CHAPTER FIVE

CONCLUSIONS AND FUTURE DIRECTIONS

**5.1 A Systematic Investigation of Exciton Transport in CPNs**

Throughout the experiments detailed in this dissertation, it has been our aim to systematically address several relevant questions regarding exciton transport in dense, nanoscale, multichromophoric systems such as CPNs. Given that defects are often unavoidable in aggregated polymer systems, it has been valuable to understand the role of defects and their effect on determining the exciton diffusion length for a given polymer. This was addressed by dye-doping and polymer blending to deliberately introduce quenchers into CPNs with known amounts of defect quenching. This strategy elucidated how ignoring defect quenchers can result in substantial underestimation of the exciton diffusion length in the absence of quenchers. For both doped systems, Monte Carlo simulations of exciton transport and energy transfer to a Possion distributed ensemble of defects and dopants were utilized to model the observed exciton decay kinetics from experimental fluorescence lifetime measurements, which in turn, led to the determination of the exciton diffusion length for PFBT in the absence of defects. In addition, modeling of polymer blended CPNs aided in determining that a dopant polymer is more likely to be in an open conformation when doped in an aggregate nanoparticle (rather than a more compact conformation) due to the high energy transfer efficiency from PFBT to the dopant polymer MEH-PPV. After determining the typical length scale of exciton transport in CPNs, the next problem was to determine how exciton transport rates are affected by changes in interchromophore spacing, and to additionally determine how the effective dimensionality of exciton transport in CPNs affects defect quenching. This was accomplished using solvent-induced swelling methods. In addition to fluorescence lifetime measurements, fluorescence anisotropy decay measurements allowed for the calculation of exciton transport rates (for moderate to high THF concentrations). Additionally, a discrete lattice model that included changes in lattice spacing (i.e., interchromophore spacing) was utilized to model the effect of swelling on exciton transport rates and to determine effective chromophore size in PFBT and MEH-PPV CPNs (~1 nm), with good agreement between experimental and model results at low-to-moderate THF concentrations. It is clear by the results of this work that an apparent compromise between fluorescence quantum yield and the rate of exciton transport exists, which can be taken advantage of in different ways depending on the desired applications for a given conjugated polymer system.

**5.2 Determination of the Intrinsic Exciton Diffusion Length in PFBT**

A novel approach was proposed for determining exciton transport parameters in conjugated polymers. Exciton dynamics of conjugated polymer nanoparticles doped with dyes were investigated by time-resolved fluorescence spectroscopy. Highly efficient energy transfer from the polymer PFBT to the dye perylene red was evident in the fluorescence spectra and excited state kinetics. Exciton transport parameters were obtained by fitting to a model that included the effects of Poisson statistics, nanoparticle size, exciton diffusion, energy transfer, and quenching by defects. The results indicate substantial quenching by defects, owing primarily to exciton diffusion, which can greatly increase the effective quenching volume of defects. Stern-Volmer quenching analysis of dye-doped CPNs yields a quenching constant of 37 per dye molecule, which corresponds to a perylene red quenching radius of 5.3 nm. The substantially higher quenching radius obtained from Stern-Volmer analysis as compared to the calculated quenching radius of 3 nm for the PFBT/perylene red pair supports the notion of exciton diffusion contributing to the observed quenching efficiency. We estimated the amount of quenching by defects, and included quenching by defects in our model and analysis, yielding an estimated exciton diffusion length of 12 nm and diffusion constant of 8.0x10-9 m2 s-1 for nanoparticles of PFBT. The results indicate that quenching by defects can lead to substantial error in determined exciton transport parameters (i.e., underestimation of *LD* by a factor of ~2), unless quenching by defects is properly taken into account in the analysis. The larger exciton diffusion length determined from the above analysis is promising for device applications requiring large exciton diffusion lengths, such as organic photovoltaic devices. Given that the analysis above results in an exciton diffusion length for a hypothetical defect-free material, for the aforementioned applications, strategies would need to be employed to reduce the contribution of defects to exciton transport (e.g. swelling methods to break up aggregate defects, or doping with reducing agents to minimize hole polaron quenchers). Additionally, the above analysis provides a general means for determining the defect density and exciton diffusion length (as well as the effect of defect quenchers on the measured *LD*) for materials that exhibit substantial fluorescence quenching in the aggregated state.

