

# Optical Properties and Electronic Structure of Polymer Nanostructures

Jack C. Wells

Computational Materials Science Group  
Computer Science and Mathematics Division  
Oak Ridge National Laboratory  
Oak Ridge, Tennessee

## Abstract

Recent advances in the synthesis and processing of polymers have resulted in uniformly oriented nanorods of a conjugated polymer (MEH-PPV) with transition moments perpendicular to the support substrate. A variety of experimental, theoretical, and simulation studies provides evidence of single-molecule, polymer nanoparticle structures with an extraordinary degree of intra-molecular order. These nanorods exhibit narrow photoluminescence emission spectra (10-15 nm fwhm) with no evidence of spectral diffusion on time scales of several hundred seconds. The distribution of center frequencies from a large ensemble of individual nanoparticle measurements shows clearly defined peaks that can be correlated with emissive chromophores corresponding to excitonic traps of integer multiples of monomer conjugation lengths. These peak frequencies are lowered from self-solvation effects on the chromophore within the core of the nanoparticle.

These discrete emission characteristics suggest exciting possibilities in photonics and molecular optoelectronics, and motivate interest in a detailed understanding of the electronic structure of the material. However, because of the size and nature of these molecules, a theoretical and computational description of their electronic structure is a challenging task. I will describe models for these macromolecules consisting of extended and stacked pi-conjugated systems, specifically oligo phenylene-vinylene (OPV), and discuss the singlet transitions between the ground and low-lying excited states from the points of view of semi-empirical and first-principles theory. An attractive feature of the methods employed is that the description of both optical excitations and charge transport may be made on the basis of the same computational description.

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