Investigation of Exciton Diffusion and Charge Transfer Dynamics in Nano Phase-Separated P3HT:PCBM blend films by Utrafast Time Resolved Fluorescence

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Electronic Supplementary Information

Excitation density calculation:

The power of the excitation pulse of 625nm, at levels of 20, 15, 10, 5, 2.5 nJ/pulse, was adjusted by the neutral density filters and used to excite samples. The diameter of the excitation spot was measured by two ways, one was to place a photo sensitive paper at the sample position and the size of the exposed area under excitation pulse was measured with a microscope. The other way was the knife-edge measurement, by moving a sharp knife edge slowly going across the pulse at the sample position, and recording the transmitted power vs. the position of the knife edge to determine the profile of the spot. The results of the two measurements agree well, giving a spot diameter of 130 μm. For pristine P3HT film, the film thickness was measured to be about 200 nm by Stylus profiler (AMBIOS TECHNOLOGY INC XP-2), the excitation volume is calculated to be $2.65\times10^{-9}\,cm^3$. The incident photons/pulse is calculated by dividing the incident power/pulse by one photon energy of 625nm, which is $3.17\times10^{-17}\,J$. 20 nJ/pulse corresponds to an incident light intensity of 6.3×10^{10} photons/pulse. The absorbance of the file at 625nm is about 0.34, corresponding to a 54.3% absorption of the incident photons, resulting in a total absorption of 3.42×10^{10} photons. The total number of the absorbed photons divide by the excitation volume results in the final excitation density: $1.29\times10^{19}\,/\,cm^3$. The blend film excitations are calculated the same way.

Solution of the rate equation:

The rate equation can be given as:

$$\frac{dN(t)}{dt}=-\frac{N(t)}{\tau_0}-4\pi R_a D\left(1+\frac{R_a}{\sqrt{2\pi Dt}}\right)N^2-4\pi R_{CT}DN_{CT}\left(1+\frac{R_{CT}}{\sqrt{\pi Dt}}\right)N(t)$$

Let $M(t)=\frac{1}{N(t)}$, we have $\frac{dM(t)}{dt}=-\frac{1}{N^2}\frac{dN(t)}{dt}$, substituting it into the above equation, we get

$$\frac{dM(t)}{dt}=\left(\frac{1}{\tau_0}+4\pi R_{CT}DN_{CT}\left(1+\frac{R_{CT}}{\sqrt{\pi Dt}}\right)\right)M(t)+4\pi R_a D\left(1+\frac{R_a}{\sqrt{2\pi Dt}}\right)$$

We can set $A=\frac{1}{\tau_0}+4\pi R_{CT}DN_{CT}$, $B=4\sqrt{\pi D}R_{CT}^2N_{CT}$, $C=4\pi R_a D$, $D^{'}=4\sqrt{\frac{\pi D}{2}}R_a^2$,

$\frac{dM}{dt}=\left(A+\frac{B}{\sqrt{t}}\right)M+\left(C+\frac{D}{\sqrt{t}}\right)$, let D$^{'}$ as D, and $P(t)=\left(A+\frac{B}{\sqrt{t}}\right)$, $Q(t)=\left(C+\frac{D}{\sqrt{t}}\right)$, we have

$$\frac{dM}{dt}=P(t)M+Q(t)$$

Let $M(t)=N^{'}(t)exp\left(\int P(t)dt\right)$, substituting it into, we get

$$exp\left(\int P(t)dt\right)\frac{d}{dt}N'(t) = Q(t)$$

So, $\frac{d}{dt}N'(t) = Q(t)exp\left(-\int P(t)dt\right)$

$$N'(t) = \int Q(t)exp\left(-\int P(t)dt\right)dt$$

Set $x = \sqrt{t}$,

$$N'(t) = \int\left(C+\frac{D}{\sqrt{t}}\right)exp\left(-\int\left(A+\frac{B}{\sqrt{t}}\right)dt\right)dt$$

