

Solvent-Induced Photoemissions of High-Energy Chromophores of Conjugated Polymer MEH-PPV: Role of Conformational Disorder

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Abstract: This study examined the photoemission behaviors of isolated chains of poly[2-methoxy, 5-(2'-ethylhexyloxy)-1,4-phenylenevinylene](MEH-PPV) dispersed in various solvents including dichloromethane, chloroform and tetrahydrofuran(THF). A change in polymer-solvent interactions in these solutions caused the MEH-PPV chains to adopt different local conformations, which in turn affected their radiative de-excitation pathways. For the polymer in dichloromethane and chloroform, in which the conjugated chains are relatively extended, photoemission occurs mostly at the long chromophores with lowest HOMO-LUMO energy gap. Their emission spectra showed a main peak at ~560 nm. Dual photoemission of high- and low-energy chromophores was observed when the conjugated chains were forced to partially collapse in a poor solvent THF. Novel high-energy peaks and a typical low-energy peak were detected at ~414 nm and ~554 nm, respectively. The observation of the high-energy peaks indicates significant suppression of the intrachain energy transfer process, which was attributed to the increase in conformational disorder in the partially collapsed coils. An analysis of the excitation spectra suggests that the high-energy peaks belong to short chromophores constituting of one or two repeat units. This study systematically investigated the effects of polymer concentration, temperature and single bond defects along the backbone on the photoemission of the high-energy chromophores.

Keywords: solvent effects, conjugation length, photophysics, fluorescence spectroscopy.

Introduction

The potential of conjugated polymers as a material for various applications such as organic light emitting diode,^{1,3} plastic solar cell,^{4,5} molecular sensor⁶ and molecular electronics⁷ has triggered researchers to investigate their physical properties including electro- and photoluminescence as well as electrical conductivity. The ideal structure of conjugated backbone constitutes of alternated single and double/triple bonds, making it a relatively rigid chain. However, the synthetic procedure usually generates some saturated bonds (or chemical defects) in the polymer backbone.⁸⁻¹¹ In addition, the conjugated backbone can fold or twist introducing physical defects when chain length exceeds the persistence length.¹²⁻¹⁹ The existence of the chemical and physical defects is an important factor that dictates the photophysics of conjugated polymers. The delocalization of π electrons or conjugation length is known to be confined between these

defects.^{9,10,15,16} Therefore, a single chain of conjugated polymer constitutes of hundreds of quasi-localized chromophores with different conjugation lengths.¹⁹ One can control the averaged value of conjugation length, which in turn affects its emission behaviors, by tuning amount of the defects along conjugated backbone. This can be achieved by adjusting chain conformation^{15-18,20-22} or incorporating a controllable quantity of chemical defects.^{9,10} Chemical modification of the polymeric architectures is also an effective method for tuning the optical properties.^{12,23,24}

In our recent studies, we demonstrated that the location of absorption and emission spectra of the well-known conjugated polymer, poly[2-methoxy, 5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) can be systematically moved by controlling the magnitude of chain collapse in solutions.²⁰⁻²² It was also found that the conformational change of MEH-PPV affected the intrachain energy transfer process. However, several molecular parameters and experimental conditions remain uninvestigated. This contribution presents our continuation efforts to understand the influences of chain

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conformation on photoemission behaviors of MEH-PPV in solutions.

Recent theoretical and experimental studies have shown that MEH-PPV chain adopts relatively extended conformation in good solvents like dichloromethane and chloroform while it partially collapses in tetrahydrofuran.¹⁵⁻¹⁸ In this study, we perform systematic experiments to explore the relationship between conformational change of MEH-PPV in dichloromethane, chloroform, tetrahydrofuran and the photoemissions of various chromophores. The magnitude of chain collapse in THF is lesser than our previous studies, implying larger separation between chromophores in single chain. Some interesting discrepancies of results are observed. We have detected novel emission peaks at relatively high-energy region. Origins of these high-energy emission peaks are explored by investigating various experimental and molecular parameters including polymer concentration, temperature and concentration of chemical defects along conjugated chain.

