

Low-Temperature Single-Molecule Spectroscopy of MEH-PPV Conjugated Polymer Molecules

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Relatively narrow bandwidth fluorescence spectra were observed from isolated single molecules of the conjugated polymer, MEH-PPV (poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene]) at low temperature. The spectroscopy reveals rich spectral information in energy relaxation pathways and structure of this important electroluminescent material. From room temperature to 20 K the fluorescence of MEH-PPV molecules was found to red-shift by ~ 20 nm along with a decreased electron–phonon coupling. The fluorescence spectra give clear evidence for efficient electronic energy funneling to a small number (one in some cases) of low-energy sites, each with an increased effective conjugation length compared to room temperature.

Introduction

The electronic and optical properties of conjugated polymers have been widely investigated due to the utility of materials of this type in various molecular optoelectronic devices, such as organic light-emitting diodes (OLED), plastic electronics, sensors, and solar cells.¹ Furthermore, many important fundamental issues regarding the electronic properties and processes of this unique class of semiconducting materials remain to be resolved. This contribution is focused on the prototypical conjugated polymer, poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV), which has been extensively investigated.^{2–7} Light absorption and emission in conjugated polymers are believed to involve quasi-localized chromophores on the polymer chains.⁸ A conjugated polymer behaves as a multi-chromophore molecular system because of a great number and broad distribution of conjugated segments on the polymer chain connected by chemical and structural defects.^{9,10} For the MEH-PPV molecules in this study, there are ~ 200 effective chromophores, each with ~ 10 – 17 repeat units in conjugation length,¹¹ in a single molecule. Absorption of photons excites different chromophores on the polymer chain.

Efficient electronic energy transfer is believed to funnel the excitation to the lowest-energy chromophores (exciton trap) with longer conjugation length during the exciton lifetime (~ 300 ps).⁸ Thus, the fluorescence properties most often characterize those of the few low-transition-energy exciton traps in a conjugated polymer molecule despite its multichromophore nature in light absorption.

The spectroscopic properties of conjugated polymers are greatly influenced by the conformational structure of the polymer chains.^{12,13} Single-molecule spectroscopy (SMS)^{14,15} has been proven very valuable in understanding the conformational and optical properties of conjugated polymers,^{8,16–18} and energy-transfer process in multichromophoric dendrimers.^{19,20} Previous single-molecule spectroscopic studies of conjugated

polymers dispersed in an inert polymer host have revealed important information in fluorescence intensity fluctuation, fluorescence wavelength distribution, and lifetime.^{8,17} Single-molecule polarization spectroscopy, combined with theoretical simulation, has provided insight into the conformations adopted by conjugated polymer molecules in a polymer matrix.^{16,21} Recently, nanostructures comprising single MEH-PPV molecules have been orientated perpendicularly to the support substrate, and highly polarized and narrow bandwidth emission was observed from these individual molecules.^{18,22} Photon antibunching effect has been reported for fluorescence of single conjugated polymer molecules, suggesting only a few or even a single emissive site per polymer chain.^{23,24} These results have contributed greatly to our understanding of the conformational property and the energy-transfer process in polymer chains.

However, due to the extreme structural heterogeneity exhibited by conjugated polymer molecules, the understanding of the energy-transfer process in conjugated polymers is still very limited, especially regarding the role of the polymer chain conformation in this important process. For example, it is unknown whether the two polymer chain conformations¹⁶—defect coil and defect cylinder—have the same energy transfer efficiency. In the present study, we investigate MEH-PPV molecules dispersed in PMMA and polystyrene using low-temperature single-molecule imaging and spectroscopy. This technique has previously been successfully employed to investigate the spectroscopic properties of single inorganic nanocrystals²⁵ and individual natural light-harvesting complexes.^{26,27} Very recently, low-temperature single-molecule spectroscopy on a rigid-rod conjugated polymer, the ladder-type poly(*p*-phenylene) (MeLPPP), has been reported, revealing a fluorescence spectral line width down to 2.5 meV at 5 K.^{28,29} In the present study, extraordinarily narrow fluorescence (for conjugated polymers) is observed from isolated MEH-PPV molecules. The very narrow bandwidth of low-temperature fluorescence enables us to resolve emission from different chromophores on the MEH-PPV polymer chain, which were mostly hidden in previous single-molecule spectroscopy at ambient temperature.^{8,16–18} These results provide spectral evidence that multiple energy-

