

Effect of Sample Preparation and Excitation Conditions on the Single Molecule Spectroscopy of Conjugated Polymers

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Extensive new single molecule spectroscopy (SMS) data on the conjugated polymer MEH–PPV at low temperature were obtained. In particular, the combined effects of sample preparation and excitation condition were explored in detail. The data confirm previous observations from this laboratory that (i) the distribution of emission maxima of single MEH–PPV molecules has a bimodal distribution and (ii) the single molecule emission spectrum of MEH–PPV exhibits few time-dependent fluctuations of the emission intensity, band shape, or spectral maxima. These data also help explain the discrepancy among the various published SMS data on this compound and suggest that environmental impurities, long irradiation times, nearby interfaces, and incomplete data sampling may account for some of the discrepancies among the published data.

Single molecule spectroscopy (SMS) has proven to be a unique tool for the investigation of conjugated polymers.^{1–18} It has allowed for the direct measurement of the inhomogeneous spectral distributions of conjugated polymers. SMS has also been used to unravel complex photodynamics in conjugated polymers involving triplet states, photo-oxidation, and various charge transfer processes that would be extremely difficult to measure by ensemble methods. SMS studies of isolated conjugated polymer chains at low temperature have been particularly revealing due to the narrower vibronic bands at these temperatures that have allowed for a more rigorous vibronic analysis.^{13–16,18,19}

There is some discrepancy among the published low-temperature SMS data for the most widely investigated conjugated polymer, poly[2-methoxy,5-(2'-ethylhexyloxy)-*p*-phenylenevinylene] (MEH–PPV).^{6,9,13–19} For example, this laboratory has reported that the distribution of emission maxima for an “ensemble” of MEH–PPV single molecules has a pronounced bimodal distribution with peaks near 2.14 and 2.22 eV at 300 K,² and 2.06 and 2.22 eV at 20 K,^{9,18} while a different laboratory reports that the distribution of emission maxima has a single peak that is significantly blue-shifted.¹⁴ Another apparent discrepancy among different papers in this field is the prevalence of high-amplitude spectral dynamical features including spectral diffusion and discrete large-amplitude fluorescence intensity “jumps”.^{14–16} Papers from some laboratories have reported that these types of spectral dynamics are quite prevalent, while our group, in contrast, have observed large-amplitude spectral dynamics in only a small fraction of investigated molecules.

In this paper, we systematically investigate potential sources of the discrepancy between our results and those reported by other laboratories. For example, Figure 1 compares single molecule spectra and distributions of emission maxima from

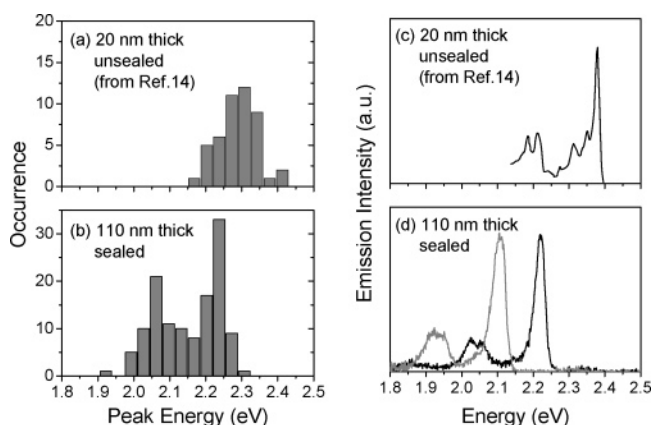


Figure 1. Comparisons of single molecule fluorescence spectra of MEH–PPV reported by different groups by measurement at different experimental conditions. (a) A distribution of emission maxima of single MEH–PPV molecules (from Figure 1 of ref 14). The MEH–PPV molecules were dispersed in an unsealed “thin” (20 nm) polystyrene film on a SiO₂-coated Si substrate at 4 K and wide-field illuminated by 488 nm at 500 W cm^{−2}. (b) An emission peak energy distribution of MEH–PPV molecules dispersed in a Au-sealed “thick” (110 nm) PMMA film on a glass coverslip at 20 K and excited by 488 nm at 200 W cm^{−2} in a confocal configuration. (c) A single molecule spectrum (from Figure 2a of ref 14) obtained at the same condition as (a). (d) Typical single molecule spectra obtained at the same condition as (b).

