

**MORPHOLOGY EFFECTS ON THE OPTICAL PROPERTIES OF PHENYLENE
VINYLENES FROM NANO-SCALE TO BULK**

Final seminar

Thomas Gregory Bjorklund, Ph.D.

Department of Chemistry

University of Illinois at Urbana-Champaign, 2003

Christopher J. Bardeen, Advisor

May 28, 03

This study looks at the effects of nano-scale morphology on the spectroscopy of phenylene vinylene molecules. A series of phenylene vinylene oligomers and polymers were synthesized (1,4-distyrylbenzene (DSB), 4,4'-bis-hexyloxy-1,4-distyrylbenzene, 1,4-bis-hexyloxy-2,5-distyrylbenzene, 4,4'-distyrylstilbene, 1,4-bis[4-(3,5-di-*tert*-butylstyryl)styryl]benzene, poly-*p*-(phenylene vinylene) (PPV), and poly[(2-methoxy-5-hexyloxy-*p*-phenylene)vinylene] (MH-PPV)). These molecules were examined as dilute solution, reprecipitated aggregates, and thin films. Spectroscopic measurements included UV/Vis absorption and fluorescence measurements, infrared absorption measurements, and time-resolved fluorescence measurements. Physical morphology measurements included AFM, SEM, TEM, and x-ray diffraction. The morphology of the PPV films was varied by using methanol and water as solvents for the precursor polymer and by blending polyvinyl alcohol (PVA) with the precursor polymer. PPV films made from methanol cast precursor have average crystallite sizes of 5 nm from calculations made from x-ray diffraction measurements. The corresponding PPV films made from water cast precursor have average crystallites of 10 nm. While the absorption spectra of the two film preparations had slightly different shapes, the fluorescence spectral shape and dynamics of the films was the same. PVA was blended with PPV to disrupt crystallite formation in the film. Even at low PVA concentrations, the blending caused the absorption spectrum to broaden and shift to higher energy while the fluorescence

spectrum changed shape and shifted to higher energy also. Blending with PVA also eliminated the temperature dependence of the fluorescence dynamics observed in neat PPV films. The addition of side groups on to the polymer to make MH-PPV also disrupts the formation of crystallites in the films and forms a different type of intermolecular emitting species than PPV. DSB molecules and the end substituted 4,4'-bis-hexyloxy-1,4-distyrylbenzene pack in an edge-to-face pattern aligning the transitions dipoles such that an H type aggregate is formed which when excited produces a Frenkel exciton. The side substituted 1,4-bis[4-(3,5-di-*tert*-butylstyryl)styryl]benzene packs in a face-to-face pattern producing an excimer species when excited. Doping other organic molecules into the DSB caused another intermolecular emitting species to appear in the fluorescence spectrum of the aggregates with a lifetime over ten times as long as non-doped DSB aggregates.