Supplementary information for Internal Structure-Mediated Ultrafast Energy Transfer in Self-Assembled Polymer-Blend Dots

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Three-dimensional (3D) diffusion model for intensity-dependent PL dynamics

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

To pure polymer nanoparticles, fitting intensity-dependent PL dynamics by 3D-diffusion model is simple, since $\beta_1 = 0$, $\gamma_1 = 0$ [1]. Only one problem is how to properly make an estimate of the effective exciton density N_e in the polymer nanoparticle solution.

Here, we estimate N_e according the following expression, $N_e = N_{abs} / V_{eff}$, where N_{abs} is the absorbed photon number of polymer nanoparticles, and V_{eff} is effective excitation volume. We use $V_{eff} = OD_{460} \times (\sigma_{460} \times N_A / 2303)^{-1} \times l^{-1} \times V_0 \times V_{particle}$, where OD_{460} is optical density of PFBT at 460 nm, $\sigma_{460} = 2.24 \times 10^{-12}$ cm^{-1} is the corresponding absorption cross section assuming $\sigma \propto r^3$ (r is the particle radius) [2], N_A is the Avogadro constant (thus $\sigma_{460} \times N_A / 2303$ is equal to molar extinction coefficient) [3], l is optical length, V_0 is the sample volume excited by pump light, which is equal to a cylinder with diameter of bottom area (~200 μm) and height l, $V_{particale}$ is the volume of single nanoparticle. According to these estimated exciton density, we could easily obtain the exciton-exciton annihilation radius R_a and isotropic diffusion constant D.

Modeling the PL quenching dynamics

Considering the Förster resonance energy transfer model, the quenching dynamics could be expressed as eqs 1 [4].

$$I(t) = I_0(t) \times \exp[-(t/\tau_{ET})^{\beta}],\ g(t) = \frac{I(t)}{I_0(t)} = \exp[-(t/\tau_{ET})^{\beta}] \qquad (1)$$

here, $I(t)$ is the normalized time-resolved fluorescence intensity in the blended particles, which is proportional to the exciton concentration at time t, $I_0(t)$ is the normalized time-resolved fluorescence intensity in PFBT nanoparticles, τ_{ET} is energy transfer time, $\beta = 0.5$ for Förster-type energy transfer, $g(t)$ is the PL intensity ratio of the time-resolved fluorescence intensity measured in the blended nanoparticles to the pure ones, which gives the true quenching kinetics by acceptor polymer molecules.

In the mean time, assuming that the dominant quenching mechanism is the energy transfer to acceptor units by dipole-dipole interaction (also Förster-type), and acceptor units are randomly distributed in the nanoparticles, the PL intensity ratio can be described as [5]

$$g(t) = \exp[-(\pi N_m^2 / N_0^2 \times t/\tau_1)^{1/2}] \qquad (2)$$

where $N_m = f \cdot \rho \cdot N_A / M$ is the concentration of acceptor polymer molecules, where f is the fraction of dopant polymer molecules in blended particles (by weight), $\rho = 1.0$ g cm^{-3} is polymer density [6], N_A is the Avogadro constant and M is the dopant polymer molecular mass [7]; N_0 is the 'critical concentration' defined as $N_0 = [(4/3)\pi R_0^3]^{-1}$, where R_0 is the Förster radius.

