

Supporting Information for:

Revising Exciton Diffusion Lengths in Polymer Dot Photocatalysts

Andjela Brnovic, Leigh Anna Hunt, Haining Tian, and Leif Hammarström*

Department of Chemistry, Ångström Laboratory, Uppsala University, SE 751 20 Uppsala,
Sweden

*Email: leif.hammarstrom@kemi.uu.se

1. Materials

All materials were used as received: PFBT or F8BT (poly(9,9-dioctylfluorene-alt-benzothiadiazole), poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)]) with average $M_n \leq 25000$ was purchased from Sigma-Aldrich; perylene red (N,N'-Bis(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxy-3,4,9,10-perylenetetracarboxylic diimide) was purchased from AK Scientific; polystyrene grafted with ethylene oxide and carboxyl groups (PS-PEG-COOH, backbone chain M_w 8500, graft chain M_w 4600, total chain M_w 36500) was purchased from Polymer Source. Experiments and measurements were carried out at room temperature under standard ambient conditions.

2. Pdots Preparation Procedure

PFBT Pdots doped with perylene red were prepared according to the modified nanoprecipitation procedure.^{1,2} Initially, tetrahydrofuran (THF) solutions of PFBT and perylene red were prepared, each having concentrations of 0.1 mg mL⁻¹ and 0.01 mg mL⁻¹, respectively. These precursor solutions were mixed in the desired ratio and sonicated to ensure homogeneity. The desired volume of PS-PEG-COOH (THF) solution was added to all mixtures and sonicated briefly where the weight ratio between PFBT and PS-PEG-COOH was maintained at either 1:1 or 1:3 (wt/wt), as specified. Subsequently, 2 mL of the mixture:PS-PEG-COOH solution was rapidly dispersed into an 8 mL bulk aqueous phase (deionized water) pre-heated at 85 °C. The dispersion was sonicated for 2 min. Finally, THF was removed by keeping the dispersions at 85 °C. Single-component PFBT Pdots were prepared according to the same procedure.

3. Dynamic Light Scattering (DLS)

Hydrodynamic diameters were determined by utilizing a Zetasizer Nano S from Malvern Instruments Nordic AB.

4. Steady-State Spectroscopy

Steady-state experiments were performed at room temperature in 1 cm quartz cuvette. Absorption measurements were carried out on a Varian Cary 5000 UV-Vis-NIR spectrophotometer. Steady-state fluorescence measurements were recorded on a Spectrofluorometer FS5 system from Edinburgh Instruments together with the Fluoracle software using a right-angle detector geometry (90° angle), and corrections were made for fluctuations in the light source and detector response. Samples were excited using 473 nm light with absorbance adjusted to 0.08 at excitation wavelength and a 5 nm emission slit width.

5. Time-Correlated Single Photon Counting (TCSPC)

Fluorescence lifetime decays in the nanosecond range were measured on a Spectrofluorometer FS5 system from Edinburgh Instruments. The excitation source was a picosecond pulsed light emitting diode (EPL-470) with an excitation wavelength of 470 nm. The instrument response function (IRF) was recorded in a 1 cm quartz cuvette using diluted Ludox® (Sigma Aldrich) solution in deionized water at 470 nm emission wavelength. All measurements were carried out at room temperature in water and THF. Sample absorbance was adjusted to 0.08 at 473 nm. All samples were measured at 540 nm emission wavelength with 1 nm emission slit width. The obtained data were fitted using the DecayFit software with either biexponential (eq S1) or Infelta-Tachiya (eq 1) reconvolution fit model:

$$f(t) = A_1 \cdot e^{-k_1 \cdot t} + A_2 \cdot e^{-k_2 \cdot t} \quad \text{eq S1}$$

where, k_1 ($k_1 = \frac{1}{\tau_1}$) and k_2 ($k_2 = \frac{1}{\tau_2}$) are rate constants and A_1 and A_2 are their relative amplitudes, respectively.