Experimental

The MEH-PPVs used in this study are obtained from two synthetic batches, designated as MEH-PPV95 and MEH-PPV98. The number averaged molecular weights (M_n) of MEH-PPV95 and MEH-PPV98, determined by GPC with polystyrene standard, are 66,000 g/mol ($M_w/M_n=4.2$) and 75,000 g/mol ($M_w/M_n=3.5$). The two polymers contain different concentration of tetrahedral defects along the backbone. The analysis of their absorption spectra indicates that about 4-6 mol% and 1-2 mol% of the defects exist in the MEH-PPV95 and MEH-PPV98, respectively. Solutions of the polymers were prepared by dissolving powder sample in different solvents (AR grade). The solutions were subjected to serial dilution to obtain desired concentration. UV/vis absorption spectra were recorded by using Analytikjena Specord S100 with 1 cm thick quartz cuvette. The emission and excitation spectra were measured from Perkin-Elmer LS55 luminescence spectrometer equipped with water circulating system to allow temperature-dependent experiments. Temperature of the sample was measured by using thermocouple immersed directly in the solution.

Results and Discussion

Absorption spectrum of the 0.02 mg/mL MEH-PPV95 in chloroform is illustrated in Figure 1(a). The spectrum exhibits a broad pattern with λ_{max} at ~ 494 nm. The broadness of the spectrum arises from an intrinsic nature of the MEH-PPV conjugated backbone, which constitutes of various chromophores with different conjugation lengths.^{19,25,26} The one with relatively short conjugation length absorbs high-energy photons (i.e. short wavelength). The location of absorption spectrum systematically moves to low-energy region upon

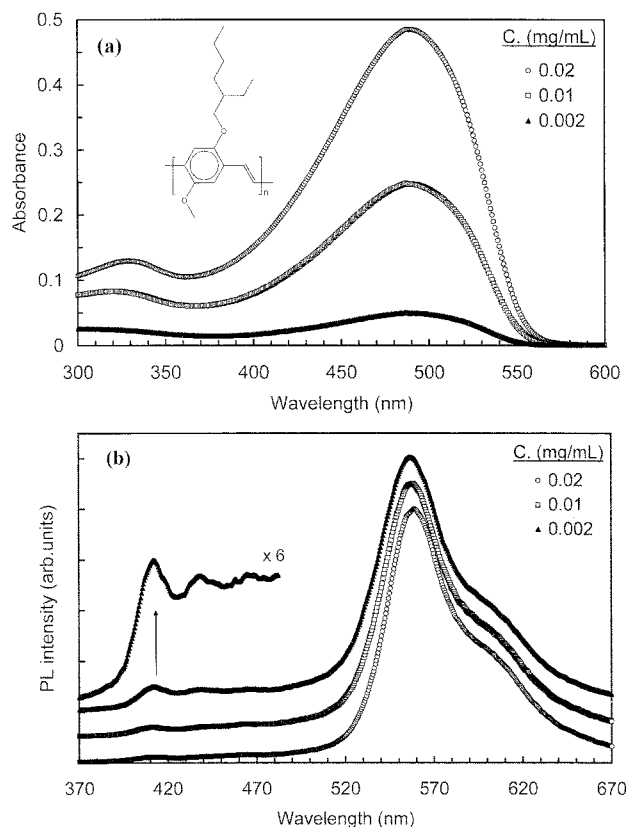


Figure 1. (a) Absorption and (b) photoluminescence (PL) spectra of MEH-PPV95 (chemical structure shown as inset) in chloroform. Excitation wavelength for PL measurements was 350 nm. PL spectra are normalized and shifted vertically for presentation. Polymer concentrations are shown in the plots. Part of PL spectrum of the 0.002 mg/mL solution is enlarged for clarity.

increasing number of repeat units in the chromophores,^{27,28} corresponding to the gradual decrease of HOMO-LUMO energy gap. The emission spectrum exhibits the same trend with increasing the length of chromophores. To gain insight information about the optical properties of each MEH-PPV chromophore, we look into the results of recent study on diheptyloxy oligophenylenevinyls (DHepO-OPV_{ns}) with repeat units ranging from 1 to 7.²⁷ The chromophores of DHepO-OPV_{ns} with one, two and three repeat units in chloroform solution exhibit absorption patterns with λ_{max} at 341, 390 and 427 nm, respectively. Since the structures of MEH-PPV and DHepO-OPV_{ns} repeat units are similar, we expect the chromophores of MEH-PPV with one, two and three repeat units to absorb light at similar energy region. This comparison is valid because slight modification of alkoxy side chain does not affect the optical properties of the chromophores.^{29,30} Theoretical calculations of HOMO-LUMO energy gap of various PPV oligomers are also consistent.³¹

