**Supporting Information**

For

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

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1. **Preparation and Characterization of Conjugated Polymer Nanoparticles**

The copolymer poly[(9,9-dioctylfluorenyl-2,7-diyl)-*co*-(1,4-benzo-{2,1',3}-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 nano-precipitation method.[1](#_ENREF_1) 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.

1. **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 qyuantum yield of PFBT and MEH-PPV CPNs. The concentration of each standard was adjusted to yield an absorbance of ~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 () of the CPN samples were calculated using the absorbance *A*, integrated fluorescence *F*, and refractive indices ** of the solvent or solvent mixture using

, (S1)

where *x* and *s* are subscripts corresponding to the sample and standard, respectively, and *s* is the quantum yield of each standard (0.92 for fluorescein in 0.01M NaOH, and 0.21 for Lucifer Yellow CH).[2-4](#_ENREF_2) Samples were purged with nitrogen for ~2 minutes in order to remove the majority of molecular oxygen prior to measurement.

1. **Reverse-Mode Time-Correlated Single Photon Counting (TCSPC) Spectroscopy**

Picosecond fluorescence lifetimes and fluorescence anisotropy decay (FAD) 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, ~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 either parallel (0°), perpendicular (90°), or at magic angle (55°) to the vertically polarized excitation pulses. All three polarization angles were utilized for FAD, magic angle polarizer orientation was adopted for TCSPC. 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.[5](#_ENREF_5),[6](#_ENREF_6) The excitation power was attenuated (usually between ~300 µW and 1 mW) to maintain a count rate of ~400 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 ~70 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.

1. **Picosecond Fluorescence Anisotropy Decay**

Polarized intensity decays collected at 0°, 90° and 55° to the vertically polarized excitation pulse were obtained via reverse-mode TCSPC (c.f. Fig 7a). The resulting polarized intensity data was utilized to construct time-resolved anisotropy decays by the relation , where , , and G is a correction factor accounting for differences in detector sensitivity to vertically and horizontally polarized light (c.f. Fig 7b). The process by which the anisotropy data is calculated from the fluorescence intensity decays at each polarizer orientation was adapted from a method by Fleming et al., and is outlined in detail below.[6](#_ENREF_6)

First, the total intensity decay law is determined from fitting the 55° data. The trial functions are single exponential for fluorescein in water and PFBT in THF, and KWW for all other samples. The parameters yielded from these fits (, or , *β*) are used as the first term of the trial decay for the 0° and 90° data. The second term in the trial decay function for the parallel or perpendicular data is given by a single exponential, so that the total trial decay function for a given sample is either a bi-exponential or a summed KWW and exponential decay

, (S2)

where the superscript indicates the polarizer orientation. The fit results are then processed to determine the rotational correlation time , and the limiting anisotropy  as follows. First, an amplitude correction factor, used to account for differences in SNR from run to run between the 55° data and the 0° (or 90°) data, is determined by**, where the corrected amplitude (LHS) is calculated by multiplying the amplitude of the second exponential term in Equation 1 by the ratio of the 55° and the 0° (or 90°) KWW amplitudes. Thus, the corrected amplitude replaces the amplitude on the second term in Equation 1.Once the amplitudes are corrected, the phenomenological correlation time is calculated by a weighted average of the 0° and 90° lifetimes,

. (S3)

In calculating r(t), the 55° terms drop out in the numerator due to the subtraction of I0(t) and I90(t), yielding

. (S4)

Evaluating Equation 3 at t = 0 yields the limiting anisotropy ,

.  (S5)

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