Global fitting was performed using DecayFit for MATLAB.

6. Exciton Quenching Volume Calculation

From an estimated PFBT density of 1 g/mL, the amount of PFBT (0.2 mg) used for preparation of Pdots and the total volumes of final solutions (6.4 mL) for both ratios, we have determined the volume of polymer per liter of the solution ($3.9 \cdot 10^{-5} \text{ l/l}$ and $3.1 \cdot 10^{-5} \text{ l/l}$ for 1:1 and 1:3 PFBT:PS-PEG-COOH wt/wt ratios, respectively).

At $\langle n \rangle = 1$ where concentrations corresponded to $2.2 \cdot 10^{-8} \text{ mol/l}$ and $3.7 \cdot 10^{-8} \text{ mol/l}$ for 1:1 and 1:3 PFBT:PS-PEG-COOH wt/wt ratios, respectively, we could estimate the number of particles per liter of solution and the quenching volume per particle (V_q).

7. Calculation of the relation of the quenching volume and the exciton diffusion length

In the reference by Berezhkovskii *et al.*, the average volume $\bar{v}(\tau)$ visited by a spherical particle with radius r undergoing Brownian motion, at times τ when $\bar{v}(\tau) \gg v_0$ ($v_0 =$ the particle volume), is given as (eq. 41 of the reference)³:

$$\bar{v}(\tau) \approx \gamma_3 r^{d-2} \bar{R}_n l^2 \quad \text{eq S2}$$

where the numerical multiplier $\gamma_3 \approx 2.917$, d is the dimensionality of the process ($d = 3$ in our case), \bar{R}_n is the number of lattice sites visited, and l is the step size of the random walk. Using the Förster radius (R_0) for energy transfer to perylene red ($r = 3.0$ nm) as the relevant particle radius for calculating the quenching volume, we obtain $v_0 = 113$ nm³, which is indeed much smaller than the estimated Pdot core volume (2,300 nm³, see the main paper and section 6 in SI), thus satisfying $\bar{v} \gg v_0$. The linear dependence on particle radius may seem counter-intuitive however, it is explained in the reference as a consequence that the fractal dimension of a Wiener trajectory equals two (for 3 and higher dimensions), thus explaining the dimensionality of the factor r^{d-2} in eq S2 (see original work for further details).

Eq 40 in the reference gives (for random walk in 3D):

$$\bar{R}_n \approx 0.718 \cdot n \quad \text{eq S3}$$

where n is the number of steps taken for a 3D system, which is given by (eq. 38):

$$n = \frac{6Dt}{l^2} \quad \text{eq S4}$$

where D is the diffusion coefficient. For 3D diffusion, the mean-square displacement $\langle x^2 \rangle = 6Dt$, from which follows that:

$$n = \frac{\langle x^2 \rangle}{l^2} \quad \text{eq S5}$$

Insertion of eq S5, eq S3 and the value of γ_3 into eq S2 gives the final expression:

$$\bar{v}(\tau) \approx 2.917 \cdot r \cdot 0.718 \cdot \langle x^2 \rangle \quad \text{eq S6}$$

The volume $\bar{v}(\tau)$ is much smaller than for a sphere with radius equal to the exciton diffusion length ($L_D = \sqrt{\langle x^2 \rangle}$). With $r = 3.0$ nm, the volume is only $\bar{v}(\tau) \approx 422$ nm³ for $L_D = 8.2$ nm, which is the radius of a sphere with a volume equal to our obtained value of $V_q \approx 2,300$ nm³ for the 1:1 PFBT:PS-PEG-COOH (wt/wt) ratio. A value of $\bar{v}(\tau) = 2,300$ nm³ corresponds to $L_D = \sqrt{\langle x^2 \rangle} \approx 19$ nm. This suggests that the intrinsic exciton diffusion length of PFBT is much longer than the ca. 8 or 12 nm reported in the previous studies as discussed in the main text.