The emission spectrum of the 0.02 mg/mL MEH-PPV95 solution constitutes of a peak at 558 nm with broad shoulder

at about 607 nm as illustrated in Figure 1(b). The emission pattern is independent of excitation energy. Using excitation wavelengths at 350, 400, 450 and 500 nm provides the emission spectra with the same shape. This result indicates that the excitation of chromophores with different conjugation lengths allows the emission to take place from the same chromophores having lowest HOMO-LUMO energy gap. In other word, the excited high-energy chromophores can efficiently transfer energy to their neighboring low-energy chromophores prior to the emission process.^{9,32-34}

In this study, we have found that the emission behaviors of high-energy chromophores depend significantly on intrinsic nature of local chain conformation. The short chromophores with conjugation length ranging from 1 to 5 repeat units emit light with relatively high energy (380-530 nm).^{9,10,27,28} Therefore, the emitted photons may be obscured by self-absorption effect in relatively concentrated solution (i.e. high absorbance).³⁵ To test this hypothesis, we carried out the photoemission measurements of the solutions with systematically diluted concentrations, 0.01 and 0.002 mg/mL, exhibiting absorbance at λ_{max} of about 0.25 and 0.05, respectively (see Figure 1(a)). The 350 nm light was used for excitation of the short chromophores. As expected, small features at relatively high-energy region emerge from the spectra upon decreasing the polymer concentration. For the 0.002 mg/mL solution, in which the self-absorption effect is significantly eliminated, small peaks at 414 and 440 nm are detected. However, the intensities of these peaks are rather weak. Therefore, its existence could be usually overlooked. We note that the absorption pattern is unchanged with the dilution, indicating that the interchain effect is minimal in this concentration range.

The intensity of high-energy peaks is found to significantly increase when the isolated MEH-PPV chain changes from extended conformation to the partially collapsed one. Figure 2 illustrates the absorption and emission spectra of MEH-PPV95 in tetrahydrofuran (THF). The polymer concentrations are adjusted to be the same as those of the chloroform solutions shown in Figure 1. The partially collapse of polymeric chains is indicated by the shift of absorption and emission spectra to relatively high energy region, which is consistent with the results from dynamic light scattering^{15,16} and computer simulation.^{17,18} The λ_{max} of absorption and emission spectra are detected at 490 and 554 nm, respectively. We observe the same concentration effect on the emission of high-energy chromophores. The intensities of the peaks at 414 and 440 nm increase with decreasing polymer concentration. However, the MEH-PPV95 chain in THF exhibits much more pronounced high-energy peaks compared to those of the solutions in chloroform with the same concentration. For the 0.002 mg/mL solution, intensities of the 414 and 554 nm peaks are almost the same. These results indicate that the emission of short chromophores is significantly enhanced when the extended MEH-PPV chain in

