Supporting information

ULTRAFAST TRANSIENT OPTICAL STUDIES OF CHARGE PAIR GENERATION AND RECOMBINATION IN POLY-3-HEXYLTHIOPHENE(P3HT):[6,6]PHENYL C61 BUTYRIC METHYL ACID ESTER (PCBM) BLEND FILMS

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Haque (2), Arkady Yarstev (3), Villy Sundstrom (3) and Jenny Nelson(*,1)

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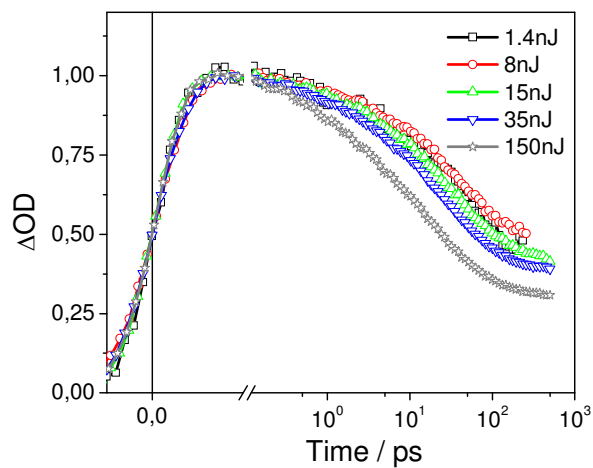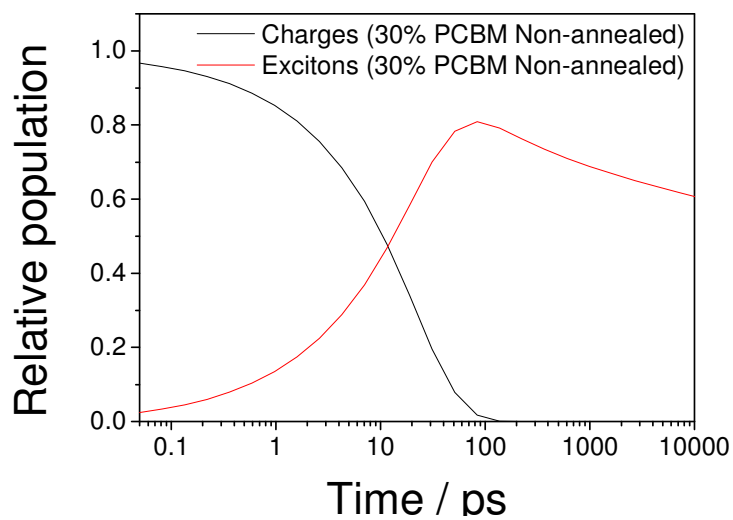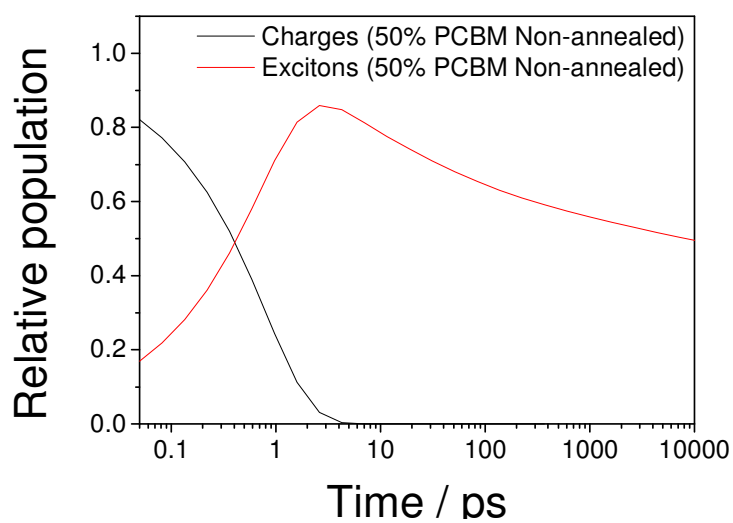1. Intensity dependence of the transient absorption kinetics.