our laboratory (Figure 1b,d) with those reported by Lupton and co-workers (Figure 1a,c). The distribution of emission maxima shown in Figure 1b has a pronounced bimodal distribution with peaks near 2.06 and 2.22 eV at 20 K.^{9,18} In contrast, the distribution in Figure 1a has a single peak at 2.35 eV at 4 K.¹⁴ A peak at 2.35 eV is surprising, since it significantly exceeds the ensemble emission maxima of bulk MEH–PPV in any other reported environment at cryogenic or room temperature.^{20–24} The discrepancy may be due to the choice of molecules used to construct the histogram. Our laboratory uses >90% of the

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investigated molecules to construct the distribution of emission maxima with no bias with respect to emission wavelength. Lupton and co-workers have selected molecules that preferentially emit in the 500–590 nm region due to experimental considerations.²⁵ Thus, the discrepancy may be a simple consequence of how single molecule data are selected for the ensemble distribution of emission maxima.

Another potential source of variations in the SMS spectra among different laboratories may be due in some cases to photochemical artifacts. Photochemical artifacts are often observed in SMS, because SMS requires an extraordinarily large number of excitations per molecule in a relatively short time period in order to achieve a useful signal-to-noise ratio. Typically, a molecule in a SMS experiment is excited hundreds of thousands to millions of times per second for a few seconds or even much longer. Under these circumstances, photodriven processes with very low probabilities may occur. For example, low quantum yield processes, such as photoelectron injection, photoisomerization, and photochemical reactions with trace impurities, have often been observed in SMS.^{26,27} Particularly problematic are multiphoton-driven processes (both simultaneous and sequential), which can be responsible for complex photochemical pathways that are difficult to anticipate.

For example, continuous single molecule irradiation can generate a large steady-state population of molecular triplet states, which can subsequently undergo a subsequent absorption of a photon or, in an even more complex situation, can undergo a reaction with the host to produce a radical which itself can undergo photophysical or photochemical processes.^{26–28} We have previously shown that photo-oxidation of single molecules of MEH–PPV can produce a long-lived cation form with a blue-shifted emission spectrum.^{2–4} A blue shift of the emission is also consistent with unambiguous photochemical studies on bulk MEH–PPV.²⁹

To minimize artifacts due to photo-oxidation, we rigorously remove oxygen and other environmental impurities by spin-coating our samples in a glovebox, transferring these samples directly from the glovebox to a vacuum chamber located within the glovebox, and then sealing the sample with a metal layer to avoid recontamination. Oxygen and other impurities can assist photo-oxidation of conjugated polymers, probably through the trapping of electrons by oxygen to form superoxide.^{3,4} Photo-induced electron injection may be a surprisingly efficient process for conjugated polymers under continuous irradiation conditions, since such irradiation generates a high steady-state probability of the conjugated polymer occupying a triplet state. A conjugated polymer molecule possessing a triplet state should have a relatively high probability of undergoing photoionization if it absorbs an additional photon. We believe that such multiphoton ionization events occur several times a second for MEH–PPV under moderate excitation conditions. If an electron scavenger such as oxygen is present, this pathway leads to photo-oxidation of the polymer chain. Additionally, if a reactive interface such as the surface layer of SiO₂ is near the MEH–PPV molecules, photo-oxidation may be assisted, because SiO₂ is known to trap negative charges in conjugated polymers.³⁰

We tested the photo-oxidation hypotheses by studying unsealed samples of MEH–PPV dispersed in thick (110 nm) and thin (20 nm) poly(methyl methacrylate) (PMMA) films, as shown in Figure 2. The data clearly show that the average emission intensity was significantly lower in the 20 nm sample. This is shown in the confocal microscopy images of a single molecule sample in Figure 2a,d and line scans of these images (Figure 2b,e). This is consistent with surface-induced photo-

