Conformational Changes and Photophysical Behavior in Poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] Thin Films Cast under an Electric Field

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Conformational Changes and Photophysical Behavior in Poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] Thin Films Cast under an Electric Field

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Thin films of the light emitting conjugated polymer poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4- phenylene vinylene] (MEH-PPV) were drop cast under a high voltage DC electric field. The conformational changes and photophysical behavior were studied systematically via steady-state and time-resolved fluorescence measurements. A clear blue shift was observed in the fluorescence spectra for thin films of MEH-PPV cast under external high electric field, and this behavior is compared to low temperature fluorescence spectra. Emission polarization measurements indicate a level of alignment of the chromophoric units when films are cast within the electric field. Moreover, an emission wavelength dependence of the fluorescence decay profiles is observed from the films cast in the absence of the electric field, but no such behavior is seen for films cast in the presence of the electric field. We interpret these observations in terms of conformational changes occurring in the polymer under the influence of the electric field, reducing the occurrence of aggregate formation.

1. Introduction

π-Conjugated polymers are the primary active components in the development of organic electronics. The structure–property relationship of solution-processable conducting polymers has been explored extensively[1–3] due to their significant impact in optoelectronic applications such as polymer light emitting diodes, field effect transistors and polymer solar cells. The self-assembly involved in thin film formation from such polymers dispersed in solution and the relationship between the supramolecular interactions and the microscopic morphology occurring upon aggregation are of importance to the optoelectronic properties of those light emitting materials in the solid-state.[4–7] Control of the molecular assembly of these conjugated materials into well-defined nanostructures to achieve ordering in thin films is desired in order to govern the performance of the organic optoelectronic devices. Although controlling the organization of conjugated polymers in the solid state is challenging due to their amorphous character combined with the large molecular weight distribution, great effort has been made to achieve surface orientation by specific processes, such as Langmuir–Blodgett methods,[8] layer-by-layer deposition,[9] aligned liquid crystal host matrices,[10–12] friction transfer,[13] tensile stretching,[14] etc. Applying an external electrical field during the film formation is an obvious measure to attempt to achieve alignment of microcrystals[15] and conjugated polymer chains.[16] However, only a few reports on the electric field induced orientation of light emitting conjugated polymer exist,[17,18] which have presented the enhancement of the charge mobility and subsequently an improvement of device performance. Scheblykin et al.[19] report the electric-field-induced photoluminescence quenching of a polymer using a diode-like arrangement, there is little reported on the photophysical behavior of the external electric field-

induced conformational changes during the formation of conjugated polymer thin films. Aggregation effects in π-conjugated molecular systems[20,21] also influence the photophysical behavior of such materials, but the effect of applied electric field on aggregation has not been widely studied.

In this work, we employed high electric field strengths (parallel to the surface of substrates) to thin films of poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) during the process of the drop casting and solvent evaporation. Steady-state and temperature-dependent fluorescence spectra give clear evidence that chain conformation has changed dramatically in these films, while time-resolved fluorescence measurements show that the fluorescence decays of these polymers can be lengthened substantially if films are formed in the presence of the external electric field.

2. Experimental Section

MEH-PPV ($M_w = 100\ 000$, Figure 1a) was purchased from Aldrich and used without further purification. The powder was dissolved into the solution of 3% (by weight) poly(methyl methacrylate) (PMMA, $M_w = 96\ 700$, Aldrich) in chlorobenzene with concentration of 0.1 mg/mL to minimize MEH-PPV aggregation during thin film formation. A total of 100 μL of this solution was then drop cast onto the 1-mm thick glass slide (2.5 cm × 2 cm) and the solvent allowed to evaporate in air for 30 min or 4 h, with or without applying an external electric field (Figure 1b), respectively. The electric field was applied using a DC power supply (HIVTRONIC Ltd. type 25-10-1,) in the range from 0 to 6000 V/cm. The absorption spectra were collected using a Varian Cary 50 Bio UV–vis spectrophotometer. A Varian Cary Eclipse fluorescence spectrophotometer was used to measure the fluorescence spectra of the conjugated polymer thin films and an Oxford Optistat[DN] liquid nitrogen cryostat was used for the temperature-dependent measurements. A picosecond time-correlated single-photon counting (TCSPC) system (Edinburgh Instruments, TCC900) was used for the fluorescence decay measurements using a microchannel plate photomultiplier (Eldy, EM132-1). The pulsed excitation (890