References

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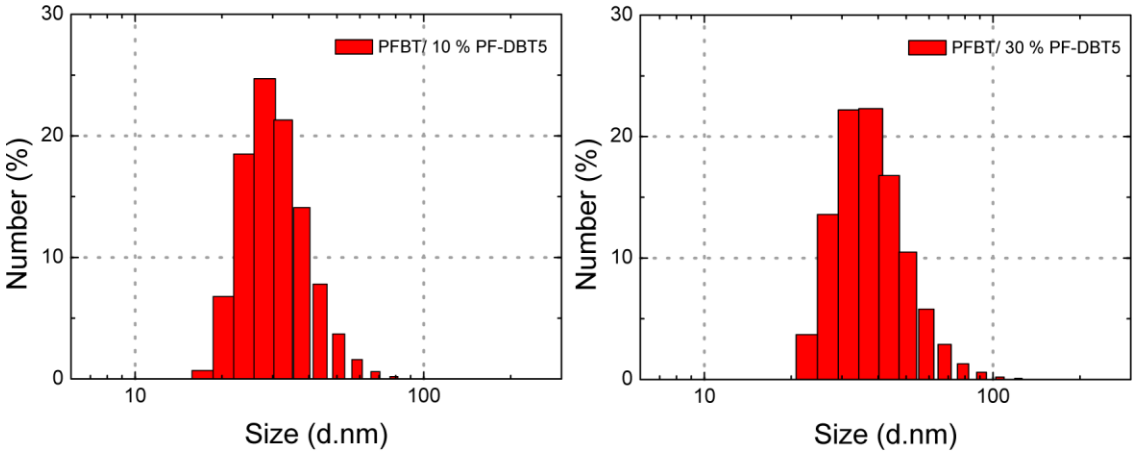

Figure S1. Dynamic light scattering measurements of blended nanoparticles with 10% and 30% dopant fraction, in which average diameter is in the range of 30-40 nm.

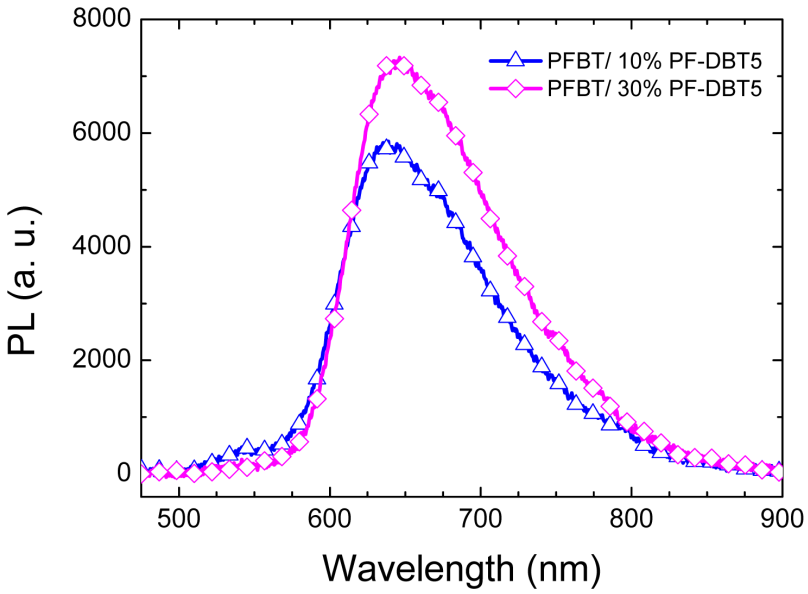

Figure S2. PL spectra for PFBT/10%PF-DBT5 and PFBT/30%PF-DBT5 nanoparticles under the same concentration and excitation condition (excited at 460 nm).