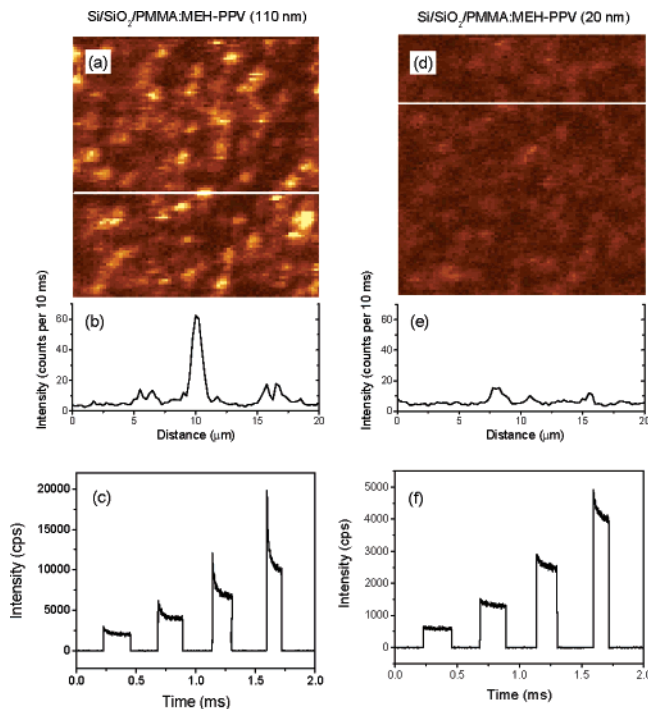


Figure 2. Comparisons of emission of MEH–PPV molecules dispersed in (a–c) “thick” and (d–f) “thin” unsealed PMMA films on SiO₂-coated Si substrates. The average intensity of about 100 molecules in a “thick” film is 6 times greater than that in a “thin” film, which is represented in the typical confocal images (a,d) and their line scans (b,d). In addition, excitation intensity modulation data are also significantly affected by the film thickness of PMMA matrixes, where MEH–PPV molecules are dispersed. (c) Ensemble of modulation data from 12 MEH–PPV molecules in a “thick” film exhibit strong initial intensity, fast decay, and large contrast ratio, while (f) ensemble of modulation data from 33 MEH–PPV molecules in a “thin” film show very weak intensity, slow decay, and small contrast ratio. The intensities of excitation square pulses are 300, 700, 1400, and 2400 W cm^{−2} from the left, respectively.

oxidation of single molecules, since photo-oxidation is known to produce a lower emission quantum yield.³⁰ We routinely use thick PMMA layers in order to avoid surface perturbations.

We also studied the triplet-state lifetime of the single molecules as a function of PMMA layer thickness, using the recently developed excitation intensity modulation technique.^{7,9} The thin layer sample showed much less fluorescence intensity modulation, indicating that triplets are rapidly quenched in the sample. We attribute this quenching to the presence of positive charges. Recently, we showed that positive charges are highly efficient quenchers of triplet states in conjugated polymer molecules.⁸ Thus, the thinner sample shows clear evidence of perturbation due to photo-oxidation.

Besides the layer thickness effect, we also have shown that sample sealing and preparation in an inert atmosphere/vacuum system combined apparatus can aid in the suppression of spurious photochemical processes. This is demonstrated in Figure 3, where most MEH–PPV molecules in our sealed samples show no intensity fluctuations under low-intensity irradiation conditions (Figure 3a), but an unsealed system in a vacuum system shows clear intensity fluctuations. This clearly shows that small amounts of impurities in the sample can greatly distort the measured single molecule spectroscopy data. Interestingly, even the relatively clean, sealed sample shows intensity fluctuation at very high irradiation intensities (as shown in Figure 3c).

It is likely that the spectral diffusion and intensity fluctuation effects observed with high-intensity CW irradiation is a