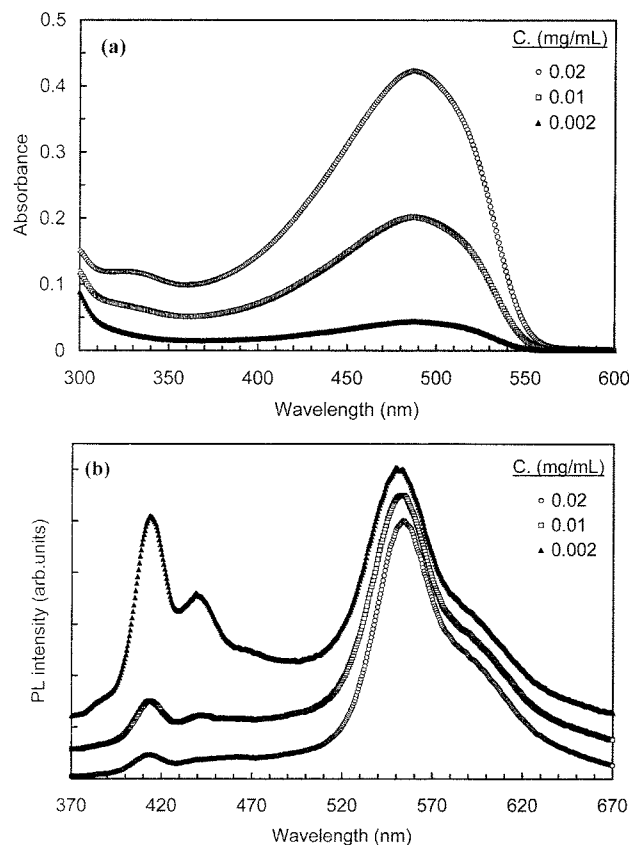


Figure 2. (a) Absorption and (b) PL spectra of MEH-PPV95 in tetrahydrofuran. Excitation wavelength for the PL measurements was 350 nm. PL spectra are normalized and shifted vertically for presentation. Polymer concentrations are shown in the plots.

chloroform is forced to partially collapse in THF. This suggests that the increase of conformational disorder in the partially collapsed chains reduces the efficiency of intrachain energy transfer.^{9,14,36,37}

The emission of high-energy chromophores in MEH-PPV was also observed in our previous studies, which investigated the polymer solutions in various alcohol solvents.^{20,21} However, the emission occurred at lower energy region. The emission peaks of high-energy chromophores were detected at ~460 nm and ~495 nm. We believe that the discrepancy of the results arises from the difference of extent of chain collapse. The blue shift of absorption spectrum of the polymer solution in THF is about 5 nm while the dispersion of MEH-PPV in alcohols causes much larger blue-shift of about 20 to 50 nm. This indicates that the magnitude of chain collapse is much higher in the alcohol solutions. The closer chromophore-chromophore distance in the highly collapsed coils should facilitate the radiative energy transfer causing the suppression of emission peaks at 414 and 440 nm. However, more investigation is needed in order to address this issue in details. It is important to note that the collapse of conjugated chains in our studies is not large

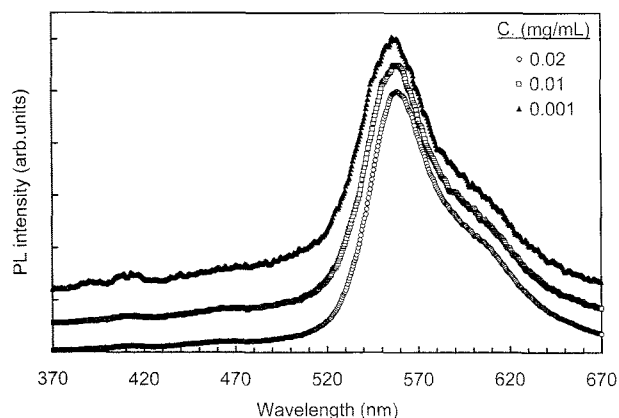


Figure 3. PL spectra of MEH-PPV95 in dichloromethane. Excitation wavelength for PL measurement was 350 nm. PL spectra are normalized and shifted vertically for presentation. Polymer concentrations are shown in the plots.

enough to cause the aggregation of chromophores in the same chain,^{10,25} indicated by the absence of red-shift peak in absorption spectrum. Therefore the energy transfer through aggregate sites, which is a more efficient pathway compared the intrachain process,^{33,34} should not exist in this system.

Since the dielectric constant of THF ($\epsilon=7.52$) is higher than that of the chloroform ($\epsilon=4.81$), one may suspect that the change of emission spectrum could arise from the variation of solvent polarity. To demonstrate that this was not the case, similar experiments were carried out by using the dichloromethane as a solvent, which exhibited higher dielectric constant ($\epsilon=8.93$). The emission spectra shown in Figure 3 do not show any peak at 414 and 440 nm. Decreasing concentration to 0.001 mg/mL allows very weak peak to be observed. Our investigation of aggregation behaviors of the MEH-PPV suggests that the dichloromethane is a better solvent compared to the chloroform. Therefore, the conjugated backbone is expected to be more extended.^{17,18} This hypothesis is supported by the absorption and emission spectra, which slightly shift to the lower energy region. The more extended chain, therefore, facilitates the intrachain energy transfer, allowing emission process to take place mostly at the chromophores with lowest HOMO-LUMO energy gap.

