{HOMO}_{\text{Donor}}$ by a number around 110 meV. See Figure S15 as an example of it.

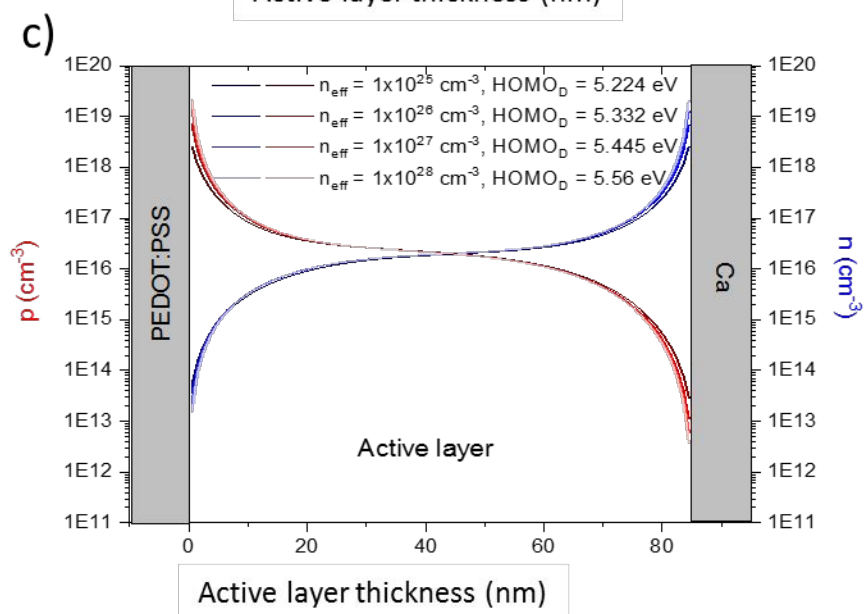
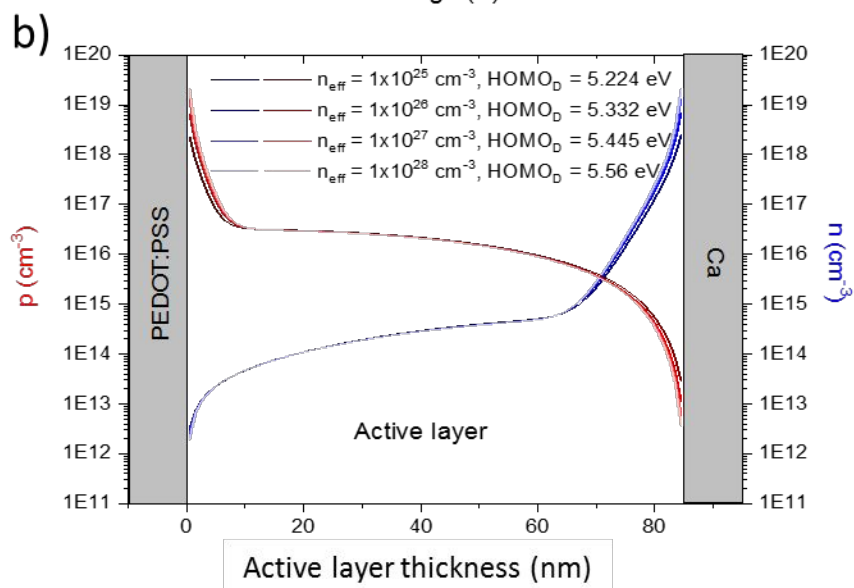
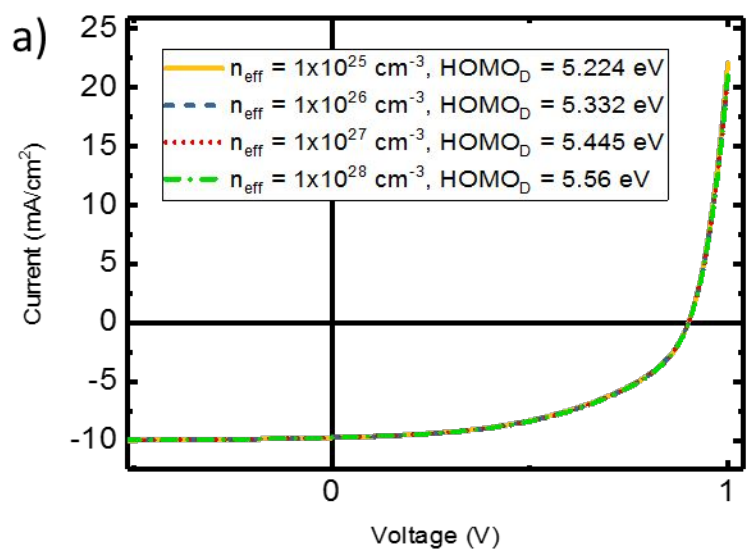


