# Conformation-dependent Room-temperature Emission Spectra of Single MEH-PPV Chains in Different Polymer Matrices

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Emission spectra of single molecules of the conjugated polymer MEH-PPV in host matrices of ZEONEX® and polystyrene are reported. Depending on the matrix, the polymer chains attain different conformations, from compact defect cylinders to extended defect coils. The conformations are correlated with photophysical properties, such as emission intensity fluctuations, and with shapes and peaks of emission spectra. The observed bimodal distribution of the spectral peaks is related to distribution in conjugated segment lengths.

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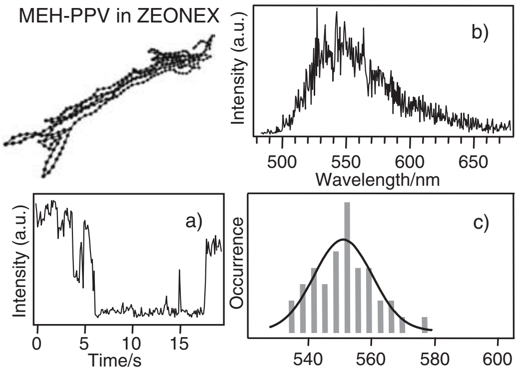

**Figure 1.** Conformation and photophysics of MEH-PPV in ZEONEX. a) Single-chain emission intensity time trace, b) single-chain emission spectrum, and c) histogram of emission spectral peaks.

Conjugated polymers are the subject of intense research as active materials for optical and electronic devices.[1,2] Photophysical processes play crucial roles in the device function. However, photophysics of conjugated polymers depends strongly on the unique conformation of individual polymer chains. As a result, many questions on the relationship between structure and optical properties remain open.[3,4]

The complexity of the study of conjugated polymer photophysics can be partially overcome by the use of single molecule spectroscopy.[5] Recently, we reported a novel fluorescence polarization microscopic method[6] and used it together with molecular dynamics simulations to reveal the conformation of individual polymer chains on a truly single-molecule level.[7] This enabled us to study photophysical properties of MEH-PPV on the same single chains and to show that the conformational state is the determining factor for the photophysical processes. Here, we use the previously determined conformations of MEH-PPV in different host matrices and correlate the structural information with single chain emission spectra.

Poly[2-methyloxy-5-(2-ethylhexyl)oxy-1,4-phenylenevinylene] (MEH-PPV, Aldrich, $M_w$ 200000, PDI 5) was dispersed by spin-coating in thin-film matrices of ZEONEX and of low-molecular weight polystyrene (PS). The film thickness was on the order of 120 nm. The experiments were carried out on an inverted fluorescence microscope[7] using the 488-nm line of $Ar^+$ ion laser for excitation. Time evolving emission spectra were taken with an EM-CCD camera and an imaging spectrograph as a series of tens of images.

Single MEH-PPV chains attain compact defect cylinder conformations in the poor-solvent matrix of ZEONEX (Figure 1). The resulting interchain interactions lead to localization of the exciton and to blinking in the emission time-traces (Figure 1a). Single-chain emission spectra measured for several tens of molecules were analyzed and their maxima were plotted in a histogram in Figure 1c. The histogram shows a single-mode Gaussian-like distribution with a center near 550 nm.

In the good-solvent matrix of polystyrene, the MEH-PPV is present in two conformations,[7] a compact oblong defect coil (type 1) and an extended disc-like defect coil (type 2), as seen in Figure 2. The two conformations lead to different photophysical behavior. The compact defect coil causes partial localization of the exciton in domains on the chain,[8] resulting in blinking of the emission (Figure 2a). In contrast, the extended coil conformation prevents any interchain interactions and the emission intensity shows only continuous changes (Figure 2b). The emission spectra of single MEH-PPV chains in polystyrene are of two types, one similar to the spectra in ZEONEX matrix with a peak near 550 nm (Figure 2c), and one with a more complex shape and a peak near 590 nm (Figure 2d). The spectral maxima from a statistical ensemble of single molecules are plotted in a histogram in Figure 2e. The histogram shows a bimodal distribution with the two bands centered at 548 and 588 nm. We have not directly measured the conformations and spectra on the same chains. Instead, we observed the blinking and bleaching behavior of individual chains during the measurements of the spectra. According to Ref. 7, we then assigned the spectra of continuously bleaching molecules to the extended defect coil (type 2) and the spectra of the blinking molecules to the compact defect coil (type 1) conformations. In the histogram (Figure 2e), the spectra of the blinking molecules (type 1) correspond to the short-wavelength band and those of the continuously bleaching molecules (type 2) to the long-wavelength band. This assignment provides the important missing link between the spectral characteristics on the one hand and the polymer microscopic structure on the other on a truly single molecule level. Previous extensive work on conjugated polymer conformation and spectral properties[5,9] resulted only in information on an average conformation of an ensemble of individual chains and did not allow study of a one-on-one correspondence between the conformation and emission spectrum of the same chain.