Origins of the high-energy emission peaks at 414 and 440 nm are further investigated by monitoring excitation spectra at different emission wavelengths as illustrated in Figure 4. The excitation spectrum measured at fixed emission wavelength of 580 nm exhibits pattern similar to the absorption spectrum. The spectrum covers from 290 to 570 nm and reaches maximum at ~ 484 nm. The excitation spectrum of the high-energy peak (i.e. at fixed emission wavelength of 430 nm) is detected at higher energy region, covering from 290 to 420 nm. Its peak is at ~ 387 nm. As discussed earlier, this energy region corresponds to the absorption of chromophores with one or two repeat units.

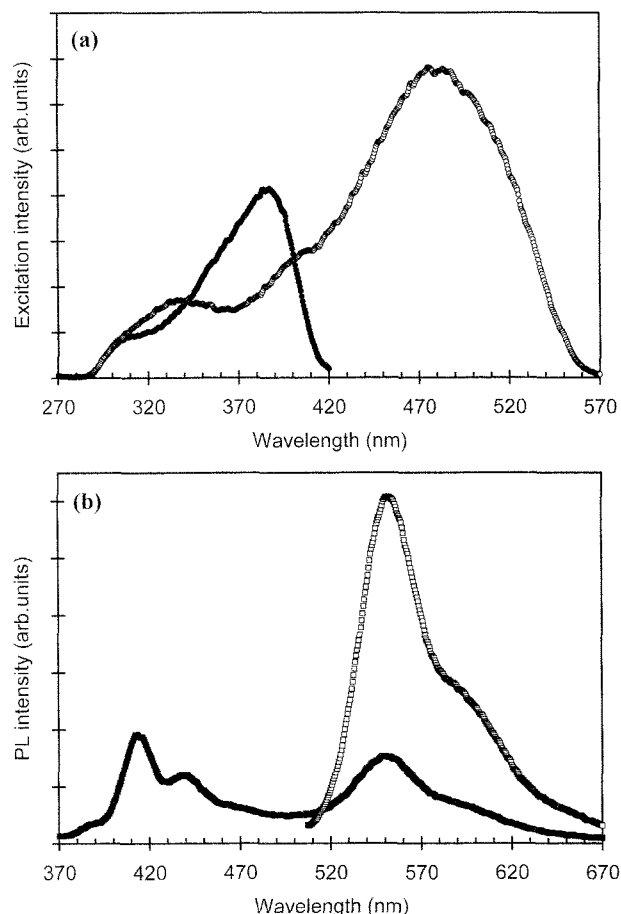


Figure 4. Excitation and PL spectra of 0.001 mg/mL MEH-PPV95 in tetrahydrofuran recorded at 20 °C. (a) Excitation spectra measured at fixed emission wavelengths of (●) 430 nm and (○) 580 nm. (b) PL spectra measured by using excitation wavelengths at (■) 350 nm and (□) 500 nm.

Therefore, the emission peaks at 414 and 440 nm are likely to arise from these short chromophores. This peak assignment is parallel to previous studies of the MEH-PPVs containing large fraction of tetrahedral defects.^{9,10} In those studies, the emission of the short chromophores was observed when the concentration of the chemical defects was increased above 70 mol%. The measurements of emission spectra by using different excitation wavelengths provide the consistent results. Using excitation wavelengths at 350 and 400 nm causes the emissions of both short and long chromophores as shown in Figure 4(b). Increasing excitation wavelengths to 450 and 500 nm, which is above the absorption region of the short chromophores, allows only the long chromophores to emit light. However, the location and pattern of emission spectra of the long chromophores are independent of the excitation wavelength.

Our previous studies have shown that the conjugation length of MEH-PPV in various solutions decreases upon increasing temperature, which is due to the increase of rota-

