

PICOSECOND TIME-RESOLVED STUDIES OF MULTIPLE ENERGY TRANSFER IN CONJUGATED POLYMER NANOPARTICLES

By Louis C. Groff II

ABSTRACT

Conjugated polymer nanoparticles (CPNs) are a model system for the study of complex, nanoscale, multichromophoric interactions. In this dissertation, we are focused on furthering our understanding of the physical picture, processes, length scales, and time scales of energy transport in conjugated polymers. In particular, we are interested in determining how parameters related to the nanoscale structure and composition of CPs affect energy transport, which is investigated using steady-state and time-resolved fluorescence spectroscopy in conjunction with Monte Carlo simulation methods. Such information could prove useful for optimizing the structure and composition of device layers (e.g., in photovoltaic devices). We additionally seek to develop brighter, red-emitting CPNs through Förster Resonance Energy Transfer (FRET) for their use in biomedical imaging applications. Analysis of dye-doped and polymer blended CPNs shows that the doped CPNs exhibit bright, red-shifted emission, owing to the highly efficient energy transfer from the host polymer PFBT to the respective dopants (the fluorescent dye perylene red in dye-doped CPNs, and the polymer MEH-PPV in blended CPNs). An exciton diffusion energy transfer model was employed to simulate exciton dynamics in doped CPNs, and additionally to determine the intrinsic exciton diffusion length for PFBT in the absence of quenching defects. Solvent-induced swelling methods were utilized to study how swelling affects the multiple energy transfer cascade to intrinsic defects and/or aggregate species in CPNs, which modulates the exciton dynamics and fluorescence properties of CPNs. Changes in the rate of exciton transport over a range of solvent compositions were measured using picosecond

fluorescence anisotropy decay (FAD). Analysis of the results indicates increased fluorescence lifetimes and fluorescence quantum yield with increasing THF concentration. Additionally, the FAD and model results indicate that the rate of exciton transport is significantly increased in the nanoparticle state compared to polymer in good solvent. The results elucidate a tradeoff between exciton transport rates and fluorescence quantum efficiency in conjugated polymer systems, which can be exploited for improvement of organic semiconductor-based devices.