$$= \int\left(C+\frac{D}{\sqrt{t}}\right)exp\left(-At-2B\sqrt{t}\right)dt$$

$$= \int\left(C+\frac{D}{x}\right)exp\left(-Ax^2-2Bx\right)2xdx$$

$$= 2\int(Cx+D)exp\left(-Ax^2-2Bx\right)dx$$

$$= \int\left[\frac{C}{A}(2Ax+2B)+2D-\frac{2BC}{A}\right]exp\left(-Ax^2-2Bx\right)dx$$

$$= \int\left\{\left[\frac{C}{A}(2Ax+2B)\right]exp\left(-Ax^2-2Bx\right)+\left[2D-\frac{2BC}{A}\right]exp\left(-Ax^2-2Bx\right)\right\}dx$$

$$= -\frac{C}{A}\int exp\left(-Ax^2-2Bx\right)d\left(-Ax^2-2Bx\right)+\left[2D-\frac{2BC}{A}\right]\int exp\left(-Ax^2-2Bx\right)dx$$

$$= -\frac{C}{A}exp\left(-Ax^2-2Bx\right)+\left[2D-\frac{2BC}{A}\right]\int exp\left[-A\left(x+\frac{B}{A}\right)^2+\frac{B^2}{A}\right]dx$$

Set $u = x+\frac{B}{A}$, we get

$$N'(t) = -\frac{C}{A}exp\left(-Ax^2-2Bx\right)+\left(2D-\frac{2BC}{A}\right)exp\left(\frac{B^2}{A}\right)\int exp\left[-Au^2\right]du$$

$$\int exp\left(-cx^2\right)dx = \sqrt{\frac{\pi}{4c}}erf\left(\sqrt{c}x\right)$$

$$N'(t) = -\frac{C}{A}exp\left(-Ax^2-2Bx\right)+\left(2D-\frac{2BC}{A}\right)exp\left(\frac{B^2}{A}\right)\sqrt{\frac{\pi}{4A}}erf\left[\sqrt{A}\left(x+\frac{B}{A}\right)\right]+E_{const}$$,

$$M(t)=\left\{-\frac{C}{A}exp\left(-Ax^2-2Bx\right)+\left(2D-\frac{2BC}{A}\right)exp\left(\frac{B^2}{A}\right)\sqrt{\frac{\pi}{4A}}erf\left[\sqrt{A}\left(x+\frac{B}{A}\right)\right]+E_{const}\right\}exp\left(\int\left(A+\frac{B}{\sqrt{t}}\right)dt\right)$$

$$=\left\{-\frac{C}{A}exp\left(-Ax^2-2Bx\right)+\left(2D-\frac{2BC}{A}\right)exp\left(\frac{B^2}{A}\right)\sqrt{\frac{\pi}{4A}}erf\left[\sqrt{A}\left(x+\frac{B}{A}\right)\right]+E_{const}\right\}exp\left(2\int\left(Ax+B\right)dx\right)$$

$$=\left\{-\frac{C}{A}exp\left(-Ax^2-2Bx\right)+\left(2D-\frac{2BC}{A}\right)exp\left(\frac{B^2}{A}\right)\sqrt{\frac{\pi}{4A}}erf\left[\sqrt{A}\left(x+\frac{B}{A}\right)\right]+E_{const}\right\}exp\left(Ax^2+2Bx\right)$$

$$=\left\{-\frac{C}{A}+\left(2D-\frac{2BC}{A}\right)exp\left(\frac{B^2}{A}\right)exp\left(Ax^2+2Bx\right)\sqrt{\frac{\pi}{4A}}erf\left[\sqrt{A}\left(x+\frac{B}{A}\right)\right]+E_{const}\,exp\left(Ax^2+2Bx\right)\right\}$$

$$=-\frac{C}{A}+\left(2D-\frac{2BC}{A}\right)exp\left(\frac{B^2}{A}\right)exp\left(At+2B\sqrt{t}\right)\sqrt{\frac{\pi}{4A}}erf\left[\sqrt{A}\left(\sqrt{t}+\frac{B}{A}\right)\right]+E_{const}\,exp\left(At+2B\sqrt{t}\right)$$

