

## Communications to the Editor

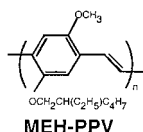
### Single-Molecule Spectroscopy of the Conjugated Polymer MEH-PPV

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Poly[2-methoxy, 5-(2'-ethyl-hexyloxy)-*p*-phenylene-vinylene] (MEH-PPV) is an important electroluminescent polymer that is used extensively in light-emitting diodes and other photonic applications because of its excellent processability and favorable electronic, and spectroscopic properties.<sup>1–3</sup> Commercially available MEH-PPV has a mass-averaged molecular weight of 996,000, with a ratio of mass to number average molecular weights of 2.2. A typical MEH-PPV molecule is comprised of



1700 monomer units. The optical states of MEH-PPV and their dynamics and dependence on the morphology of MEH-PPV are under active investigation.<sup>1–4</sup> It is generally accepted that the optical coherence length for MEH-PPV is  $\sim 10$ – $15$  monomer units,<sup>5,6</sup> and that absorption spectrum is due to the overlapping singlet single absorption of about a hundred weakly coupled, localized quasi chromophores. Correspondingly, the excitations (excitons) are believed to be localized on the order of tens of monomer units, but capable of undergoing energy migration during the singlet excited state lifetime ( $\sim 200$  ps).<sup>7,8</sup>

This paper describes single-molecule spectroscopy<sup>9</sup> on MEH-PPV molecules that were isolated (at about 0.2 molecules per  $\mu\text{m}^2$ ) in a polystyrene spin-coated polymer thin (50 nm–1000 nm) film. Single-molecule fluorescence images, spectra, and intensity kinetic traces (transients) were obtained with a home-built, sample-scanning fluorescence confocal microscope.<sup>10</sup> Molecules were continuously irradiated at 488 nm, which is close to the

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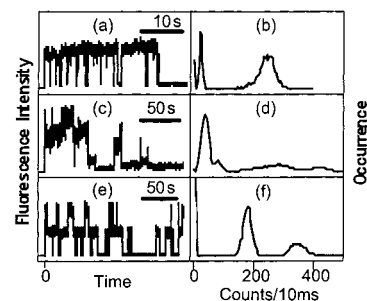
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**Figure 1.** The intensity transients of single molecules (left) and corresponding intensity histograms (right). Panels a–d are from two MEH-PPV single molecules. Panels e–f are the simulation of an intensity transient and the corresponding intensity histogram for a single molecule with two discrete intensity levels.

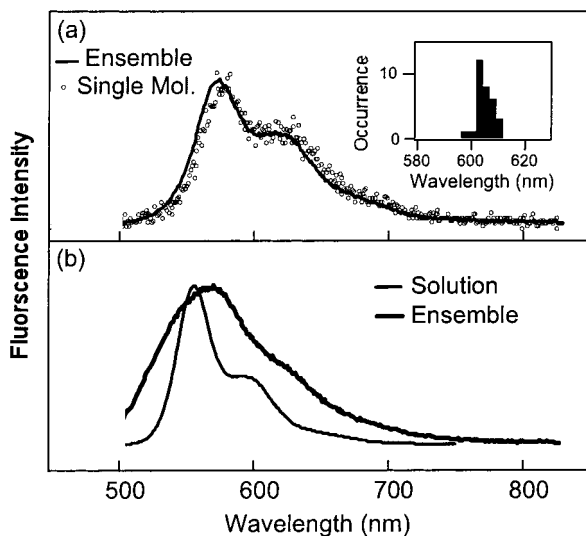
peak of the absorption spectrum. This should generate excitons at random locations along the polymer chain. Typical single-molecule fluorescence intensity vs irradiation time “transients” of MEH-PPV are shown in Figure 1a,c. The transients exhibit large-amplitude, discrete intensity fluctuations. Analogous transients were observed for MEH-PPV, for thin or thick polymer films, for MEH-PPV in a polystyrene or poly(methyl methacrylate) host, and even for MEH-PPV molecules directly on a glass substrate without a polymer host. Many of the transients exhibit a small number (typically 2 or 3) of quasi discrete intensity levels. This is demonstrated by parts b and d of Figure 1, which are intensity histograms of the transients displayed in parts a and c of this figure, respectively, and by parts e and f of Figure 1, which show simulated data for an emitting molecule with two discrete intensity levels. Analogous intensity jumps have been reported for the conjugated polymer dPPV-dPPyV.<sup>11</sup>

An individual intensity jump occurs within one counting period (typically 10 ms) and appears to be due to a single photochemical event. The time interval between jumps is on the millisecond to tens of seconds time scale. The decrease in fluorescence signal is attributed to quenching of singlet excitons of MEH-PPV by reversibly formed, long-lived, photogenerated fluorescence “quencher defect”. The transition from a higher intensity level to a lower one is assigned to the photochemical generation of the quencher defect and from a lower to a higher level to the thermal repair of the quencher defect. Candidates for the quencher defect include the dipolaron, i.e., a separated radical cation/radical anion pair, and certain photooxidation intermediates for conjugated polymers, which have been reported to be efficient singlet excited state quenchers.<sup>12</sup> The quenching efficiency of a single quencher defect was estimated by the fluorescence intensity drop that occurred on the transition from a higher to lower intensity level. The intensity drops were typically  $\sim 20\%$  or greater.