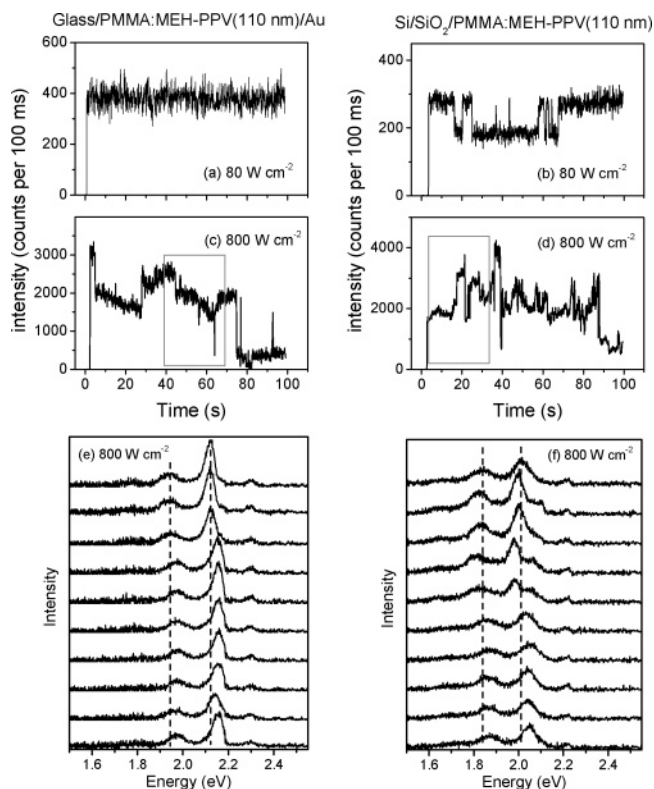


Figure 3. Effect of excitation intensity on “flickering” and spectral diffusion of single MEH-PPV molecules dispersed in sealed (left) and unsealed (right) PMMA films. (a–d) Typical transients of emission intensity of MEH-PPV single molecules at 20 K were recorded with a 0.1 s acquisition time. At the low excitation intensity, most of MEH-PPV molecules (>90%) in a sealed PMMA film (a) exhibit stable emission in intensity and spectral shape for longer than 1 min, which was consistently observed in ref 18, while more than half of the molecules in an unsealed PMMA film (b) show “flickering” emission intensity within 1 min. On the other hand, at the higher excitation intensity, emission of molecules in both sealed and unsealed PMMA films becomes unstable in intensity, spectral shape, and position. While the transients (c,d) were recorded at the higher excitation intensity (800 W cm^{-2}), consecutive 3 s emission spectra were acquired at the same time. The bottom panels (e,f) are 10 consecutive representative spectra, and the corresponding periods for (e,f) are marked as the gray boxes in the transients (c,d), respectively.

photochemical effect. Multiphoton ionization apparently leads to ejection of the electron far from the single molecule chain, which is ultimately trapped by a residual impurity or sample substrate interface. In any case, the intensity fluctuations and associated fluctuations of the emission band shape and emission maxima (Figure 3e,f) are clearly primarily photochemically or photophysically driven. In other words, they are not a statistically significant intrinsic thermal behavior of MEH-PPV. The reports of prevalent intensity fluctuations and spectral diffusion reports may be due to such photochemical effects.¹⁶ For example, in the samples where MEH-PPV molecules are in direct contact with the SiO_2 interface, photochemical artifacts might be expected to be more severe,³⁰ since the MEH-PPV molecules are not protected by polymer encapsulation. Finally, in some published experiments, MEH-PPV was encapsulated by the poly(vinyl alcohol) (PVA). PVA is known to be highly perturbative in SMS experiments due to photochemistry involving hydroxyl groups.²⁶

Further evidence that the highly blue-shifted spectra can be induced by photochemical artifacts was obtained by examining the spectroscopy of MEH-PPV single molecules before and after brief irradiation by high peak intensity femtosecond pulses.

