

Probing Inter-chain Interactions in Organic Semi-conductors

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Applications of conjugated polymers in photovoltaics and displays drive the need to understand how morphology and aggregation affect emission yields, spectra, and the facility with which charges are generated and migrate through the sample. It is known that solvent-polymer interactions in solution critically affect the properties of thin films formed when these solutions are cast onto substrates. Here, the aggregation of conjugated polymers in commonly used organic solvents is investigated using fluorescence correlation spectroscopy (FCS), burst analysis, microscopy, and ultrafast spectroscopy. P3HTs and PPVs are shown to form weakly-bonded non-emissive aggregates in toluene that persist even at picomolar concentrations. These aggregates cause a substantial decrease in the bulk emission intensity in solution but do not affect the fluorescence spectra or lifetimes.[1] In contrast, aggregates formed from more polar solvents such as tetrahydrofuran (THF) are significantly more emissive though their fluorescence lifetimes and yields are also reduced compared to monomeric chains. These differences are understood by monitoring the stimulated emission evolution of the two aggregate types. In addition, the propensity for charge separation leading to emission quenching is probed using transient absorption. Overall, our results show how FCS and burst analysis can be used to diagnose the presence of non-emissive aggregates at ultra-low concentrations. They furthermore demonstrate that chain-chain interactions in dilute solution have a negative impact on the emission properties and overall quality of spin cast thin films that can be reversed through judicious sample processing. Finally, initial efforts to explore the relationship between solvent-driven chain conformation and emission quenching behavior *via* molecular dynamics simulations will be described.

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References:

[1] E.C. Wu, R.E. Stubbs, L. A. Peteanu*, R. Jemison, R. D. McCullough, and J. Wildeman, *Journal of Physical Chemistry B* (in review)