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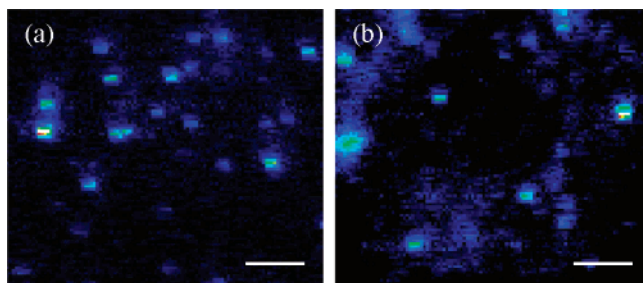


Figure 1. Wide-field fluorescence images of MEH-PPV molecules dispersed in PMMA matrix under 488 nm excitation at (a) room temperature, 300 K, and (b) low temperature, 20 K. The scale bars in both images are 10 μm .

transfer channels are present in a conjugated polymer chain. The low-temperature study presents much richer spectral information of isolated MEH-PPV molecules, which should help to further understanding of the optical properties of conjugated polymer materials.

Experimental Section

MEH-PPV used in the present study was supplied by Uniax Corp. The MEH-PPV molecules have a number-averaged molecular weight of 453,000 and a polydispersity of 2.2, with ~ 1700 monomer units in a typical polymer chain. Appropriate concentrations of MEH-PPV solutions were prepared by dissolving MEH-PPV molecules in solutions of 1% (by weight) polystyrene ($M_w = 44,000$, Aldrich) in toluene, 5% PMMA ($M_w = 96,700$, Aldrich) in toluene, or 1.5% PMMA in chloroform. The solution was spin-cast onto a 1-mm thick quartz disk to yield a uniform film with a thickness of ~ 100 nm as measured by an atomic force microscope (AFM). The quartz disk was mounted to the coldfinger of a liquid helium optical cryostat (Janis ST300-MS) by using the thermal-conductive grease (Apiezon N). The coldfinger temperature was 8 K. Actual sample temperature should be higher than 10 K, mainly due to IR radiation and the poor thermal conductivity of the substrate. We estimate it to be 20 K.

Wide-field imaging of MEH-PPV molecules was conducted by using an optical microscope (Zeiss Axio100) in the epifluorescence mode. The noncollimated excitation laser light was focused by a microscope objective ($\times 40$, NA 0.6) to a spot of ~ 50 μm on the sample. Typical excitation laser power was 0.25 mW, corresponding to an excitation intensity of 100 W/cm². The fluorescence was collected by the same objective, passed through a dichroic mirror, filtered by a Notch filter, and focused by a tube lens to the entrance slit of a spectrometer (Acton SP150) equipped with a liquid nitrogen-cooled CCD detector (Roper Scientific). The spectrometer was equipped with a mirror and a 300 groove/mm grating, used for fluorescence imaging and spectral measurement, respectively.

In fluorescence polarization measurement with 488 nm excitation, the dichroic mirror was checked to make sure that it does not cause transmission polarization distortion at MEH-PPV fluorescence wavelength. A circularly polarized 488 nm light was used to excite the sample. A polarization analyzer was placed before the spectrometer. The images were recorded by the CCD for different analyzer polarization directions.

Results and Discussion

Figure 1 shows the typical wide-field fluorescence images of single MEH-PPV molecules under 488 nm excitation at 300 and 20 K respectively. The low coverage of MEH-PPV

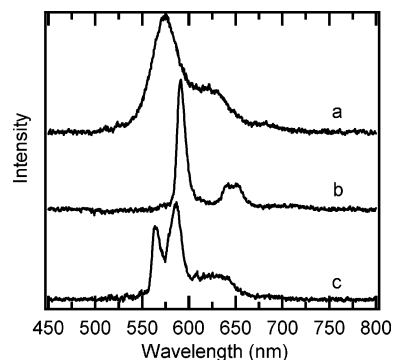


Figure 2. Comparison of room-temperature and low-temperature single-molecule fluorescence spectra of MEH-PPV. (a) A typical single-molecule spectrum of MEH-PPV at 300 K. (b) A single-molecule spectrum of MEH-PPV at 20 K characteristic of single-chromophore emission. (c) A single-molecule fluorescence spectrum of MEH-PPV at 20 K characteristic of multichromophore emission.

molecules on the substrate, $< 1/100$ μm^2 , ensures that single individual molecules are being excited and detected. The bright spots in the images correspond to individual MEH-PPV molecules. The signal-to-noise is lower at 20 K than at room temperature, principally resulting from a large increase in the background emission from the polymer matrix at low temperature. Due to the low partial pressure of O₂ in the vacuum cryostat, and the slow diffusion of O₂ in polymer film,⁸ MEH-PPV molecules were observed to be very photostable. (Photo-oxidation is the dominant photochemical process for MEH-PPV.) Typically, the molecules could withstand over 1 h of irradiation without photobleaching.