The calculations above should be taken as approximate. Random walk in the Pdots is limited by the core, and the walks will be reflected at the interfaces. This will increase the walk into volumes already passed, and decrease the value of $\bar{v}(\tau)$.

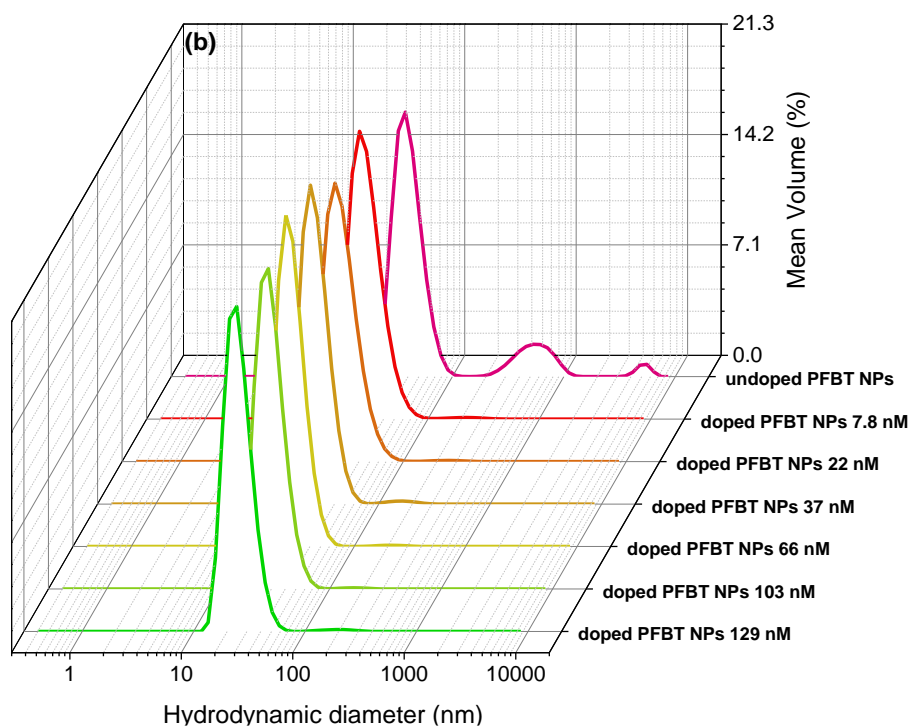
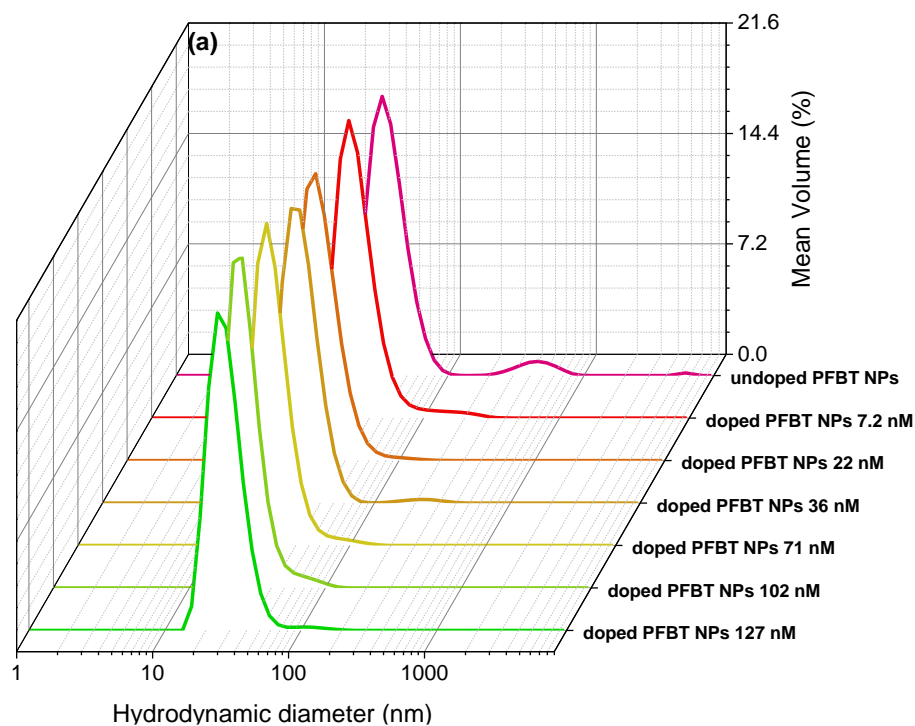