So we can give

$$N(t)=\frac{1}{-\frac{C}{A}+\left(2D-\frac{2BC}{A}\right)exp\left(\frac{B^2}{A}\right)exp\left(At+2B\sqrt{t}\right)\sqrt{\frac{\pi}{4A}}erf\left[\sqrt{A}\left(\sqrt{t}+\frac{B}{A}\right)\right]+E_{const}\,exp\left(At+2B\sqrt{t}\right)}$$

According to initial condition，N(0)=N_0 when t=0，so,

$$E_{const}=\frac{1}{N_0}+\frac{C}{A}-\left(2D-\frac{2BC}{A}\right)exp\left(\frac{B^2}{A}\right)\sqrt{\frac{\pi}{4A}}erf\left(\frac{B}{\sqrt{A}}\right)$$

and

$$N(t)=\frac{1}{-\frac{C}{A}+\left(2D-\frac{2BC}{A}\right)exp\left(\frac{B^2}{A}\right)exp\left(At+2B\sqrt{t}\right)\sqrt{\frac{\pi}{4A}}erf\left[\sqrt{A}\left(\sqrt{t}+\frac{B}{A}\right)\right]+\left[\frac{1}{N_0}+\frac{C}{A}-\left(2D-\frac{2BC}{A}\right)exp\left(\frac{B^2}{A}\right)\sqrt{\frac{\pi}{4A}}erf\left(\frac{B}{\sqrt{A}}\right)\right]exp\left(At+2B\sqrt{t}\right)}$$

Finally, it can be simplified as following form:

$$N(t)=\frac{N_0\,exp\left(-\frac{t}{\tau_0}-\gamma_1 t-2\beta_1\sqrt{t}\right)}{1+\frac{\gamma_2}{\frac{1}{\tau_0}+\gamma_1}\left[1-exp\left(-\frac{t}{\tau_0}-\gamma_1 t-2\beta_1\sqrt{t}\right)\right]+\sqrt{\frac{\pi}{\frac{1}{\tau_0}+\gamma_1}}\left(\beta_2-\frac{\beta_1\gamma_2}{\frac{1}{\tau_0}+\gamma_1}\right)exp\left(\frac{\beta_1^2}{\frac{1}{\tau_0}+\gamma_1}\right)\left[erf\left(\sqrt{\frac{t}{\tau_0}+\gamma_1 t}+\frac{\beta_1}{\sqrt{\frac{1}{\tau_0}+\gamma_1}}\right)-erf\left(\frac{\beta_1}{\sqrt{\frac{1}{\tau_0}+\gamma_1}}\right)\right]}$$

Where $\gamma_1=4\pi R_{CT}DN_{CT}$, $\gamma_2=4\pi R_a DN_0$, $\beta_1=4\sqrt{\pi D}R_{CT}^2N_{CT}$, $\beta_2=4\sqrt{\frac{\pi D}{2}}R_a^2N_0$.

For the pristine P3HT film, N_{CT}=0, so the solution for exciton-exciton annihilate only can be expressed as:

$$N(t)=\frac{N_0\,exp\left(-t/\tau_0\right)}{1+4\pi R_a DN_0\tau_0\left[1-exp\left(-t/\tau_0\right)\right]+4\pi\sqrt{\frac{D\tau_0}{2}}R_a^2N_0\,erf\left(\sqrt{t/\tau_0}\right)}$$

For the blend film, if the excitation power is low enough, the exciton-exciton annihilate is absent, so for the charge transfer only we have

$$N(t) = N_0 \exp\left[-(\frac{1}{\tau_0} + 4\pi R_{CT} D N_{CT})t - 8\sqrt{\pi D} R_{CT}^2 N_{CT} \sqrt{t} \right]$$