Figure S15. V_{OC} can be adjusted either by adjusting the HOMO level or the effective charge density. (a) Simulated JV response-, **(b)** densities of charges through the active layer at short circuit - , **(c)** densities of charges through the active layer at open circuit - of the solar cell presented in Figure S14, for different sets of effective densities of states and $HOMO_{Donor}$ levels. Other parameters are common to all cases: $LUMO_A = 4$ eV; generation efficiency = 0.823; $\mu_e = 1 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{ s}^{-1}$, $\mu_h = 1 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{ s}^{-1}$ (these mobility values are taken from reference⁹) and the reduction to Langevin recombination $\zeta = k_{2,TDCF} / k_{Langevin} = 4.33 \times 10^{-2}$.

Concerning the chosen effective densities of states, keep in mind as examples that the density of thiophene rings in perfect P3HT crystal would be in the order of $4 \times 10^{27} \text{ m}^{-3}$ (inter-monomer distances 3.85 Å, π -stacking distance 3.83 Å and distance along the alkyl side chain 16.8 Å,¹⁰ and neglecting the tilting of the unit cell) while if you consider the conjugation length (or a long D/A molecule) as one of your reference lengths and less ordered systems you would end up in densities in the order 10^{25} m^{-3} .

A consequence is that it is also possible to reproduce the experimental V_{OC} while using the experimental $HOMO_D$ level of 5.7 eV obtained for TQ1.¹¹ But this would correspond to an unrealistic effective states density of around $1 \times 10^{29} \text{ m}^{-3}$. More reasonably, an effective states density around $1 \times 10^{26} \text{ m}^{-3}$ would correspond to a CT-related energy loss in the range of 370 meV (difference between the experimental HOMO of TQ1 and the value we have to input to the model to reproduce V_{OC}). Either way, it must be stressed that in our modelization, V_{OC} is artificially adjusted, and that only the photocurrent generation and extraction should be discussed to validate the input parameters.

S6.3. Estimation of $k_{2,TA}$

The charge extraction is governed by field-independent and density-independent mobilities ($\mu_{h,SCLC} = 1 \times 10^{-5} \text{ cm}^2 \text{s}^{-1} \text{V}^{-1}$ and $\mu_{e,SCLC} = 1 \times 10^{-3} \text{ cm}^2 \text{s}^{-1} \text{V}^{-1}$)⁹ and the internal electric field, and competes with Langevin recombination ($R_{Langevin} = k_{Langevin} np = ((\mu_e + \mu_h) / (q \epsilon_0 \epsilon_r)) np$), attenuated by

an empirical reduction factor derived from $k_{2,TA}$ or $k_{2,TDCF}$ (see Table 1). The relative dielectric constant of the active layer was also estimated by ellipsometry.

There is an inter-dependence between the steady state charge density and the n -dependent recombination prefactor $k_{2,TA} = \gamma n^{\lambda-1}$. As a result $k_{2,TA} (n = n_{oc})$ was determined iteratively:

- 1) A first estimate of n_{oc} was obtained using the Setfos simulation with a recombination coefficient given by $k_{2,TDCF}$.
- 2) $k_{2,TA} (n = n_{oc})$ was calculated.
- 3) The simulation was ran again with the updated recombination coefficient.
- 4) The new value of n_{oc} was taken from the simulation and the new $k_{2,TA} (n = n_{oc})$ computed and the situation ran again.

