**Manuscript Title:**

Measurement of Exciton Transport in Conjugated Polymer Nanoparticles

**Authors:**

Louis C. Groff, Xiaoli Wang and Jason D. McNeill

**Corresponding Author:**

Jason D. McNeill

Department of Chemistry

Clemson University

Clemson, SC 29634 USA

Phone: (864) 656-4065

E-mail: mcneill@clemson.edu

**Manuscript Type:**

Article

**Journal Section:**

C4: Physical Processes in Nanomaterials and Nanostructures

Dear Editors,

Thank you for your prompt consideration of our manuscript. Attached is the revised manuscript (jp-2013-07065h). The authors would also like to thank the editors and reviewers for their kind comments and thoughtful suggestions. We have revised the manuscript in response to the reviewers’ suggestions and highlighted the revised text in the manuscript. A point-by-point response and a list of changes are on the following pages. We hope that you will find that the reviewers’ concerns have been addressed adequately. Since the reviews were positive and the issues raised were minor, we expect that you will find that further review is not necessary.

Sincerely,

Jason D. McNeill

**Point-by-point response to editors’ comments:**

1. Reference formatting is incorrect. (#10-11-12-13 on the checklist)  
       (a) Article Titles are now required with ALL titles to be written in title case.  
       (b) Last Page numbers are required.

**Response:** These items have been corrected according to the guidelines laid out in the checklist.

1. Figure 4 is not mentioned in the text.
2. Figure 6 is mentioned (pg 14) not is not shown.

**Response:** The mention of Fig. 6 was intended to read “Fig. 4,” and has been corrected in the manuscript, which should address both of the above mentioned items.

**Point-by-point response to reviewers’ comments:**

**Reviewer 1**

**Comments:**

This work reports experimental study of exciton transport in conjugated polymers using a doping dye molecule as a probe with time-resolved fluorescence.  A diffusion model was used to account for the key features and determine the diffusion length of interest.  The work is well designed and carefully executed.  The results are of good quality and the analysis is thorough and insightful.

I only have one minor question for the authors to consider: in the model, is dye is probably assumed to be very small, equivalent to a point.  Is it possible to include a finite size of the dye molecule in the model?  In relation, since the dye does have a finite size, could or how would this affect the data interpretation?

**Response:** The simulations use a continuum model to handle the structure of the polymer. While the dyes are essentially points within this continuum, the model can to some degree be adjusted to correct for finite dye volume effects, e.g., by adjusting the Förster radius. In addition, in prior publications, we had previously performed simulations using a fixed lattice, with lattice constants similar to dye dimensions, and obtained similar results. Furthermore, the doping percentages are small, while the quenching efficiencies are high. Discussion of this reasoning, addressing these points relevant to the reviewer’s question, have been added to the manuscript.

**Reviewer 3**

**Major comments:**

1. The percentage of dopant inside the CPN is completely determined based on the concentration ratio of dopant and CPN. Percentage of dye doping is based on the assumption of “…. expecting most of the dye is incorporating into the CPN….” For the homogeneity of the sample they used brief sonication. Authors need to make comments on the homogeneity and elaborate the CPN preparation procedure mentioning sonication time, frequency for sonication, temperature etc. How the authors assumed that all the dyes were incorporated into the core? Is there any experimental proof that all the perylene dyes were incorporated into the core?

**Response:** The sonication time of our sample is ~30 s at 40 kHz and room temperature. This has been clarified in the main text, and the Supporting Information. In our 2008 J. Phys. Chem. C publication, we performed centrifugal concentration of a sample of Coumarin 6 doped polyfluorene CPNs and measured the absorbance and fluorescence of the filtrate. Negligible absorbance and very weak fluorescence from Coumarin 6 was observed, indicating that the majority of the dye is embedded in the polymer matrix. The process was repeated a few weeks later and no dye leakage was observed. We expect similar results due to the similarities of the current system to the previously studied system. The lack of additional spectral signatures due to dye leakage or aggregate formation in the UV-Vis spectra further supports this notion, along with the high measured energy transfer efficiency at low dopant concentrations. This has been added to the manuscript and Supporting Information.

1. For simulation a modeling of exciton diffusion and energy transfer are imported here. To obtained the desired result they varied several parameters but they assumed the nanoparticles as a sphere only and they gave priority to quenching by defects- but why they only restricted the simulation with spherical particle and quenching by defects only? Apart from AFM is there any indication that the CPN are spherical?

**Response:** Regarding the assumption of quenching by defects, this is justified based on prior results reported by us and others that the primary quenching species is hole polarons (i.e., cations). However, we are purposely somewhat vague about the nature of the quenching defect, since our proposed modeling approach should be valid for different types of defects. Perhaps we mistakenly gave the impression that the defects are synthetic defects or other particular type of defect, and we have changed the manuscript to remove that ambiguity. Additionally, the assumption of the existence of quenchers is a key part of the model we are testing--the assumption is provisional, and if there were no quenching species evident in the results, we would have obtained a defect concentration of zero.

Regarding the assumption of spherical shape, we and others have addressed this previously. Some discussion of simulations assuming spherical versus cubic particle, with references, has been added to the manuscript.

**Minor comments:**

1. Diffusion length LD = (2nDτ)^1/2 , but author claim that the diffusion length increased by factor of two where the lifetime of excited state is reduced. This needs elaboration for the non-expert readers.

**Response:** This has been clarified in the main text, by modifying the text to clarify the definition of LD employed.

1. Although there is red shift in the emission maxima but the quantum yield of CPN is getting lowered with the increment of dopant (perelene dye) amount, with this result how the author claims that such CPN is useful for multicolour imaging and tracking purpose?

**Response:** At low-to-moderate doping levels, the fluorescence quantum yield remains at or above 0.10. Since there is typically overlap between the emission spectrum of autofluorescence (which typically exhibits a small Stokes shift) and that of the fluorescent label, there is usually a tradeoff when choosing a filter set, between maximizing the fraction of the emission spectrum collected and rejection of autofluorescence. Therefore, an increased separation between excitation and emission typically leads to higher signal levels and better rejection of autofluorescence. We have modified the text in order to clarify this issue.

1. Fig 3a, undoped decay looks quite wavy in nature and is there any rise in the initial part?

**Response:** There is no rise in the initial part--emission is prompt, to within the time resolution of the setup. The waviness apparent in some of the decay traces is possibly due to afterpulsing in the single-photon APD detector, stray reflections in the apparatus reaching the detector, or nonlinearities in the time-amplitude converter (TAC) or multi-channel analyzer (MCA) within the TCSPC setup. These effects are prominent only in samples with a lifetime greater than ~2 ns. The effect on the determined fluorescence lifetimes is minor, and has been cross-checked with several standard dyes, including fluorescein in 0.01 M NaOH (τ = 4 ns), Coumarin 6 in ethanol (τ = 2.5 ns), and perylene red in THF (τ = 5.6 ns). All lifetimes measured were within 10% of literature values. A paragraph discussing the validation of the apparatus and addressing these concerns has been added to the Supporting Information.

1. Fig 4b in the inset needs scale for X-axis.

**Response:** An appropriate scale has been added to the X-axis of the inset in Fig. 4b.