

# Supporting Information

For

## Effect of Solvent-Induced Swelling on Exciton Transport in Conjugated Polymer Nanoparticles

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### A. Preparation and Characterization of Conjugated Polymer Nanoparticles

The copolymer poly[(9,9-dioctylfluorenyl-2,7-diyl)-*co*-(1,4-benzo-<sup>1</sup>-thiadiazole)] (PFBT, MW 10,000, polydispersity 1.7), and the poly(phenylene vinylene) derivative poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV, MW 200,000, polydispersity, 4.0) were purchased from ADS Dyes, Inc. (Quebec, Canada). The fluorescent dye fluorescein was purchased from Life Technologies (Invitrogen, Eugene, OR). The fluorescent dye Lucifer Yellow CH dipotassium salt (LY, 1 mg/mL in water), solvent tetrahydrofuran (THF, anhydrous, inhibitor-free, 99.9%) and sodium hydroxide (SigmaUltra, minimum 98%) were purchased from Sigma-Aldrich (Milwaukee, WI). All materials were used as provided without further purification.

The preparation of fluorescent nanoparticles was performed via a previously described nanoprecipitation method.<sup>2</sup> The conjugated polymers PFBT and MEH-PPV were dissolved in THF by gentle agitation and prepared at a concentration of 1000 ppm. An aliquot of each stock solution was used to prepare precursor solutions at 20 ppm. A 2 mL quantity of a given precursor solution

was rapidly added into 8 mL of deionized water under bath sonication at a frequency of 40 kHz and room temperature. Removal of THF was accomplished by the following procedure. Nanoparticle suspensions were placed in a vacuum oven under nitrogen flow for 8 hours at room temperature in order to remove enough THF to prevent bumping during the subsequent evacuation step. Nitrogen flow was ceased and samples were pumped down to an atmosphere of <10 torr using a two-stage rotary vane pump. The samples were heated at ~40 °C for 6-7 hours to remove most of the remaining THF. The total volume of liquid was reduced by typically 60% during the vacuum evaporation process. The aqueous samples were vacuum filtered through a glass fiber prefilter to remove larger aggregates and a 0.1 µm PVDF membrane filter (Millipore). The resulting suspensions are clear (not turbid) and stable for months with no visible signs of aggregation.

UV-Vis absorption spectra were acquired using a Shimadzu UV2101PC scanning spectrophotometer with 1 cm quartz cuvettes. Fluorescence spectra and fluorescence quantum yield were measured using a commercial fluorimeter (Quantamaster, Photon Technology International) using 1 cm quartz cuvettes.

In addition to nanoparticles in water and polymer in THF, swelled nanoparticle samples were prepared by diluting an aliquot of concentrated nanoparticle suspension with the appropriate volume of water, followed by slowly adding THF to produce 3 mL of suspension with volume ratios of THF/water between 0.2 and 0.95. Each sample was gently agitated to ensure solution homogeneity. The sample absorbance was kept at or under ~0.05 (~0.02 for 95% THF). Samples were purged with nitrogen for ~2 minutes, limiting THF losses for higher % THF samples.

## B. Measurement of Fluorescence Quantum Yield

The standard fluorescent dyes fluorescein and Lucifer yellow CH, dissolved in 0.01 M NaOH and water, respectively, were used to determine the fluorescence quantum yield of PFBT and MEH-PPV CPNs. The concentration of each standard was adjusted to yield an absorbance of  $\sim 0.05$  at 473 nm for fluorescein, and 450 nm for Lucifer yellow CH. The concentrations of the CPN samples were adjusted to match the absorbance at each excitation wavelength. The fluorescence quantum yield ( $\Phi$ ) of the CPN samples were calculated using the absorbance  $A$ , integrated fluorescence  $F$ , and refractive indices  $\eta$  of the solvent or solvent mixture using

$$\Phi = \frac{A_s}{A_x} \frac{F_x}{F_s} \left( \frac{\eta_x}{\eta_s} \right)^2 \Phi_s, \quad (S1)$$

where  $x$  and  $s$  are subscripts corresponding to the sample and standard, respectively, and  $\Phi_s$  is the quantum yield of each standard (0.92 for fluorescein in 0.01M NaOH, and 0.21 for Lucifer Yellow CH).<sup>3-5</sup> Samples were purged with nitrogen for  $\sim 2$  minutes in order to remove the majority of molecular oxygen prior to measurement.