Similar spectroscopic behaviors are observed in the present study with polystyrene and PMMA as the host matrix, although it was previously shown by room-temperature SMS that the photophysical properties of individual molecules of MEH-PPV depend on the nature of the host matrix.³⁰ In addition, polystyrene polymer matrix exhibits stronger background emission at 20 K than PMMA. The results discussed below were mainly based on measurements with PMMA as the inert matrix.

Narrow Fluorescence at Low Temperature. Typical 20 K single-molecule fluorescence spectra of MEH-PPV polymer is shown in Figure 2, compared to the typical 300 K single-molecule spectrum. Two types of low-temperature spectra were observed: single-chromophore type fluorescence and multichromophore type fluorescence, exemplified by the spectra b and c in Figure 2, respectively. As expected, the 20 K spectra are much narrower than the 300 K spectra, with the spectral line width (full width at half-maximum, fwhm) decreasing from ~ 37 nm (or ~ 1120 cm⁻¹ in energy) at 300 K to 10 nm (~ 300 cm⁻¹ in energy) at 20 K. The 0–0 and 0–1 vibronic peaks are more clearly resolved in the 20 K single-chromophore type fluorescence (spectrum b in Figure 2), the narrowest and best resolved spectrum ever reported for MEH-PPV molecules. This spectrum is also narrower than the fluorescence spectra of PPV oligomers dispersed in PMMA matrix at 77 K.³¹ We note that the multichromophore type single-molecule fluorescence spectrum has previously been observed at 300 K,⁸ but they are more prominent at 20 K because of the narrow spectral line width achieved at low temperature.

The narrow, single-chromophore type 20 K single-molecule spectrum of MEH-PPV in Figure 2 reveals two active vibrational modes, similar to the phonon replica structure observed in PPV film at 16 K.³² The two vibrational modes are located at ~ 1580 and 1290 cm⁻¹, respectively, both corresponding to C–C vibrations on the polymer chain backbone.

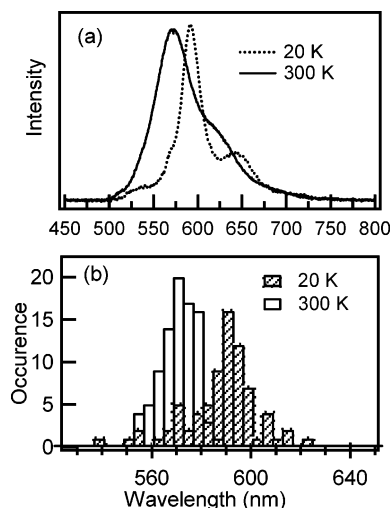


Figure 3. (a) Ensemble fluorescence spectra of single MEH-PPV molecules at 300 K (solid line) and 20 K (dotted line). (b) Distribution of the peak wavelength of single-molecule fluorescence spectra of MEH-PPV at 300 K (open bar) and 20 K (filled bar).

The relative intensity of the phonon replicas with respect to the zero-phonon line is also very different at low temperature than at room temperature. This effect is best characterized by the Huang–Rhys parameter, S , which describes the strength of the electron–phonon coupling in a molecule. The zero-temperature Franck–Condon factors are related to S by the following equation:^{3,33}

$$\frac{I_{n-0}}{I_{0-0}} = \frac{S^n e^{-S}}{n!}$$

The value of S can be determined from the 1–0 transition intensity relative to 0–0 transition intensity:³³

$$S = \frac{I_{1-0}}{I_{0-0}}$$

The typical 20 K narrow single-chromophore fluorescence spectrum in Figure 2 gives $S_{20K} = 0.18$. Deconvolution analysis of the 300 K spectrum in Figure 2 results in $S_{300K} = 0.34$. A decreased S parameter at 20 K implies a longer effective conjugation length and a more delocalized exciton wavelength over more repeat units in the polymer chain, which could result from the freezing out of the torsion modes of polymer chains at low temperature.³