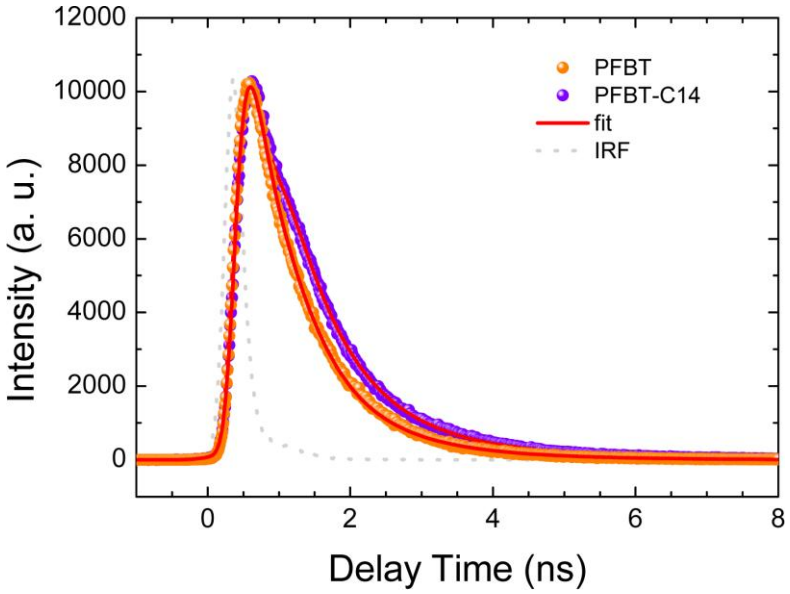

Figure S3. TCSPC data for PFBT and PFBT-C14 nanoparticles at 405 nm excitation.

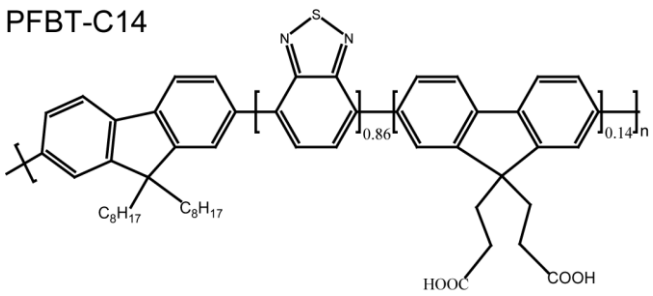

Figure S4. Molecular structure of functionalized polymer PFBT with side-chain carboxylic acid groups at molar fraction of 14%.