## C. Reverse-Mode Time-Correlated Single Photon Counting (TCSPC) Spectroscopy

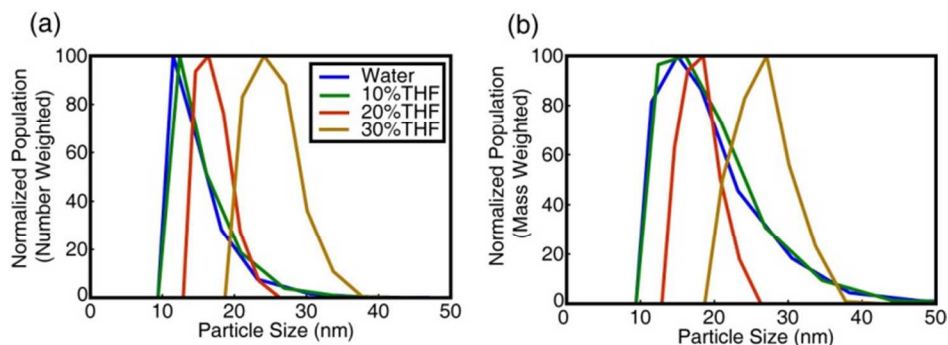
Picosecond fluorescence lifetimes were measured under nitrogen using a home-built setup for time-correlated single photon counting (TCSPC) spectroscopy operating in reverse mode. Frequency doubled pulses (420 nm) from a passively mode-locked Ti:Sapphire laser (Coherent Mira 900, 840 nm pulses,  $\sim 150$  fs pulsewidth) were used as the excitation source for the nanoparticle samples. Sample emission was collected with perpendicular geometry to the excitation source after passing through a 460 nm long pass filter, and a calcite Glan-Taylor polarizer (Thorlabs, GT10-A) oriented at magic angle ( $55^\circ$ ) to the vertically polarized excitation

pulses. The output of a single photon avalanche photodiode (APD, id Quantique, id100-50) was used as the start timing pulse for a time-to-amplitude converter (TAC, Canberra Model 2145), and the output of a fast PIN diode (Thorlabs, DET210) was used as the stop pulse, in a standard reverse-mode configuration.<sup>6,7</sup> The excitation power was attenuated (usually between  $\sim 300 \mu\text{W}$  and  $1 \text{ mW}$ ) to maintain a count rate of  $\sim 400 \text{ kHz}$  as measured at the APD. The analog TAC output was digitized using a multi-channel analyzer (FastComTec, MCA-3A). Before and after each measurement, an instrument response function (IRF) was measured using scattered excitation light from a dilute suspension of polystyrene microspheres. The width of the IRF was determined to be  $\sim 70 \text{ ps}$  (fwhm). Typical peak signal-to-noise ratios (SNR) were between 200:1 (80%-100% THF samples) and 500:1 (IRF and low-mid % THF samples). The reported information was collated from a total of two samples per concentration of THF, and 3-5 scans per sample. Intensity decays were collected for 5-20 minutes to obtain the above mentioned SNR values, depending on the lifetime of the sample.

#### **D. Dynamic Light Scattering (DLS) Measurements of Swelled CPNs**

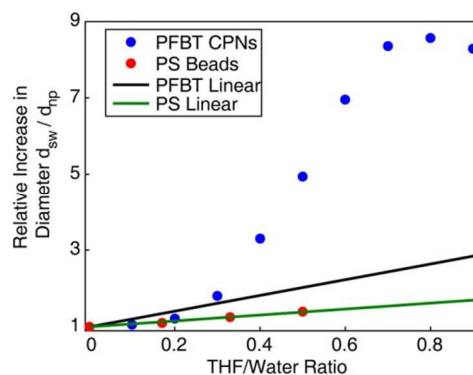
The size distributions of swelled PFBT CPNs were determined via dynamic light scattering (DLS) of PFBT CPN suspensions at various THF/water ratios using a Nanobrook Omni spectrometer (Brookhaven Instruments Corporation, Holtsville, NY) with BIC Particle Solutions Software (Version 3.1). Swelled PFBT CPN samples were prepared according to the swelling procedure given above, with an absorbance of  $\sim 0.1$  at  $450 \text{ nm}$ . The acquisition time for each measurement was 180 seconds. Data was collected at a count rate of  $500 \text{ kcounts/s}$ , with a scattering angle of  $90^\circ$ , and at  $25^\circ\text{C}$ . The viscosity correction for the various THF and water mixtures was obtained from Nayak et al.<sup>8</sup> Polystyrene spheres (Invitrogen,  $24 \text{ nm}$ ) were used as a

size standard. Both the number-averaged sizes and mass-averaged sizes were measured (c.f. Fig. S1). A polydispersity index of 2.42 was calculated from the ratio of mass-averaged particle size over number-averaged particle size, and remained constant within the range of 0%-30% THF.



**Fig. S1.** Dynamic light scattering (DLS) results for PFBT CPNs in 0%-30% THF/water mixtures. (a) Number weighted particle size distribution, (b) mass weighted particle size distribution.

The results illustrate that the swelling is highly nonlinear at THF concentrations beyond 30% THF (c.f. Fig. S2), and the results indicate that a second, larger population emerges at concentrations of 40% THF and higher. The DLS results are fit linearly within the range of THF from 0% to 30%, where a single population exists ( $R^2 = 0.763$ ). The linear fit curve is then used to extrapolate the simulated inter-chromophore spacing from the mean particle diameter for concentrations of 40% THF and higher. The DLS results are compared to swelling measurements using optical microscopy via Carson, et al.,<sup>9</sup> which is fit linearly ( $R^2 = 0.987$ ), and extrapolated to determine simulated inter-chromophore spacing in the same fashion as the DLS results.



**Fig. S2.** Swelling of PFBT CPNs and polystyrene (PS) beads with THF. Relative increase in mean particle diameter due to swelling as determined by dynamic light scattering measurements of PFBT CPNs (number average particle size, blue), with linear fit curve (black) to the low THF concentration data, and optical microscopy measurements on swelled polystyrene beads via Carson, et al. (red), with linear fit (green).

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