Figure S1. DLS results with the particle size distribution for single-component and doped PFBT Pdots at 1:1 (a) and 1:3 (b) (wt/wt) ratio. Average particle size for single-component PFBT and doped PFBT Pdots is 30 nm for the 1:1 (wt/wt) ratio and 29.7 nm for the 1:3 (wt/wt) ratio.

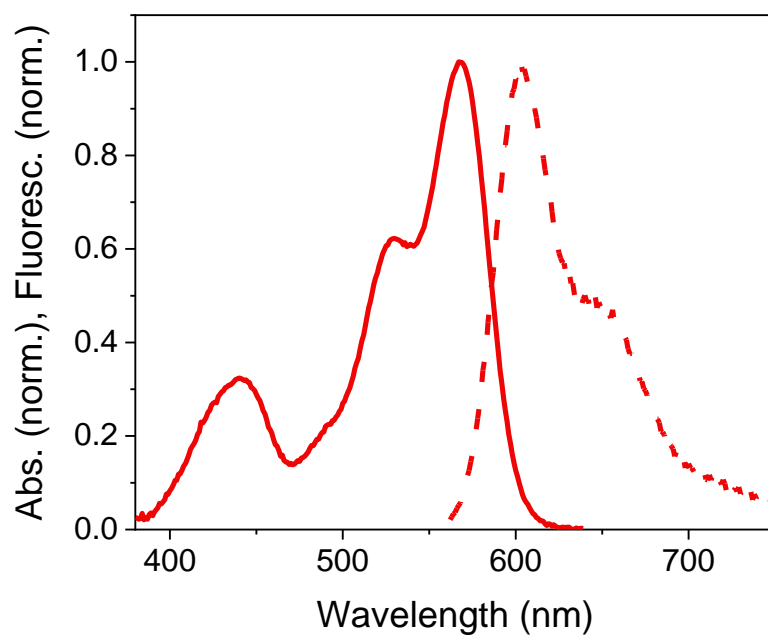


Figure S2. Absorption (solid) and fluorescence (dashed) spectra of perylene red dissolved in THF.