**5.3 Investigating Exciton Transport Rates in CPNs Through Swelling**

Many key processes in conjugated polymers are strongly influenced by multiple energy transfer (i.e., exciton diffusion). We investigated the effect of solvent-induced swelling on the kinetics of multiple energy transfer in nanoparticles of the conjugated polymers PFBT and MEH-PPV. Multiple incoherent energy transfer events between equivalent chromophores results in loss of fluorescence polarization, which can be observed in the fluorescence anisotropy decay kinetics. Additionally, multiple energy transfer affects the rate of quenching by defects. We found that the rate of energy transfer between like chromophores is highly sensitive to solvent effects, occurring at a rate of 1.1109 s-1 for PFBT dissolved in THF, and 3.3109 s-1 for MEH-PPV dissolved in THF. In both moderately swelled and aqueous nanoparticle suspsensions of PFBT and MEH-PPV, the rate of energy transfer is increased by a factor of 10-60 (with the highest energy transfer rates corresponding to MEH-PPV CPNs). A discrete cubic lattice model incorporating distance-dependent multiple energy transfer and quenching by defects was employed to elucidate the relationships between solvent-induced swelling, fluorescence quantum yield, and decay kinetics. The simulation results show good agreement with experimental results at low to moderate THF concentrations. The results support quenching by defects or polarons, amplified by multiple energy transfer, as a likely explanation for the typically low fluorescence quantum yield of conjugated polymer particles as compared to the free polymer in solution as well as similar effects observed in thin films. In addition, the effect of dimensionality on fluorescence quenching by defects was determined by comparing a 3D spherical particle to an ensemble of 1D linear polymer chains with equivalent amounts of chromophores and defects. It was calculated that defect quenching is substantially reduced by ~80% in the 1D ensemble compared to a 3D particle, indicating that interchain exciton transport (or intrachain transport in folded chains) contributes substantially to quenching by defects.

**5.4 Future Prospects**

There are several directions that have already been pursued or are currently being pursued to study CPNs further. It is beneficial to understand the details of charge-transfer complex formation, recombination, and transport in CPNs (i.e., polaron formation and polaron diffusion). Single molecule microscopy has been done previously to examine charge carrier transport in CPNs, but was restricted in the observable time scale (50 frames/s).{Yu, 2009 #57}{Yu, 2012 #58} The previous results suggested that polaron dynamics were occurring at rates below the time resolution of the instrument. Work is currently being pursued to examine polaron transport on the sub-millisecond time scale, in an effort to better understand the rates of charge-transfer complex formation and recombination in CPNs, which are crucial to effective device performance.

Additionally, we may examine the effect of chain length on exciton dynamics and transport rates by investigating nanoscale oligomer aggregates via steady-state and time resolved spectroscopic methods. Some work has already been done on oligophenylene-vinylene (OPV) and oligothiophene (OT) nano-aggregates by Spano, which suggests somewhat different excitonic behavior in the aggregated state. In particular, conjugated oligomer aggregates seem to blue-shift (i.e., form H-aggregates) as opposed to the common red-shifting (J-aggregation) seen in conjugated polymer aggregates.{Spano, 2006 #219} However, it is also possible to form oligomer aggregates which display J-aggregate characteristics, {Spano, 2003 #220} which would make oligomer nanoparticles of other monomer structures (e.g. oligofluorenes or oligo-FBTs) worth studying. For example, it could be of interest to determine at which chain length J-aggregation dominates over H-aggregation (and/or if mixed aggregation is observed). Another useful aspect to H-aggregation is that lifetimes are usually longer, which could lead to longer exciton transport due to the extended lifetime of the H-aggregate state, which could be probed using methods we have already employed using CPN samples.