A longer conjugated length of polymer chains should also be manifested by a red-shift in the fluorescence spectrum of a polymer molecule at 20 K. The single-molecule spectra from ~ 80 molecules, at 300 and 20 K, respectively, are added up to obtain the ensemble spectra of MEH-PPV molecules, shown in Figure 3a. The 20 K ensemble spectrum is red-shifted by ~ 20 nm compared to the 300 K spectrum. Figure 3b displays the single-molecule fluorescence peak wavelength distribution for 300 and 20 K, respectively. In constructing the 20 K distribution, all the 0–0 peaks in a multichromophore type spectrum are counted, thus resulting in a broader distribution at 20 K in Figure 3b. Consistent with the ensemble spectra, the peak wavelength distribution also shows a ~ 20 nm red-shift from 300 to 20 K. Harrison et al. observed a similar ~ 20 nm red-shift in MEH-PPV thin film fluorescence from 300 to 20 K.³⁴ Although we could not follow the spectral change of the same MEH-PPV molecule with decreasing temperature, our statistical results are

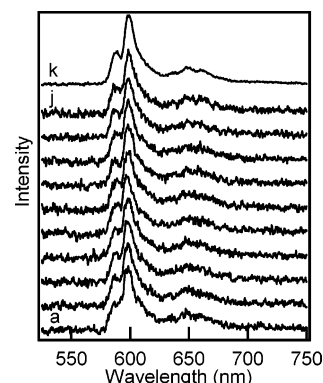


Figure 4. Consecutive 1-min fluorescence spectra of a multichromophore-emitting MEH-PPV molecule at 20 K under continuous-wave 488 nm excitation (a–j) and a 6-min spectrum of the same molecule (k). No spectral diffusion is observed.

convincing that the fluorescence of MEH-PPV molecules is red-shifted by ~ 20 nm from 300 to 20 K.

The effective conjugation length in MEH-PPV molecules can be estimated on the basis of the calculation by Chang et al.³⁵ The zero-order transition energy for a MEH-PPV oligomer with N repeat units is $E(N) = E_0 + 2\beta \cos[\pi/(N+1)]$ where $E_0 = 34,400 \text{ cm}^{-1}$ and $\beta = -8800 \text{ cm}^{-1}$.³⁵ Fluorescence close to 590 nm has been assigned to oligomer $N = 8$ by Kumar et al.²² Using the equation given above, the transition energy difference between oligomer $N = 8$ and $N = 6$ is calculated to be 680 cm^{-1} , very close to the fluorescence distribution peak energy difference from 300 to 20 K. (Wavelength 569 nm to 590 nm corresponds to 625 cm^{-1} energy difference.) Thus, the average fluorescence peak wavelength 569 nm at 300 K corresponds to a conjugated segment length of 6 repeat units. At 20 K, the red-shifted emission peak at 590 nm is estimated to relate to an increase in an effective conjugation length by 2 repeat units.

Multichromophore Fluorescence. More than 50% of the MEH-PPV molecules studied show the multichromophore type fluorescence spectra. Figure 4 displays 10 consecutive 1-min spectra and an additional 6-min spectrum of a multichromophore emitting MEH-PPV molecule at 20 K. The spectra show very little spectral diffusion within the time resolution of 1 min over this long time period, unlike those observed in 300 K spectra of MEH-PPV on glass cast from toluene solution.¹⁷ We also prepared samples in chloroform. Identical spectral behavior was observed. The multiple peaks in Figure 4 are apparently not due to spectral diffusion. Rather, depending on the polymer chain conformation, two or more segments in the polymer can emit simultaneously, if the energy-transfer interaction between them is very weak.

Occasionally, slow blinking can be observed in single MEH-PPV molecule fluorescence at 20 K. Figure 5 shows the intensity transients for two MEH-PPV molecules under continuous wave 488 nm excitation at 20 K. These transients were obtained from 2 s fluorescence intensity imaged consecutively for total ~ 20 min. Any blinking off/on events faster than 2 s are not observable with this CCD imaging method. Most fluorescence transients exhibit fluctuation by $\lesssim 30\%$, as in Figure 5a, possibly resulting from faster blinking events and photon noise. Figure 5b shows an intensity transient with a ~ 200 -s off-time period. The blinking off/on could be due to reversible photoinduced generation of quenchers on the polymer chain involving O_2 , which is the dominant mechanism for room-temperature blinking of MEH-PPV.⁸ In our low-temperature setup, the sample is in high vacuum; also the O_2 diffusion in PMMA matrix at 20 K

