

## Temperature Dependence of Exciton Diffusion in Conjugated Polymers

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### SOLUTION OF THE DIFFUSION EQUATION

Here we present the derivation of the exciton density  $n$  in the polymer film spin-coated on top of the cross-linked fullerene network from the diffusion equation (1):

$$\frac{\partial n(x, t)}{\partial t} = -\frac{n(x, t)}{\tau} + D \frac{\partial^2 n(x, t)}{\partial x^2} + G(x, t) - S(x)n(x, t). \quad (\text{S.1})$$

Here  $x$  is the spatial coordinate,  $t$  denotes the time,  $\tau$  represents the exciton lifetime in a quencher free reference sample,  $D$  is the diffusion coefficient,  $G(x, t)$  is the exciton generation term and finally  $S(x)$  represents the exciton quenching. Due to the fast and uniform excitation the generation term  $G(x, t)$  can be replaced by the following initial condition:

$$n(x, 0) = N_0. \quad (\text{S.2})$$

The exciton quenching term  $S(x)$  corresponds to the interface quenching and can be replaced by boundary conditions. The quenching efficiency of the polymer-fullerene interface can be safely assumed to be 100%:

$$n(L, t) = 0, \quad (\text{S.3})$$

where  $L$  is the polymer thickness (Figure S1).

We found experimentally that the free interface of a spin-coated MDMO-PPV film quenches excitons with efficiency compared to that of the polymer-fullerene interface. The pristine films spin-coated on quartz substrate exhibit shorter decay times as the polymer thickness is decreased. The most pronounced thickness dependence appears in the range of 5 – 50 nm, while more than 200 nm thick samples do not show variations in PL decay times. Such a thickness dependence is similar to that of polymer-fullerene heterostructures (see Figure 1) and is the signature of the diffusion limited interface quenching.

To quantify the quenching efficiency at the free interface we extracted the exciton diffusion length from both types of samples: polymer-fullerene heterostructures and pristine films. For the heterostructures we solved Eq. (S.1) assuming that both interfaces are perfect quenchers, whereas for the pristine films we assumed that excitons

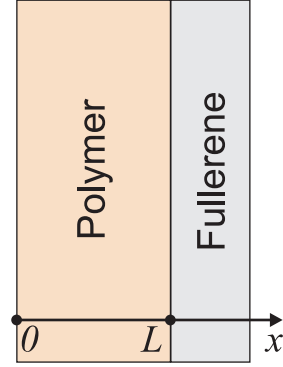


FIG. S1: Sketch of the two layers in a heterostructured sample. The choice of coordinates used in the diffusion equation (S.1) is shown.

are efficiently quenched only at the free interface. By applying these models to the experimental data we found the same values of the exciton diffusion length from both types of samples. This clarifies the choice of the boundary conditions and shows that the free interface indeed is efficient exciton quencher. In our following publication we will discuss the exciton quenching at the free interface in more detail and will relate it to the morphology of a spin-coated MDMO-PPV film.

Thus due to the efficient exciton quenching at the free interface the second boundary condition is:

$$n(0, t) = 0. \quad (\text{S.4})$$

In such a way Eq. (S.1) is simplified to the Cauchy problem:

$$\begin{cases} \frac{\partial n(x, t)}{\partial t} = -\frac{n(x, t)}{\tau} + D \frac{\partial^2 n(x, t)}{\partial x^2} \\ n(x, 0) = N_0 \\ n(0, t) = n(L, t) = 0 \end{cases} \quad (\text{S.5})$$

We seek the solution in the form:  $n(x, t) = T(t)X(x)$ , then the variables in Eq. (S.5) can be separated:

$$\frac{1}{T} \frac{\partial T}{\partial t} + \frac{1}{\tau} = D \frac{1}{X} \frac{\partial^2 X}{\partial x^2} = -\lambda^2, \quad (\text{S.6})$$

where  $\lambda$  is a constant. The obtained expression splits into two equations, which determine  $T(t)$  and  $X(x)$ :

$$\begin{aligned} T(t) &= e^{-t/\tau} e^{-\lambda^2 t}, \\ X(x) &= A \cos(\omega x) + B \sin(\omega x), \end{aligned} \quad (\text{S.7})$$

where  $A$  and  $B$  are constants, and  $\omega^2 = \lambda^2/D$ . By applying the boundary conditions we get:

$$\begin{aligned} A &= 0, \\ \omega_k &= \frac{\pi k}{L}, \quad k = 0, \pm 1, \pm 2, \dots \end{aligned} \quad (\text{S.8})$$

Then the exciton density is the linear combination of the partial solutions:

$$n(x, t) = e^{-t/\tau} \sum_{k=1}^{\infty} B_k e^{-D\omega_k^2 t} \sin \omega_k x. \quad (\text{S.9})$$

Constants  $B_k$  are determined using the initial condition (S.2):

$$B_k = \frac{2N_0}{L} \frac{1 - (-1)^k}{\omega_k}. \quad (\text{S.10})$$

Since  $B_k$  turns to zero for every even index  $k$ , we can simplify (S.10) by introducing the always odd index:

$$B_{2m-1} = \frac{4N_0}{L} \frac{1}{\omega_{2m-1}}, \quad m = 1, 2, 3, \dots \quad (\text{S.11})$$

In such a way we obtained the exciton density in a polymer film with both quenching interfaces:

$$n(x, t) = \frac{4N_0}{L} e^{-t/\tau} \sum_{m=1}^{\infty} \frac{e^{-D\omega_{2m-1}^2 t}}{\omega_{2m-1}} \sin \omega_{2m-1} x. \quad (\text{S.12})$$

Then the PL decay is proportional to the integral of the obtained expression over the sample thickness  $L$ :

$$PL(t) \propto n(t) = \frac{8N_0}{L} e^{-t/\tau} \sum_{n=1}^{\infty} \frac{e^{-D\omega_{2n-1}^2 t}}{\omega_{2n-1}^2}. \quad (\text{S.13})$$

We model the experimental PL decay that is normalized to unity at zero time  $PL(0) = 1$ . The normalization of (S.13) and expansion of  $\omega_{2n-1}$  lead to the expression (2) that we use for the modelling:

$$n_{\text{normalized}}(t) = \frac{8}{\pi^2} R(t) \sum_{n=1}^{\infty} \frac{e^{-Dt\pi^2(2n-1)^2/L^2}}{(2n-1)^2}, \quad (\text{S.14})$$

where  $R(t)$  is the normalized PL decay of a thick reference sample:

$$R(t) = \lim_{L \rightarrow \infty} n_{\text{normalized}}(t). \quad (\text{S.15})$$

It is important to note, that the exciton diffusion coefficient is the only fit parameter in (S.14).

To extract the exciton diffusion length we model the relative quenching efficiency  $Q(L)$ :

$$Q(L) = 1 - \frac{\int_0^L dx \int_0^\infty dt n_{\text{two quenching int.}}(x, t)}{\int_0^L dx \int_0^\infty dt n_{\text{not quenching int.}}(x, t)}. \quad (\text{S.16})$$

It is easy to show that the integral over the time and thickness of the exciton density in the sample that does not contain quenching interfaces is simply  $N_0 L \tau$ . Then by integrating (S.13) and by setting  $L_D = \sqrt{D\tau}$  we get the final expression for the relative quenching efficiency:

$$Q(L) = \frac{2L_D}{L} \tanh \frac{L}{2L_D}. \quad (\text{S.17})$$

The resulting equation is labeled as (4) in the article and used to extract the exciton diffusion length  $L_D$ , which is the only fit parameter here.