**Supporting Information**
for

# Multiple Energy Transfer Dynamics in Blended Conjugated Polymer Nanoparticles

*Xiaoli Wang*[†], *Louis C. Groff*[†], *and Jason D. McNeill**[†]

[†]Department of Chemistry, Clemson University, Clemson, SC, USA 29634

## 1. Calculation of fluorescence quantum yield

The fluorescent dye fluorescein in 0.01 M sodium hydroxide was used as standard to determine the fluorescence quantum yield of CPN sample. All the CPN samples and fluorescein standard solution were diluted to yield an absorbance of ~0.05 at excitation wavelength 473 nm. The calculation of sample quantum yield employed the following equation with the literature quantum yield value of 0.92 for fluorescein standard.[1,2]

$$\phi_f(x) = \frac{A_s F_x n_x^2}{A_x F_s n_s^2} \phi_f(s) \quad \text{(S1)}$$

Where $\phi_f$ is the fluorescence quantum yield, A is the absorbance at the excitation wavelength, F is the integrated area under the corrected fluorescence emission curve, and n is the solvent refractive index. Subscripts *s* and *x* represent standard and unknown sample, respectively. The results of the quantum yield measurements are given in Table 1 in the main text.

## 2. Förster radius calculation between donor and acceptor

The calculation of Förster radius ($R_0$) is using,

$$R_0^{\,6} = \frac{9000 \ln(10) \phi_D \kappa^2}{128 \pi^5 N_A n^4} \int_0^\infty f_D(\lambda)\, \varepsilon(\lambda) \lambda^4 d\lambda$$

Where $N_A$ is Avogadro's number; n is the refractive index of donor PFBT at peak emission wavelength (1.9);[3] $\kappa^2$, the orientation factor is assumed as 2/3;[4] $\phi_D$, $f_D(\lambda)$, $\varepsilon_A(\lambda)$ are the quantum yield of donor PFBT, normalized fluorescence spectra of donor, and extinction coefficient of acceptor MEH-PPV in THF solution, respectively. The calculation yields a 9.8 nm Förster radius between PFBT and MEH-PPV.

**3. Fluorescence lifetime fitting results**

The picosecond lifetime data were fitted by nonlinear least-squares minimization, using convolution of a trial decay function with the instrument response function. The trial functions employed were single exponential, bi-exponential, and the stretched exponential (Kohlrausch-Williams-Watts, KWW) function ($F(t) = Ae^{-(t/\tau)^{\beta}}$). The detailed fitting results are shown in Table S1 and Table S2.

**Table S1 PFBT lifetime fitting result**

| Sample | Single exponential | Bi-exponential | | | | | KWW | |
|---|---|---|---|---|---|---|---|---|
| | $\tau$ | $\tau_1$ | $n_1$ | $\tau_2$ | $n_2$ | $\tau_{avg}$ | $\tau$ | $\beta$ |
| 0% | 567 | 250 | 0.32 | 1016 | 0.68 | 770 | 317 | 0.64 |
| 0.5% | 344 | 155 | 0.34 | 619 | 0.66 | 458 | 184 | 0.63 |
| 1% | 331 | 180 | 0.42 | 694 | 0.58 | 473 | 166 | 0.61 |
| 2% | 318 | 133 | 0.33 | 584 | 0.67 | 431 | 153 | 0.60 |
| 4% | 277 | 136 | 0.40 | 578 | 0.60 | 397 | 117 | 0.57 |
| 6% | 262 | 137 | 0.43 | 576 | 0.57 | 384 | 114 | 0.58 |
| 10% | 245 | 128 | 0.44 | 554 | 0.56 | 364 | 89 | 0.54 |
| PFBT in THF | 3356 | 204 | 0.005 | 3398 | 0.995 | 3380 | 3288 | 0.97 |