Figure S.I. 1: Excitation power dependence of TA kinetic traces from annealed 50 wt.% PCBM blend film, for excitation and probe wavelengths of 550 nm and 1000 nm, respectively. The traces are normalized as explained in the text. The data show that the kinetics are insensitive to excitation intensity below about 20 nJ/pulse.
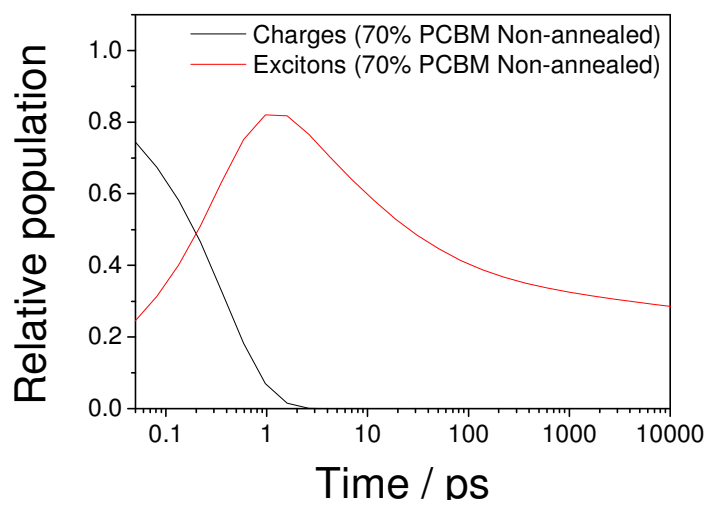
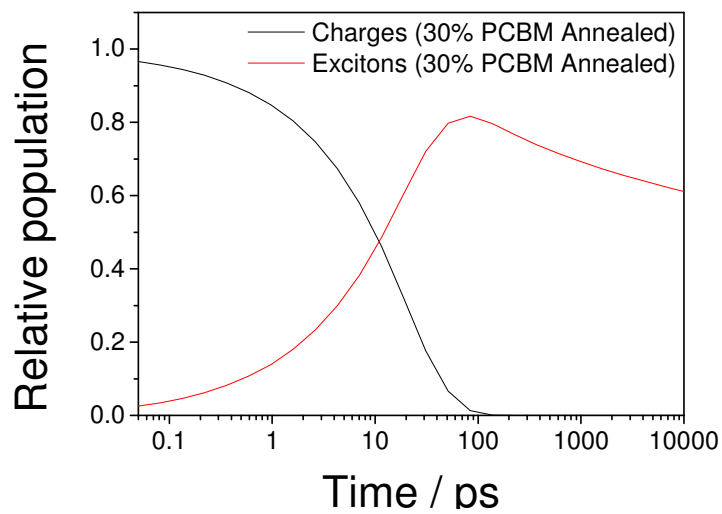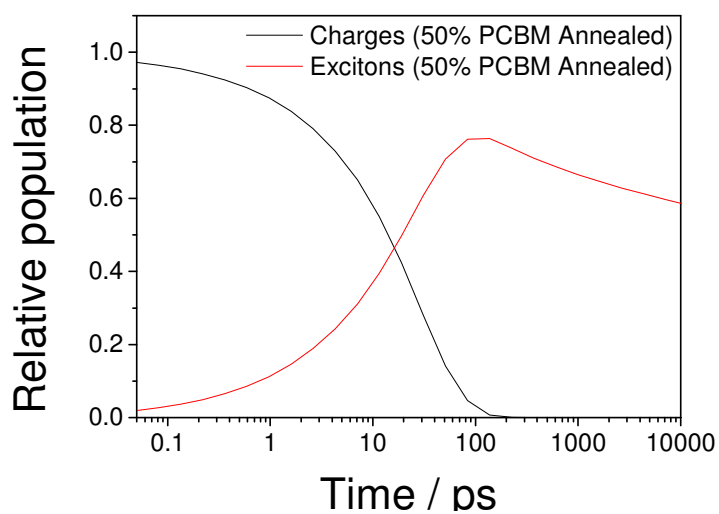2. Fitted exciton and polaron evolution for all blend films.

(a)

(b)

(c)

(d)

(e)

(f)

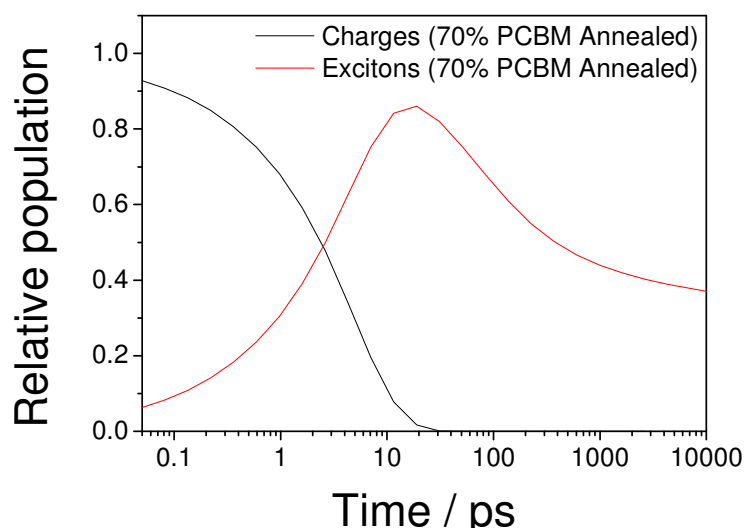**Figure S.I. 2:**. Fitted evolution of exciton (black) and polaron (red) populations as a function of time (in ps) after excitation, for all six blend films studied. ((a), (b), (c): non annealed films; (d), (e), (f):) In all cases a qualitatively similar behaviour is seen, where exciton decay coincides with a growth in charge population, and is followed by decay of charges. The rate of exciton decay

