Single Molecule Fluorescence Spectroscopy of Luminescent Conjugated Polymers with Different Chain Length

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Abstract – ***Fluorescence intensity traces of different length luminescent conjugated polymers are studied by single molecule spectroscopy. The fundamental difference between one and three-dimensional system is used to explain the discrepancy in the photophysics of different chain length.***

The unique advantage of single molecule experiments is the ability to observe phenomena such as the distribution of individual spectrum and transient intensity variation that are obscured in ensemble measurements. It is possible to verify the statistical assumptions used in the ensemble of molecules. Single-molecule fluorescence has been applied on conjugated polymers to investigate the multiple chromophore system [1-4]. In this conference, we present the fluorescent comparison of single poly(phenylene-vinylene)s (PPV)s with various length. Polymer with short length (~ 24 rep. units) exhibits mainly a rod-like structure, while the polymer with much longer length (>1000 units) forms defect cylinder or defect-coiled structure. The conformational difference makes energy transfer as well as charge transfer via different paths in the quasi-one dimensional system and the 3-D folded structure. [5-7]

The fluorescence time trace from single molecules was observed for over one hundred molecules of both polymers. For rod-like polymer, most of the traces exhibit jumps between few steps. Spectral changes companion with the stepwise intensity jump, but the reverse was not held. Rod-like structure with/without kink is used to explain the equal/nonequal intensity step size of the time trace, as well as the polarization dependence. Spectral change as the function of time reflects the distribution of effective chain length in the polymer. This implies the inefficient energy transfer along the polymer backbone. On the contrary, long chain polymer exhibits defect-coiled or defect-cylinder structure. The 3-D folded structure facilitates energy transfer through surrounding folded segments. Molecular oxygen plays important role to quench the emission, hence influences the fluorescence from the polymer. Comparing the sample with different protecting methods, intrinsic fluorescence behavior can be studied. [8, 9] In addition, understanding the initial quenching process provides more information about the polymer conformation and the relationship to its photophysics.

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