**Table S2 MEH-PPV lifetime fitting result**

| Sample | Single exponential | Bi-exponential | | | | | KWW | |
|---|---|---|---|---|---|---|---|---|
| | $\tau$ | $\tau_1$ | $n_1$ | $\tau_2$ | $n_2$ | $\tau_{avg}$ | $\tau$ | $\beta$ |
| 4% | 759 | 522 | 0.54 | 1647 | 0.46 | 1031 | 609 | 0.79 |
| 6% | 744 | 423 | 0.41 | 1376 | 0.59 | 978 | 539 | 0.74 |
| 10% | 590 | 373 | 0.51 | 1406 | 0.49 | 868 | 396 | 0.71 |
| MEH-PPV NPs | 77 | 17 | 0.47 | 240 | 0.53 | 134 | 3 | 0.31 |
| MEH-PPV in THF | 295 | 226 | 0.70 | 1016 | 0.30 | 436 | 227 | 0.79 |

$\tau_{avg} = \tau_{1*} n_1 + \tau_{2*} n_2$

All lifetimes are in ps.

**4. Radiative ($k_r$) and non-radiative ($k_{nr}$) rates**

The radiative and non-radiative rates of PFBT in THF and unblended PFBT nanoparticles were determined through following steps. The quantum yield and lifetime of PFBT in THF were 0.66 and 3400 ps, while for PFBT nanoparticles, 0.13 and 770 ps

were obtained. From the quantum yield and lifetime expressions, $\phi = k_r/(k_r + k_{nr})$ and $\tau = 1/(k_r + k_{nr})$, radiative rates for PFBT polymer in THF and unblended PFBT nanoparticles were and $1.69\times10^8$ $s^{-1}$. The non-radiative rates were determined to be $1.0\times10^8$ $s^{-1}$ (polymer in THF) and $1.13\times10^9$ $s^{-1}$(unblended PFBT NPs).

The radiative and non-radiative rates of MEH-PPV in THF and pure MEH-PPV nanoparticles were also calculated. The quantum yield and lifetime of MEH-PPV in THF were 0.21 and 440 ps, while for MEH-PPV nanoparticles, 0.05 and 130 ps were obtained. The radiative rate and non-radiative rate for MEH-PPV in THF were calculated to be $4.77\times10^8$ $s^{-1}$ and $1.80\times10^9$ $s^{-1}$, while the results for MEH-PPV nanoparticles were obtained as $3.85\times10^8$ $s^{-1}$ and $7.31\times10^9$ $s^{-1}$.

**5. Simulation results without consideration of acceptor polydispersity**

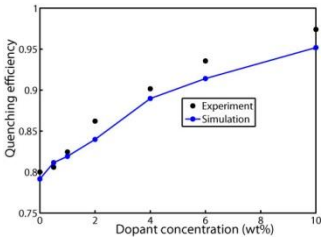


**Figure S1** Comparison of simulated quenching efficiency (blue dot with line) and experimental (black dot) data vs. dopant concentration (wt%).

If we assume the acceptor has PDI = 1, the simulated quenching efficiency is shown in Figure S1. Since the low molecular weight chains are ignored in the simulation, the average polymer chain numbers per particle are very low. For example, the calculated average chain number per particle for 6% blending sample is ~1 polymer chain per particle. In this case, some of the particles do not have acceptor based on Poisson statistics. This assumption leads to a lower quenching efficiency compared to the experimental data as shown in Figure S1.

**Reference**

1. Weber, G.; Teale, F. W. J. Determination of the Absolute Quantum Yield of Fluorescent Solutions. *Trans. Faraday Soc.* **1957,** 53, 646-655.

2. Fery-Forgues, S.; Lavabre, D. Are Fluorescence Quantum Yields So Tricky to Measure? A Demonstration using Familiar Stationery Products. *J. Chem. Educ.* **1999,** 76, 1260-1264.

3. Campoy-Quiles, M.; Heliotis, G.; Xia, R. D.; Ariu, M.; Pintani, M.; Etchegoin, P.; Bradley, D. D. C. Ellipsometric Characterization of the Optical Constants of Polyfluorene Gain Media. *Adv. Funct. Mater.* **2005,** 15, 925-933.
4. Lakowicz, J. R., *Principles of Fluorescence Spectroscopy*. Third Ed.; Springer: 2006.