and polaron appearance is fastest for those cases where the fitted value of L is short. Although the 50 and 70 wt.% non-annealed cases were fit with eq (3) rather than eq. (2) in the main text to allow for the non exponential exciton decay, the qualitative trend with L reducing as PCBM content increases is the same as for the cases fit with eq.(2).

3. Solution of the diffusion equation

Equation (1) is the diffusion equation with a sink term. This equation can be solved using Fourier series. Together with the initial condition that $X(0, x) = 1/L$ for $0 < x < L$, the solution is:

$$X(t,x) = \sum_{nodd} \frac{4}{\pi n L} \exp\left[-\left(\frac{\pi^2 n^2 L_{ex}^2}{L^2}+1\right)\frac{t}{\tau_r}\right]\sin\left(\frac{n\pi x}{L}\right) \tag{1.1}$$

where the sum is taken over odd values of n and we have used the definition of the exciton diffusion length $L_{ex} = \sqrt{D\tau_r}$.

This expression for $X(t,x)$ can be used to obtain both the total number of excitons at time t per absorbed photon, $\xi(t)$, and the instantaneous charge pair generation rate $\gamma(t)$ by integrating the appropriate terms over space:

$$\xi(t) = \int_0^L X(t,x)dx = \sum_{nodd} \frac{8}{\pi^2 n^2} \exp\left[-\left(\frac{\pi^2 n^2 L_{ex}^2}{L^2}+1\right)\frac{t}{\tau_r}\right] \tag{1.2}$$

$$\gamma(t) = \int_0^L D\frac{d^2 X}{dx^2}dx = \sum_{nodd} \frac{8L_{ex}^2}{L^2\tau_r} \exp\left[-\left(\frac{\pi^2 n^2 L_{ex}^2}{L^2}+1\right)\frac{t}{\tau_r}\right] \tag{1.3}$$

4. Functional form for the time evolution of charges.

Equation (2) in the main text of the paper is used to describe the time evolution of charges. It reads:

$$p(t) = \exp\left(\frac{-\tau_b}{\tau_g}\right)\exp\left(\frac{\tau_b^2}{t\tau_g + \tau_b\tau_g}\right)\left(1 + \frac{t}{\tau_b}\right)^{-\alpha}$$

(2.1)

where τ_b is the timescale for bimolecular recombination and τ_g the natural time for exponential decay. The aim if this expression is to behave as an exponential for times shorter than τ_b and as power law for times longer than τ_b. The reasoning for wanting this behaviour is explained in the main text, briefly we desire the recombination of charge to behave geminately (i.e. as an exponential) at brief times and non-geminately (i.e. as a power law) for longer times. In this section we show that equation (2) does indeed behave thus.

First, rescale all times by τ_b so that $t = \hat{t}\tau_b$ and $\hat{\tau}_g\tau_b = \tau_g$ and rearrange equation 1 to obtain:

$$p(\hat{t}) = \exp\left(\frac{1}{\hat{\tau}_g}\left(\frac{1}{1+\hat{t}} - 1\right)\right)(1 + \hat{t})^{-\alpha}$$

(2.2)

If $\hat{t}$ is much smaller than 1, we can use a Taylor series to write:

$$\frac{1}{1+\hat{t}} - 1 \approx -\hat{t}$$
$$(1 + \hat{t})^{-\alpha} \approx 1$$

(2.3)

Hence:

$$p(\hat{t}) = \exp\left(-\frac{\hat{t}}{\hat{\tau}_g}\right)$$

(2.4)

If, conversely, $\hat{t}$ is much larger than 1, we can write:

$$\frac{1}{1+\hat{t}} - 1 \approx -1$$

(2.5)

and hence:

$$p(\hat{t}) = \exp\left(-\frac{\hat{t}}{\hat{\tau}_g}\right)(1+t)^{-\alpha} \qquad\qquad (2.6)$$

where the exponential prefactor describes the percentage of charges that recombine geminately.