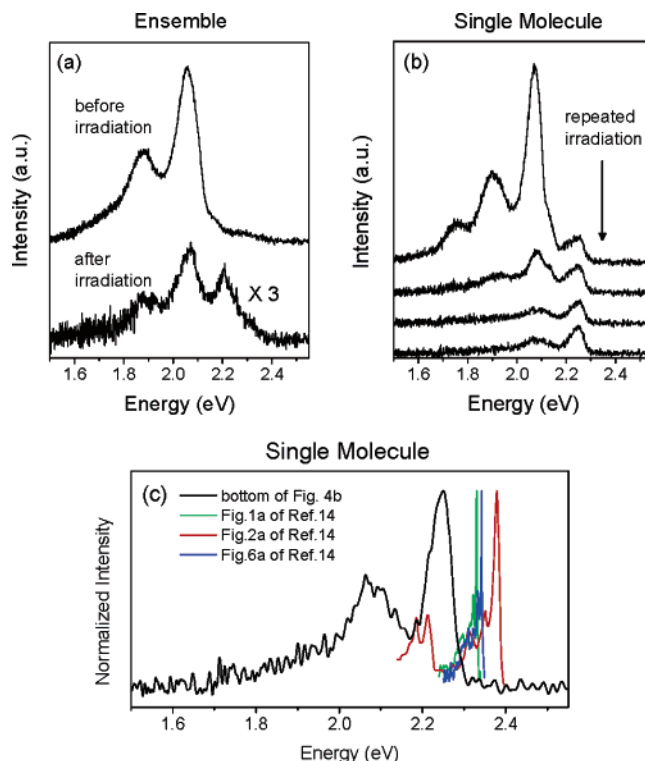


Figure 4. (a) Comparison of the ensemble spectra of 50 single MEH-PPV molecules dispersed in a Au-sealed 110-nm-thick PMMA matrix at 20 K measured before and after femtosecond pulse irradiation. The femtosecond pulse was irradiated by scanning the beam over the whole area with an average intensity of 130 W cm^{-2} for an average irradiation time of 0.5 s for a molecule. The CW excitation intensity for spectrum measurement was 160 W cm^{-2} . (b) Irreversible spectral progression of a single MEH-PPV molecule are shown in spectra measured between repeated irradiations of femtosecond pulses on the molecule with an intensity of $\sim 10 \text{ W cm}^{-2}$ for 3 s. (c) An emission spectrum of a photodamaged MEH-PPV molecule after repeated femtosecond pulse irradiation (the bottom of Figure 4b) is compared with emission spectra of MEH-PPV molecules reported by Lupton and co-workers.¹⁴

Since multiphoton processes are highly excitation intensity dependent, irradiation with femtosecond pulses should dramatically increase the quantum yield of photo-oxidation. Before irradiation, the emission spectra of our sample were observed to peak at low energy as expected from our previous studies (see Figure 4a,b). In contrast, after irradiation, the SMS spectra exhibited a large blue shift and a concomitant drop in emission quantum yield. Thus, unequivocal generation of photochemically damaged MEH-PPV produces the same trends observed in the SMS data of Lupton and co-workers (Figure 4c).

In summary, new experiments on the effect of sample preparation and excitation conditions on the single molecule spectroscopy of MEH-PPV have verified, as previously reported from this laboratory, that (i) the distribution of emission maxima of MEH-PPV exhibits a dual peak emission histogram and (ii) the emission intensity, band shape, and spectral maxima exhibit few fluctuations. Additionally, the potential role of photochemical artifacts in the SMS of MEH-PPV was extensively investigated.

Samples of poly[2-methoxy,5-(2'-ethylhexyloxy)-*p*-phenylenevinylene] (MEH-PPV, Uniax, $M_w \approx 1\,000\,000$) were prepared by the following procedure. MEH-PPV was diluted in a toluene solution of poly(methyl methacrylate) (PMMA, Aldrich), and the solution was spin-coated on a glass coverslip or a SiO_2 -coated Si wafer in a N_2 -filled glovebox. The PMMA film thickness was 110 or 20 nm. For sealed samples, the

PMMA-coated glass coverslip was transferred directly to a thermal evaporator, and a gold film (200 nm thick) was evaporated on the PMMA layer. Then, both sealed and unsealed samples were transferred into a cryostat and kept under a vacuum of $<10^{-5}$ mbar. The experimental setup for the low-temperature scanning confocal microscope is described elsewhere.^{9,18} Briefly, the 488 nm line of an Ar ion laser was focused to a spot diameter of ~ 700 nm using a $40\times$, 0.6 NA objective lens. Images were obtained by moving an entire cryostat on a motor-driven x - y stage (Newport, ILS50CCHA). The fluorescence signal was split into two beams: One was directed to an avalanche photodiode, and the other was directed to a spectrometer composed of a monochromator and a CCD. For the photodamaging study by femtosecond laser pulses, 200 fs pulses centered at 488 nm (width of 5 nm, repetition rate of 250 kHz) were generated by an optical parametric amplifier (Coherent, OPA 9400) pumped by a regenerative amplifier. The femtosecond beam was introduced collinear with the CW beam using a beam splitter. The pulse duration at the sample position is estimated to be ~ 1 ps due to dispersion mainly by the objective lens.³¹ For excitation intensity modulation experiments,^{7,9} a sequence of excitation pulses was repetitively generated by an acousto-optic modulator and a programmable function generator. The signal from the APD was synchronized to a multichannel scaler.

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