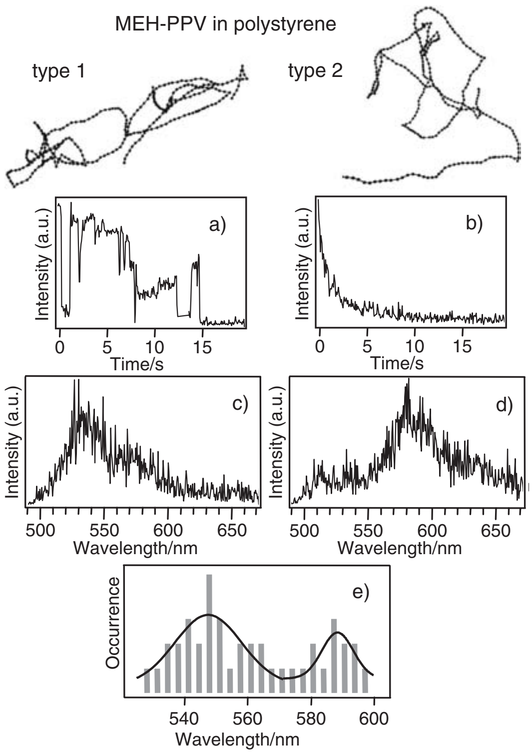

**Figure 2.** Conformation and photophysics of MEH-PPV in low molecular weight polystyrene. Type 1: oblong defect coil; Type 2: extended defect coil. Single chain emission intensity time traces of a) type 1 and b) type 2 conformations. Single-chain emission spectra of c) blinking and d) continuously bleaching molecules. e) Histogram of emission spectral peaks.

There has been a continuing interest in the spectral properties and their origin in the PPV family of conjugated polymers,[9–19] both in the bulk and on a single-chain level. Bimodal distribution of spectral maxima of single chains has been reported before[15] and ascribed to aggregation between different parts of the chain, similar to that proposed to explain spectral properties in solution.[13] Our results point to the interpretation of the long-wavelength spectra as being due to the presence of longer conjugation length segments. The long-wavelength spectra (Figure 2d) correspond to the extended defect-coil conformation where the lack of close proximity and contact between different parts of the chain prevent intersegment interactions (aggregation) and allow for uninterrupted sections of the $\pi$-electron conjugation. Spectra of these longer segments are red-shifted and are superimposed on the shorter-wavelength bands of the remaining segments, resulting in the observed composite spectral shapes, with an overall peak shifted to around 590 nm. On the other hand, in the case of compact defect coils (Figure 2c) and the defect cylinders (Figure 1b) local inhomogeneities (domains) or closer chain packing interrupt the conjugation and lead to a blue shift in the emission spectra. In solutions, torsional motion of the backbone in extended chains was suggested to interrupt the conjugation and cause a blue shift of fluorescence.[14] Such torsional motion is absent in our samples due to the solid-state nature of the films. A recent theoretical work[20] also ruled out aggregation as a cause of the red shift and proposed longer conjugation length in planar sections of the chain as the origin of spectral red shift. Our results thus confirm this interpretation.

In conclusion, we have obtained for the first time a link between chain conformation and fluorescence spectra of the conjugated polymer MEH-PPV. The spectra can be interpreted in therms of the length of the conjugated segments present in the individual chains.

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