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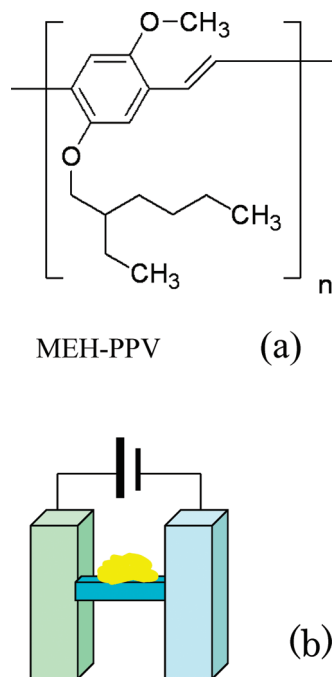
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Figure 1. (a) Chemical structure of MEH-PPV and (b) the schematic diagram of electric field generator for film formation.

nm) source was a cavity-dumped mode-locked titanium sapphire laser (Coherent Mira 900, APE PulseSwitch) pumped by a solid state laser (Coherent Verdi 10). After reduction of the pulse frequency to 5.4 MHz and frequency doubling (to 445 nm), the laser beam was attenuated to reduce the detected photon count rate to less than 0.5% of the excitation source repetition rate. Pure nitrogen was blown onto the surface of the thin films during fluorescence measurements to minimize photo bleaching and other degradation of the conjugated polymers.

3. Results and Discussion

Steady-state absorption and fluorescence spectra provide information relating to the conformational structure of conjugated polymers. Absorption spectra, excitation spectra and fluorescence spectra of MEH-PPV thin films cast under different applied external electrical field strengths (0, 4000, and 6000 V/cm) are shown in Figure 2a−c, respectively. With an increase in the voltage being applied during the process of film casting, the absorption band becomes significantly narrower and shifts to the blue considerably. The maxima of the absorption spectra lie at 508, 493, and 475 nm for thin films cast under electric field strengths of 0, 4000, and 6000 V/cm, respectively. Similarly, clear blue shifts can be observed in the excitation and fluorescence spectra of these films. The peak position (in region I) of the emission spectrum shifts from 593 to 584 nm upon increasing the electric field from 0 to 6000 V/cm. Moreover, the shoulder in the longer wavelength region (region II) is reduced significantly and an obvious shoulder in the shorter wavelength region (region III) appears with increasing applied voltage during the film formation process. The changes in the shape of the spectra, the blue-shift of the peak position, and therefore the difference of the Stokes shifts, as a function of applied field are not likely to be due to reduced energy migration efficiency from the higher energy, short conjugation length segments to the lowest energy, long segment lengths unit of the polymer chain, since spectral shifts occur in both the absorption and emission spectra. These results are more indicative of conformational changes occurring in the polymer as the
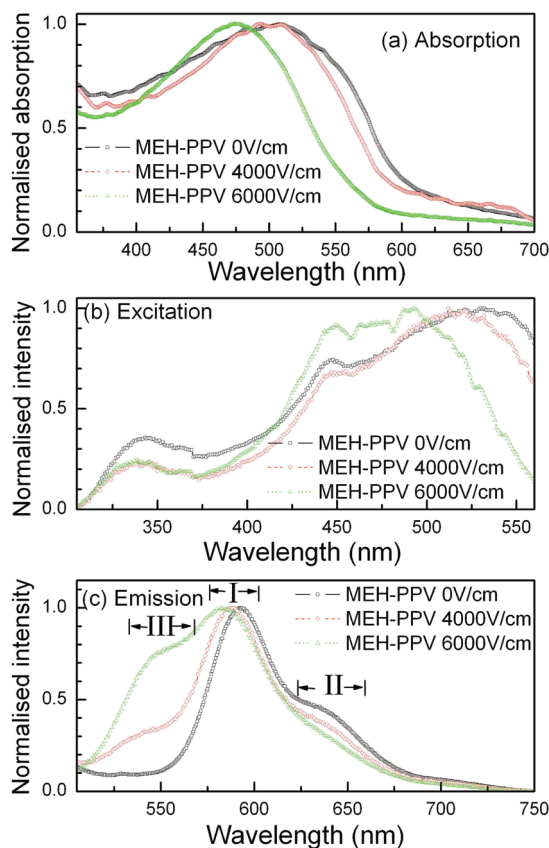