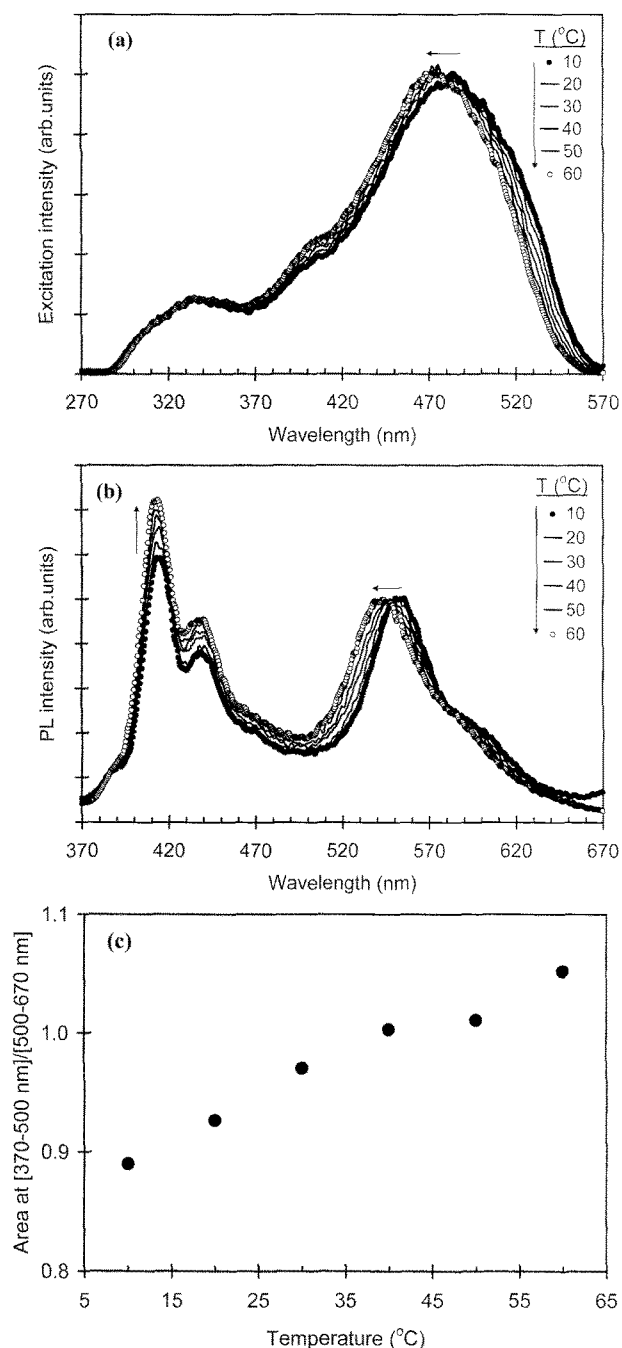


Figure 5. (a) Excitation and (b) PL spectra of 0.001 mg/mL MEH-PPV95 in tetrahydrofuran measured as a function of temperature. Excitation spectra were measured at fixed emission wavelength of 580 nm. Excitation wavelength for PL measurements was 350 nm. The spectra are normalized for comparison purpose. (c) Plot of ratios of integrated areas of PL spectra $[(370-500 \text{ nm})/(500-670 \text{ nm})]$ as a function of temperature.

tional dynamics of phenyl ring along the conjugated backbone.^{20,22} In this study, the effect of temperature on the conjugation length of MEH-PPV in THF is consistent with the previous results. Figure 5(a) illustrates the temperature

dependent of excitation spectra measured at fixed emission wavelength of 580 nm. It is clear that increasing temperature is accompanied by a blue shift of spectra, corresponding to the decrease of HOMO-LUMO energy gap. Moreover, the increase of rotational dynamics of phenyl rings at elevated temperature is found to reduce the efficiency of energy transfer along the conjugated backbone. Figure 5(b) shows the emission spectra measured as a function of temperature. The change of emission spectra is thermo-reversible. The peak at $\sim 550 \text{ nm}$, belonging to the long chromophores, gradually shifts to high-energy region upon increasing temperature, consistent with the corresponding excitation spectra. The emission spectra of the short chromophores at 414 nm, however, respond differently to the temperature change. Its location appears unchanged. The intensity of the high-energy peak compared to that of the low-energy peak systematically increases with the temperature. The variation of the relative intensities is further illustrated in Figure 5(c), which plots the ratios of integrated areas of the two regions. This result indicates that the emission of short chromophores is enhanced at elevated temperature, reflecting the suppression of intrachain energy transfer.