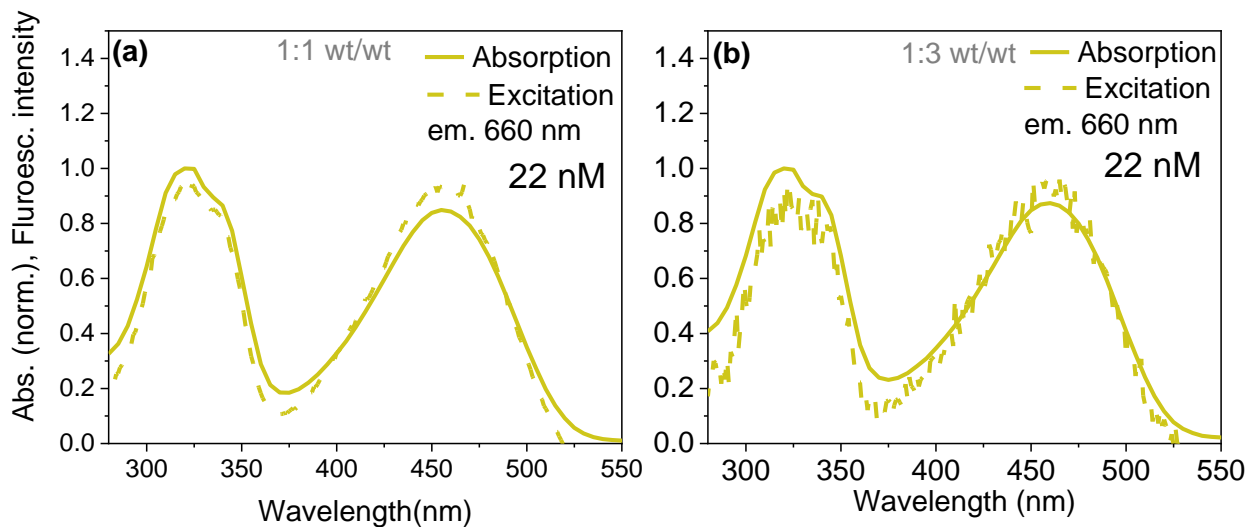


Figure S3. Absorption (solid) and excitation (dashed) spectra monitored at 660 nm emission wavelength of PFBT Pdots with 1:1 (a) and 1:3 (b) (wt/wt) ratios (doped with 22 nM concentration of perylene red).

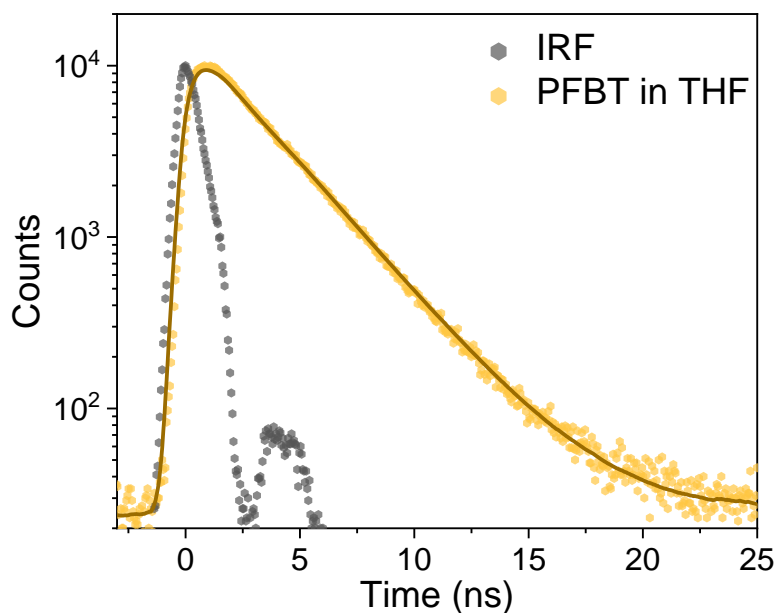


Figure S4. Fluorescence decay trace of PFBT dissolved in THF fitted using single-exponential decay function and convoluted with IRF.

- (1) Wang, L.; Fernández-Terán, R.; Zhang, L.; Fernandes, D. L. A.; Tian, L.; Chen, H.; Tian, H. Organic Polymer Dots as Photocatalysts for Visible Light-Driven Hydrogen Generation. *Angewandte Chemie International Edition* **2016**, *55*, 12306–12310.
- (2) Liu, A.; Gedda, L.; Axelsson, M.; Pavliuk, M.; Edwards, K.; Hammarström, L.; Tian, H. Panchromatic Ternary Polymer Dots Involving Sub-Picosecond Energy and Charge Transfer for Efficient and Stable Photocatalytic Hydrogen Evolution. *J Am Chem Soc* **2021**, *143*, 2875–2885.
- (3) Berezhkovskii, A. M.; Makhnovskii, Yu. A.; Suris, R. A. Wiener Sausage Volume Moments, *J Stat Phys*, **1989**, *57*, 333–346.