Figure 2. (a) Absorption, (b) excitation, and (c) fluorescence spectra of MEH-PPV thin films cast under different values of external electrical field (0, 4000, and 6000 V/cm).

film forms under the influence of the strong electric field, with the absorption and emission becoming predominantly associated with higher energy, shorter conjugation length segments. Elongation of the polymer in the direction of the electric field, which might be expected to increase the average effective conjugation length of the chromophores, and hence a *red* shift in the spectra, is also clearly not the cause of the spectral changes observed. It has been reported previously that the weakly coupled ground-state aggregates resulting from the intramolecular chain−chain contacts lead to the "red" emitting form in the spectra of single polymer chains.[22−24] The ensemble spectra, constructed by summing a large number of single polymer chain spectra, therefore contains the spectral feature toward the red showing clear vibronic structure due to the existence of the aggregates. Thus, the electric-field-induced reduction of the shoulder in region II may be attributable to decreased intramolecular chain−chain contacts, decreasing the number of red-emitting (aggregate) sites in the polymer films, resulting in an apparent blue-shift by biasing the spectrum toward the blue absorbing and emitting chromophores. The films prepared under the electric field influence were redissolved in the solvent and the fluorescence emission spectrum recorded (not shown here). Upon redissolution, the emission maximum exhibits a reversible trend back toward that of the original solutions, but the spectrum is a little broader (in the blue) than that of the film prior to electric field casting. The reversible nature (although incomplete) of the spectral shifts indicates that electric-field-induced conformational changes do exist in the films. The increased "blue" portion in the redissolved solution, presumably contributed from shorter conjugation length segments, suggests some degree of deterioration of the polymer due to the application of the electric field.
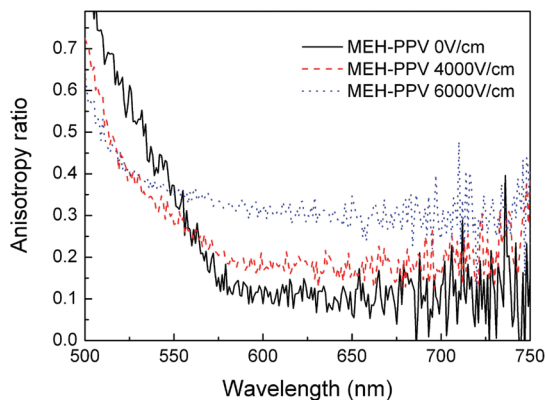
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Figure 3. Fluorescence anisotropy of MEH-PPV thin films cast under different values of external electrical field (0, 4000, and 6000 V/cm).
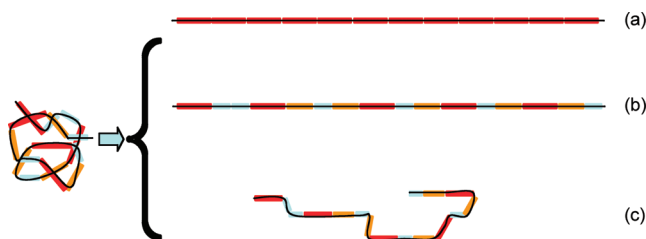

Figure 4. Schematic diagrams of proposed conformational changes under the influence of the applied electric field during film formation (description in text).

Figure 5. Temperature-dependent fluorescence spectra of MEH-PPV thin films cast under external electric field of (a) 0 and (b) 6000 V/cm.