This processed was followed until converging to a self-consistent system where the value of n_{oc} obtained from the simulation is the same as used to calculated $k_{2,TA} (n = n_{oc})$. The same *modus operandi* was used to calculated $k_{2,TA} (n = n_{sc})$. Note that HOMO_{Donor} had to be readjusted at each iteration to keep the V_{OC} at its experimental value of 0.9 V. Note also that for the estimation of n from setfos simulation we used the average of $\sqrt{np}$ across the active layer thickness. As can be seen in Figure S15b and S15c, while n and p are largely varying through the active layer thickness, their product is more stable and is the quantity relevant for calculating the non-geminate recombination rate.

Table S2: Successive iteration of setfos to determine the self-consistent couple ($k_{2,SC}$, n_{SC}). The HOMO level of the active layer is updated at every iteration to match the experimental V_{OC} of 0.9 V. $\langle \sqrt{np} \rangle_{d,SC}$ is the charge density averaged through the device thickness d under short circuit condition (see figure S16b for the first iteration). Convergence is reached after 2 iterations.

Iteration	$k_{2,initial}$ [cm ³ .s ⁻¹]	$\zeta_{initial} =$ $k_{2,initial}/k_{Langevin}$	$HOMO_D^{(b)}$	$<\sqrt{np}>_{d,SC}$ [cm ⁻³]	New $k_{2,SC}$ [cm ³ .s ⁻¹]	New ζ
(0)	2.32×10 ⁻¹¹ (a)	4.33×10 ⁻²	5.332 eV	3.02 ×10 ¹⁵	3.97 ×10 ⁻¹⁴	7.48 ×10 ⁻⁵
(1)	3.97×10 ⁻¹¹	7.48×10 ⁻²	5.253 eV	4.94 ×10 ¹⁵	7.14 ×10 ⁻¹⁴	1.35 ×10 ⁻⁴
(2)	7.14×10⁻¹⁴	1.35×10⁻⁴	5.256 eV	4.95 ×10 ¹⁵	7.16 ×10⁻¹⁴	1.35 ×10⁻⁴

(a) First estimate of the recombination coefficient extracted from the TDCF fit (Figure S12 b). (b) HOMO adjusted to have V_{OC} matching the experimental value, considering an effective charge density of 10²⁶ m⁻³ (see Figure S15)

Table S3: Successive iteration of setfos to determine the self-consistent couple ($k_{2,OC}$, n_{OC}). The initial recombination coefficient is extracted from the TDCF fit (Figure S14 b). The HOMO level of the active layer is updated at every iteration to match the experimental V_{OC} of 0.9 V. $<\sqrt{np}>_{d,OC}$ is the charge density averaged through the device thickness d under open circuit condition (see figure S16c for the first iteration). Convergence is a priori reached after a bit more than 8 iterations (a guess was used to speed up the last iteration).

Iteration	$k_{2,initial}$ [cm ³ .s ⁻¹]	$\zeta_{initial} =$ $k_{2,initial}/k_{Langevin}$	$HOMO_D^{(b)}$	$<\sqrt{np}>_{d,OC}$ [cm ⁻³]	New $k_{2,OC}$ [cm ³ .s ⁻¹]	New ζ
(0)	2.32×10 ⁻¹¹ (a)	4.33×10 ⁻²	5.332 eV	1.75 ×10 ¹⁶	3.26 ×10 ⁻¹³	6.14 ×10 ⁻⁴
(1)	3.26 ×10 ⁻¹³	6.14 ×10 ⁻⁴	5.266 eV	1.14 ×10 ¹⁷	3.08 ×10 ⁻¹²	5.8 ×10 ⁻³
(2)	3.08 ×10 ⁻¹²	5.8 ×10 ⁻³	5.293 eV	4.5 ×10 ¹⁶	1.01 ×10 ⁻¹²	1.9 ×10 ⁻³
(3)	1.01 ×10 ⁻¹²	1.9 ×10 ⁻³	5.278 eV	7.31 ×10 ¹⁶	1.8 ×10 ⁻¹²	3.4 ×10 ⁻³
(4)	1.8 ×10 ⁻¹²	3.4 ×10 ⁻³	5.285 eV	5.73 ×10 ¹⁶	1.35 ×10 ⁻¹²	2.54 ×10 ⁻³
(5)	1.35 ×10 ⁻¹²	2.54 ×10 ⁻³	5.281 eV	6.5 ×10 ¹⁶	1.57 ×10 ⁻¹²	2.95 ×10 ⁻³
(6)	1.57 ×10 ⁻¹²	2.95 ×10 ⁻³	5.283 eV	6.09 ×10 ¹⁶	1.45 ×10 ⁻¹²	2.73×10 ⁻³
(7)	1.45 ×10 ⁻¹²	2.73×10 ⁻³	5.282 eV	6.3 ×10 ¹⁶	1.51 ×10 ⁻¹²	2.84 ×10 ⁻³
(8)	1.48 ×10⁻¹²	2.8 ×10⁻³	5.282eV	6.24 ×10 ¹⁶	1.49 ×10⁻¹²	2.81 ×10⁻³