On the basis of a typical quenching efficiency of 20% or greater for MEH-PPV, the intramolecular electronic energy migration length must correspond to at least 400 nm, i.e.,  $\sim 20\%$  of an average single polymer molecule extended chain length. Furthermore, on the basis of a typical excited-state lifetime for MEH-PPV of  $\sim 200$  ps, the implied electronic energy diffusion constant from a simple 3-dimensional bimolecular quenching model is greater than  $4 \text{ cm}^2/\text{s}$ . This is more than a factor of 40 greater

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**Figure 2.** (a) The “ensemble” fluorescence spectrum of 33 MEH-PPV single molecules in a thin-film sample (the solid line) and a typical spectrum for only one of the molecules in the ensemble (dots). The inset is the histogram of first moments of these 33 single molecules. (b) The fluorescence spectrum of 0.01 g/L MEH-PPV in toluene solution (thin line) and the total spectrum of 39 MEH-PPV single molecules in a photolyzed thin-film sample (thick line).

than the bulk diffusion constant for energy migration in pure MEH-PPV films.<sup>13</sup>

The extraordinarily fast diffusion at the molecular level for MEH-PPV could be the consequence of directed energy migration by an energy “funnel” created by the distribution of “chromophoric” energy sites in the polymer.<sup>4</sup> In this model, the funnel directs excitons in polymer molecules to the bottom of the funnel, perhaps partly by a Förster mechanism. For unphotolyzed molecules, the bottom of the funnel is a shallow trap for the singlet exciton and corresponds to the location of the exciton during most of the excited-state lifetime because of rapid energy transfer to the site. After many irradiation cycles, the bottom of the funnel is converted to a quencher site by a photochemical process. After the quencher site is “installed” at the bottom of the funnel, the subsequently generated excitons are directed to the quencher by the funnel and efficiently quenched.

Single-molecule fluorescence spectra of MEH-PPV were recorded one at a time for tens of molecules for each freshly prepared thin-film sample. The spectra were recorded for a relatively short period (<2 s) to minimize photolysis. Figure 2a compares single-molecule and ensemble spectra (sum of several single-molecule spectra) of isolated MEH-PPV molecules in a polystyrene matrix. These spectra are in reasonable agreement with the ordinary fluorescence spectrum of MEH-PPV in dilute toluene solution (thin-line, Figure 2b).

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The single-molecule spectroscopy of many of the samples (e.g., Figure 2a) exhibited highly uniform spectra, despite a large molecular-weight distribution and the expected presence of numerous chemical and structural defects. This is further demonstrated by considering the distribution of first moments  $\langle\lambda\rangle$  of the spectra shown in the insert in Figure 2a. This suggests that chemical defects do not correspond to low-energy traps in the distribution of localized excited state energies, but instead, they apparently shift the distribution toward higher energy by disrupting conjugation along the polymer chain. Thus, the low-energy fluorescence trap sites (at bottom of the “funnel”) apparently simply correspond to straight-chain, conjugated regions of the polymer.

After extensive irradiation, the ensemble spectra (thick line, Figure 2b) exhibited a significant blueshift due presumably to numerous photochemical defects.<sup>14</sup> Some thin-film samples exhibited highly variable, blueshifted spectra even before extensive irradiation, which may be the result of photolysis during the confocal imaging scan.

Further insight into the photophysics of MEH-PPV was obtained by measuring the laboratory frame polarized light spectroscopy of many single MEH-PPV molecules. These data were used to estimate the *ensemble average polarization anisotropy* of the fluorescence  $\langle r_{\parallel} \rangle$  and fluorescence-excitation  $\langle r_{\text{ex}} \rangle$  of the MEH-PPV molecules, respectively  $\langle r_{\text{ex}} \rangle = 0.42 \pm 0.09$  and  $\langle r_{\parallel} \rangle = 0.4 \pm 0.1$ . The value  $r$  is defined as

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} \quad (1)$$

where  $I_{\parallel}$  and  $I_{\perp}$  represent the intensities for single-molecule excitation (or fluorescence) parallel and perpendicular to the direction of maximum excitation (or fluorescence) in the molecular frame.

The experimental fluorescence and fluorescence-excitation anisotropies are much larger than those predicted for a polymer with a Gaussian random coil conformation,<sup>15</sup> which is the reported conformation for MEH-PPV in solution.<sup>5</sup> The anisotropy data herein suggests a considerably more ordered conformation, at least for MEH-PPV in polymer thin films. Furthermore, the conformational order of MEH-PPV may be a critical factor in the previously reported anisotropic optical properties of pure MEH-PPV film.<sup>3</sup>

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**Supporting Information Available:** Detailed information is available on the experimental and theoretical methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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