Since the MEH-PPV used in this study was synthesized via Gilch's route, some single bond defects (or tetrahedral defects) normally existed along the conjugated backbone.^{8,11} The concentration of the defect is an important parameter dictating the individual chain conformation and the efficiency of intrachain energy transfer.^{9,14} It is possible that our results could stem from this molecular parameter. Therefore, we further investigate emission behaviors of the high-energy chromophores by using the MEH-PPV98 obtained from different synthetic batch. The MEH-PPV95 and MEH-PPV98 contain different amount of single bond defect along the polymer backbone as indicated by their absorption spectra in chloroform (see Figure 6). The spectra of MEH-PPV95 and MEH-PPV98 exhibit λ_{max} at about 494 and

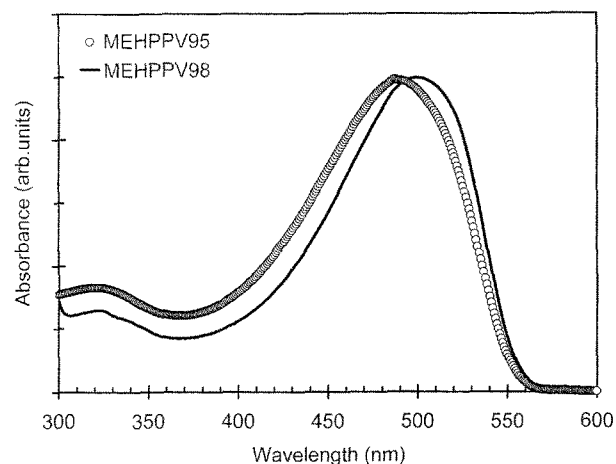


Figure 6. Absorption spectra of dilute solutions of MEH-PPV95 and MEH-PPV98 in chloroform.

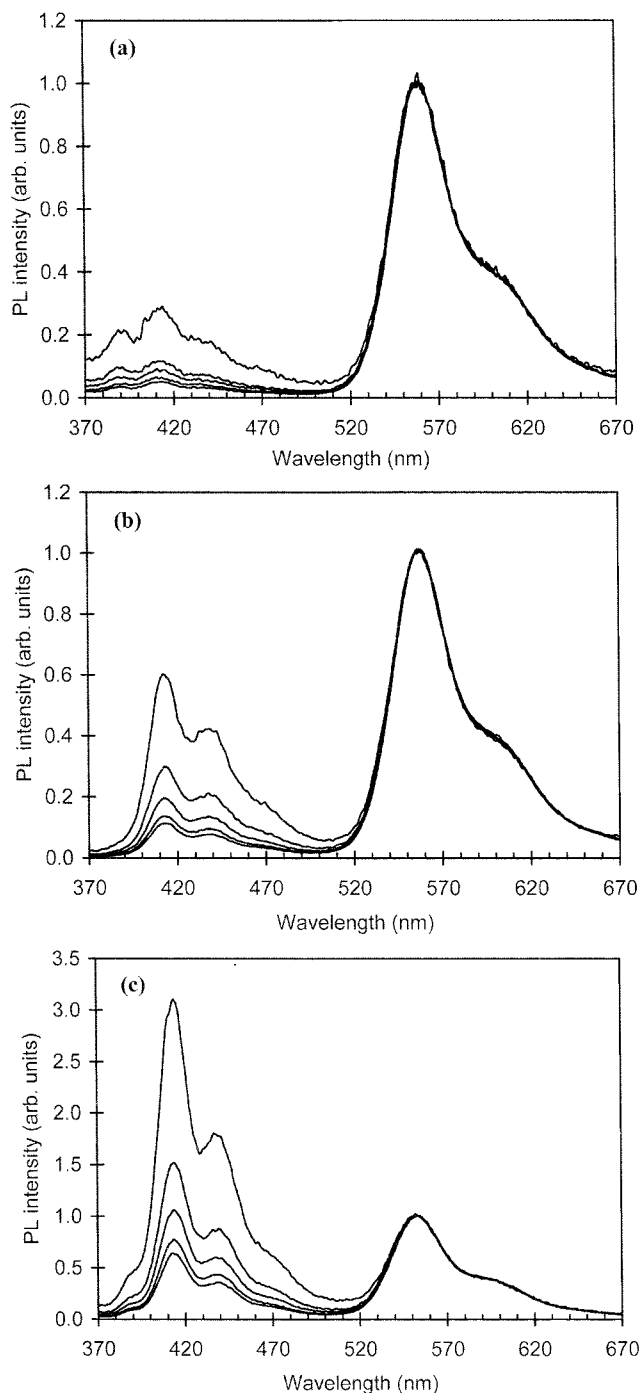


Figure 7. PL spectra of MEH-PPV98 in (a) dichloromethane, (b) chloroform, and (c) tetrahydrofuran. Excitation wavelength for PL measurements was 350 nm. Polymer concentrations ranging from bottom to top are 0.001, 0.0008, 0.0006, 0.0004, 0.0002 mg/mL. The spectra are normalized for comparison.