(a) First estimate of the recombination coefficient extracted from the TDCF fit (Figure S12b). (b) HOMO adjusted to have V_{OC} matching the experimental value, considering an effective charge density of 10²⁶ m⁻³ (see Figure S15)

S7. Simulation of steady-state triplet density

As written in the main, the text, the steady state triplet density was calculated by solving the triplets rate equation: $dT/dt = \alpha R - k_{TT}T^2 = 0$ for static conditions.

The charge recombination is decomposed between the recombination of bound pairs R_{CT} and that of separated charges R_{SC} . $R = R_{CT} + R_{SC}$

In the frame of the 2-pool model, R_{CT} and R_{SC} are independent. The fact that separated charges do not recombine through CT states is seen for example in the fact that for high fluences, the overall charge density starts to decrease before CT recombination sets in (see Figure 3d) if separated charges were recombining into CT states, the overall charge density would not change, similarly, we see triplet formation before the end of the CT lifetime (3 ns), for those fluences (Figure 3e).

R_{CT} , under steady state condition is thus calculated directly from their generation: $R_{CT} = G_{CT} = (1-f)G$ in our system with G the rate of photon absorption as calculated by optical simulation. See Figure S16. On the other hand, we have the empirical separated charges recombination rate: $R_{SC} = k_{\lambda}n^{\lambda+1}$. Due to the very asymmetric charge densities across the device (see Figure 4) we used for the charge density in that calculation the local geometric average of electron and hole densities $\sqrt{np}$ (for each depth within the active layer). Note that triplet diffusion was neglected for calculating the local triplets density. As shown by the obtained profile, and in contrast to those of charges, triplet densities are found to be pretty uniform across the device thickness (Figure 4), thus validating the neglect of diffusion.

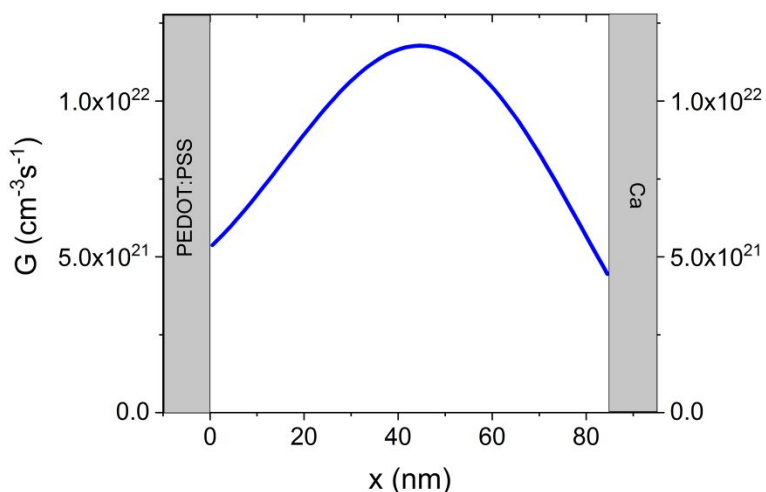


Figure S16: Simulated profile of the exciton generation rate across the active layer thickness. Of these excitons, a fraction f is converted into free charges and a fraction $(1-f)$ remains as coulombically at the heterojunction's interface. No excitation loss prior to charge transfer was found in this material system.

S8. References

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