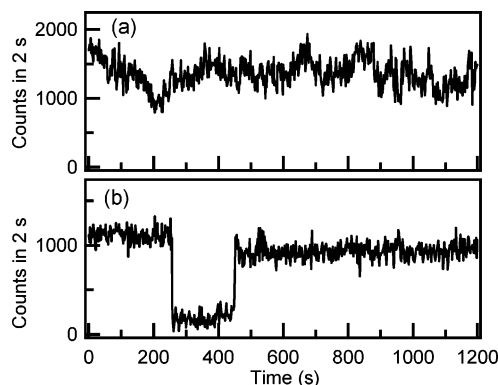


Figure 5. Fluorescence intensity transient of two single MEH-PPV molecules at 20 K under continuous wave 488 nm excitation. The bin width is 2 s.

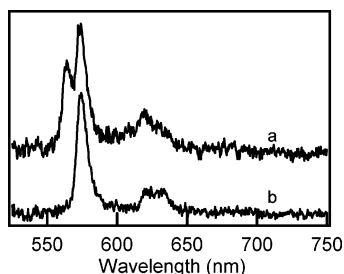


Figure 6. Two 20 K fluorescence spectra of a single MEH-PPV molecule showing the photobleaching of one of the emitting chromophore.

is very slow. This could explain why the blinking is not frequent, and also the observed long off-time period.

Figure 6 shows two fluorescence spectra of a same MEH-PPV molecule, indicating the change from multichromophore type to single-chromophore type. Initially two chromophores are both emitting. Then the blue chromophore blinks off or is photobleached, leaving only the red chromophore emitting. The red chromophore emission position does not change whether the blue one is on or off. This is indicative of essentially two independent low-energy exciton traps for this MEH-PPV molecule at low temperature. Published room-temperature single-molecule MEH-PPV data also shows evidence of multiple trapping sites in a single molecule.^{8,17} In particular, the average quenching depth of only 30% for photogenerated nonradiative traps in MEH-PPV indicates that energy can only migrate a fraction ($\sim 1/3$) of a typical MEH-PPV molecule. This suggests that energy transfer occurs approximately independently within domains within a single molecule. The results on low-temperature MEH-PPV is consistent with the domain concept³⁶ although, considering the sharpness of the spectra at low temperature, the domains may have more to do with spectral overlaps among the various donors and acceptors in the energy funneling process than with simply the intramolecular distance.²⁸

Insights into the MEH-PPV conformations responsible for the multi- and single-chromophore type emission can be found in previous theoretical simulation and experimental investigation¹⁶ of MEH-PPV molecules with tetrahedral chemical defects resulting from incomplete elimination in polymer synthesis, where carbon-carbon double bonds in the phenylene-vinylene backbone are replaced by single bonds. Two distinct conformations predicted by simulation are the defect coil and the defect cylinder structure. The defect coil is a loose and extended structure involving rodlike segments joined by defects, while the defect cylinder has a much compact, ordered, collapsed form. The fluorescence of conjugated polymers often reflects the

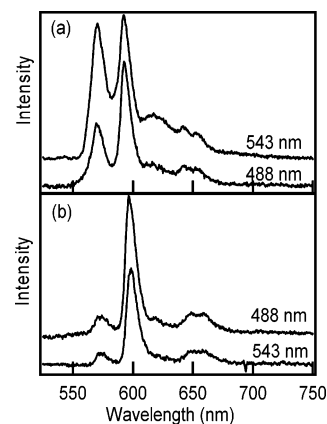


Figure 7. (a, b) Fluorescence spectra of two MEH-PPV molecules at 20 K under 488 and 543 nm excitation. The emission peak positions are the same under 488 and 543 nm excitation.

spectral properties of lowest-energy chromophores (exciton traps) with long conjugation length, due to the efficient electronic energy transfer. Depending on the conformational structure of a MEH-PPV polymer chain, it is not necessary that a molecule has only one funneling channel leading to only one low-energy chromophore. This might be most probable for the MEH-PPV molecule adopting the ordered defect cylinder conformation, where the individual segments are parallel and close to each other, and intrachain energy transfer to the lowest-energy chromophore is thought to be very efficient and complete. For MEH-PPV molecules with a defect coil conformation, it is possible that there are more than one energy funneling channel, for example, with two low-energy chromophores located on the two different ends with a separation longer than the Förster radius. In this case, where the two low-energy chromophores are relatively independent, a multichromophore type fluorescence spectrum, as shown in Figure 2, is expected.