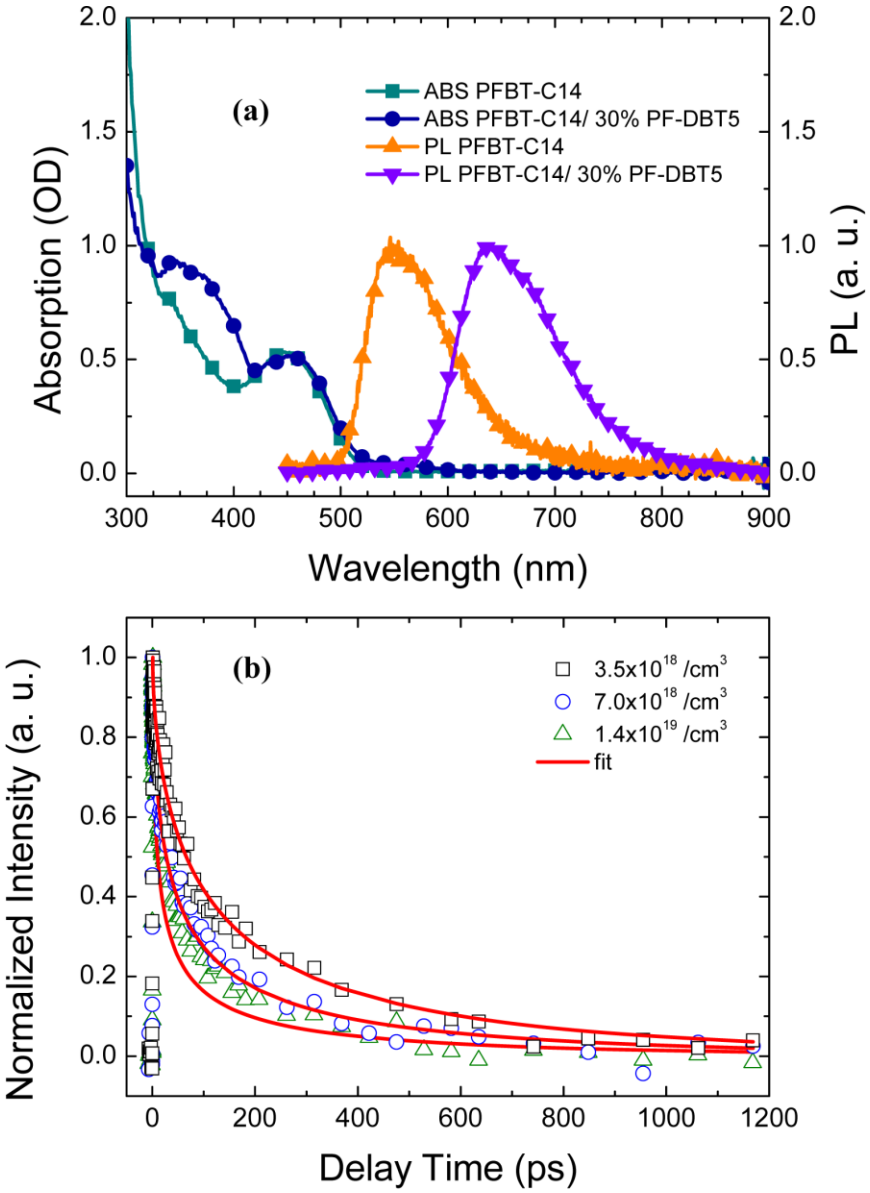

Figure S5. (a) Steady-state absorption and normalized PL spectra for pure PFBT-C14 nanoparticles and blended PFBT-C14/30%PF-DBT5 nanoparticles. (b) Intensity-dependent PL dynamics probed at 550 nm for PFBT-C14 nanoparticles at 460 nm excitation. Red solid lines represent the fitting results by 3D diffusion model.

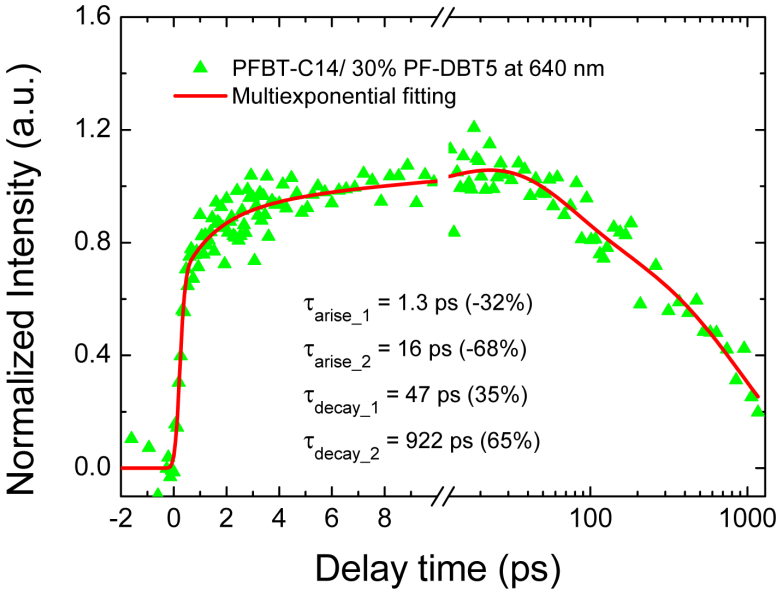

Figure S6. Multiexponential fitting for femtosecond time-resolved fluorescence dynamics of acceptor emission for PFBT-C14/ 30%PF-DBT5 nanoparticles.

Table S1. Multiple exponential analyses of TCSPC data for PFBT and PFBT-C14 nanoparticles. τ_1 was used for modeling R_0 and τ_{ET}.

	τ_1/ns	τ_2/ns	τ_{ave}/ns
PFBT	0.54 (0.81)	1.29 (0.19)	0.68
PFBT-C14	0.71 (0.84)	1.64 (0.16)	0.86