504 nm, respectively. By using known correlation between λ_{max} of the absorption spectrum and concentration of the defect,⁹ we estimate about 4-6 and 1-2 mol% of the defect in MEH-PPV95 and MEH-PPV98, respectively.

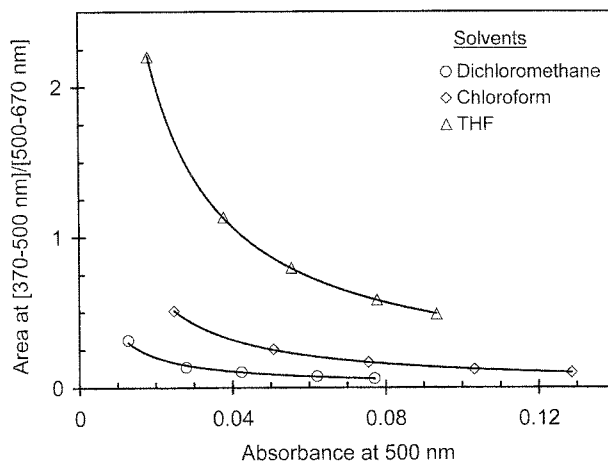


Figure 8. Ratios of integrated peak areas of PL spectra in Figure 7 as a function of absorbance at 500 nm. The ratios are calculated from the area of high-energy band (370-500 nm) relative to the area of low-energy band (500-670 nm). Solid lines are fitted to power law equations: (dichloromethane) $y=0.38x^{-0.90}$; $R^2=0.993$, (chloroform) $y=1.40x^{-1.03}$; $R^2=0.999$, $y=3.99x^{-0.94}$; $R^2=0.999$.

Although the MEH-PPV98 contains fewer amounts of single bond defect, we still observe similar emission behaviors of the high-energy chromophores. Decreasing concentration of polymer is accompanied by the increase of emission intensity at 414 and 440 nm. The emission of the short chromophores increases when the solvents are changed from dichloromethane, chloroform and THF, respectively. Figure 7 illustrates the emission spectra of MEH-PPV98 in these solvents. The concentrations range from 0.001 to 0.0002 mg/mL. It is clear that the relative emission intensity of the short chromophores systematically increases with decreasing polymer concentrations. This result is summarized in Figure 8, where ratios of integrated areas of the two regions are plotted as a function of the absorbance at 500 nm. We also observe that the data can be fitted to power law equations. The intensity of the 414 nm peak increases significantly at the very low polymer concentration. It is not trivial to compare the emission behaviors of the MEH-PPV95 and MEH-PPV98 because other molecular parameters including molecular weight, polydispersity and the rigidity of backbone are different. In addition, the molar absorption coefficient of the two polymers is not the same. However, the result obtained from the MEH-PPV95 and MEH-PPV98 is consistent, confirming our major finding. We expect that introducing higher amount of tetrahedral defects should affect the emission of the short chromophores.

Conclusions

We demonstrate that emission behaviors and intrachain energy transfer of the MEH-PPV chromophores with different conjugation lengths depend significantly on chain con-

formation. For high concentration solutions, the emission of short chromophores, which takes place at relatively high-energy region, is usually obscured by the self-absorption effect. Therefore, the emission spectra exhibiting a peak at ~560 nm represent only the electronic properties of long chromophores with lowest HOMO-LUMO energy gap. The self-absorption effect is significantly reduced in the diluted concentration allowing the high-energy peaks at ~414 nm and ~440 nm to be revealed. The measurements of excitation spectra suggest that these peaks belong to short chromophores constituting of one or two repeat units. We also have found that the emission of the short chromophores is enhanced when the conjugated chain is forced to partially collapse in THF. This is attributed to the suppression of intrachain energy transfer process due to the increase of conformational disorder. Increasing rotational dynamics of phenyl rings in the conjugated backbone achieved at elevated temperature promotes the emission of short chromophores as well. The investigation of two synthetic batches of MEH-PPVs containing 4-6 and 1-2 mol% of tetrahedral defects provides consistent results.

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