Further insight into energy transfer in MEH-PPV molecules results from the fluorescence measurement by two-color excitation. The fluorescence spectra of the same MEH-PPV molecules at 20 K were measured under 488 and 543 nm excitation, respectively. Figure 7 shows the fluorescence spectra of two MEH-PPV molecules under excitation by these two wavelengths. Both excitation wavelengths give very similar fluorescence spectra, except slight deviation in spectral peak relative intensity. Although the two different excitation wavelengths excite different chromophores on the polymer chain, the fluorescence spectral positions do not change measurably, implying that the electronic energy is funneled to the same low-energy segments regardless of initial excitation energy.

Fluorescence Polarization. The absorption anisotropy of single MEH-PPV molecules has previously been measured to infer their conformational structure.^{16,21} Because MEH-PPV molecules at 20 K are photostable for a long period, we could use CCD imaging technique to determine the fluorescence polarization. Figure 8a displays the fluorescence intensity I change with the analyzer polarization direction θ for a molecule at 20 K. The data were fit with the equation,

$$I(\theta) = I_0(1 + M \cos 2(\theta - \phi))$$

where M is polarization anisotropy and ϕ is the phase angle. The values of M and phase angle ϕ for 15 single molecules are plotted in Figure 8b. The phase angle is randomly distributed, indicating no polarization distortion from the optical components. The average M value is about 0.46, very close to the

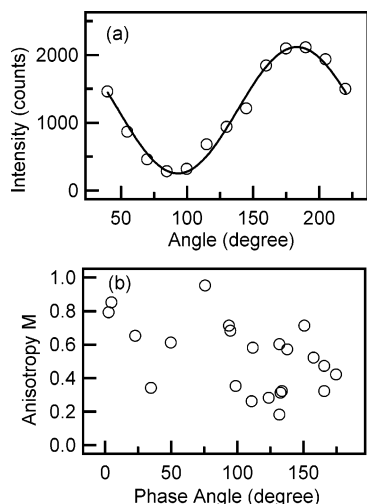


Figure 8. Fluorescence polarization of single MEH-PPV molecules. (a) Fluorescence intensity of a single MEH-PPV molecule at 20 K as a function of analyzer angle. The solid curve is the fit to a sine-squared function. (b) Plot of the fluorescence polarization anisotropy M vs polarization phase angle.

value of the absorption anisotropy obtained previously for MEH-PPV molecules.^{16,21} Ideally, single-chromophore type emission should show high polarization. Some molecules measured do show high M value close to 1. Most of the molecules have intermediate polarization anisotropy. This is consistent with the spectral property that most molecules are multichromophore type. A direct correlation of fluorescence spectrum with absorption and emission anisotropy would enable us to determine the conformation of the MEH-PPV molecules giving different types of fluorescence spectra, but this has not yet been accomplished.

Temperature Effect on Energy Transfer. The red-shift and concomitant decreasing Huang–Rhys parameter in fluorescence spectra of MEH-PPV at low temperature are usually interpreted as a result of increased segment conjugation length due to the freezing out of the torsional modes at low temperature.³ However, some evidence suggests an additional mechanism involving temperature dependence of the energy-transfer process itself might be a factor.^{37,38} Based on this mechanism, there are fewer stationary, low-energy exciton traps available at high temperature. The excitons cannot migrate easily and are more localized by conformational relaxation (self-trapping) at high temperature. This appears to explain the temperature dependence of the fluorescence spectra for some oligomers. To address this issue, further investigation on the temperature dependence of the single-molecule fluorescence spectra from the same MEH-PPV molecules is under way.

Summary and Conclusion

We have observed extremely narrow bandwidth fluorescence from single MEH-PPV molecules at low temperature (20 K). The narrow fluorescence line width enables us to distinguish two types of single-molecule fluorescence spectra of MEH-PPV, characteristic of single-chromophore emission and multichromophore emission, respectively. With decreasing temperature from 300 to 20 K, the ensemble fluorescence of single MEH-PPV molecules is red-shifted by 20 nm, with a concomitant decrease in electron–phonon interaction. This demonstrates that the emission at low temperature is due to excitons delocalized over longer conjugated segments on the polymer chain. The observation of multichromophore type single-molecule fluores-

cence spectra indicates that multiple energy-transfer channels are present in a single MEH-PPV molecule, which probably depend on the conformational structure of a polymer chain. Further temperature-dependent single-molecule spectroscopy study of MEH-PPV molecules should yield more insights into the energy-transfer process in conjugated polymer molecules.

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