Polarized fluorescence spectra were also recorded to further understand the conformation changes in the polymer films. The fluorescence anisotropy ratio, R, is defined in terms of the fluorescence spectra resolved with vertically polarized excitation and a vertical emission polarization analyzer, I_{VV}, versus a horizontal polarization analyzer, I_{VH}, emission as[25]

$$R = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}} \quad (1)$$

where the factor $G = I_{HV}/I_{HH}$ accounts for polarization bias in the detection system. The emission anisotropy spectra of the thin films prepared under different electric fields are shown in Figure 3. It can be seen clearly that the value of R is enhanced from 0.1 to 0.3 (particularly in the major emission region (570−650 nm)) with increasing electric field applied during the film formation process. This is indicative of a higher level of alignment of the chromophoric segments of the polymer chain in the direction of the electric field applied during film formation, achieved through the interaction of the electric field with the high polarizability of the polymer. Previous observations of polymer chain alignment have been reported using polymer samples[25] more dilute than used in the current study. The relatively more concentrated samples used in our work leads to less homogeneous dispersion of the polymer within the film resulting in more aggregate formation, particularly in the absence of the applied electric field. As the applied electric field is increased, and aggregation is apparently inhibited, the average degree of alignment of the chromophoric segments is seen to increase. A schematic representation of this interpretation is shown in Figure 4. The schematic on the left represents the random coil of the polymer chain in the solution prior to film formation, showing the distribution of conjugation length segments. Figure 4(a) illustrates what might be expected if the chain became fully extended and aligned under the influence
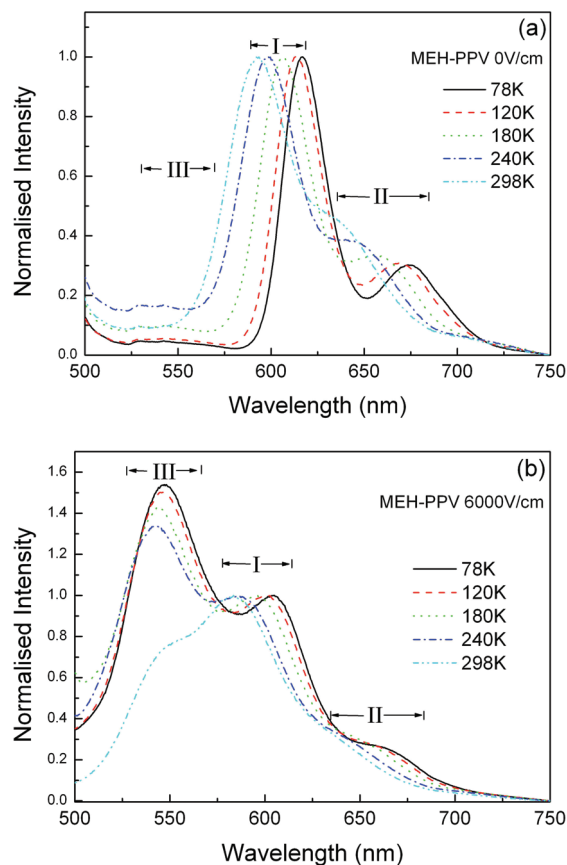
of the electric field, forming a narrow distribution of longer conjugation length segments. Figure 4b represents full alignment of the chromophoric units, but no change in the average conjugation length of the polymer. Neither of these descriptions explains our experimental results. Figure 4c illustrates partial alignment of the chromophoric segments resulting in increased emission anisotropy, with no change in the average conjugation length, but extends the distance between segments, thus reducing the possibility of intrachain interactions (aggregation and possibly energy migration). This picture is consistent with our observations.

Fluorescence spectra of MEH-PPV at low temperature can give clear featured structures, which resolve emission from different conformational structures of the conjugated polymer chains.[26,27] We therefore performed temperature-dependent fluorescence measurements for the thin films cast in the absence and presence of an external electric field (6000 V/cm) to better clarify the conformational changes of the conjugated polymer chains (Figure 5). In the case where no field has been applied (Figure 5a), as the temperature is decreased the expected enhancement in the structure of the emission bands is observed, but the general structure is maintained and there is a clear red-shift of the emission spectrum. This is attributed to a concomitant decrease in electron−phonon interactions and increased effective conjugation length compared to room temperature.[27] The sharper fluorescence bands enable us to distinguish the different emission components in the films. Although there is a slight rise showing a weak emission in region III, no clear peak can be seen in these spectra. However, in Figure 5b, which shows the fluorescence spectra for a thin film cast under the presence of the electric field (6000 V/cm), the spectral changes
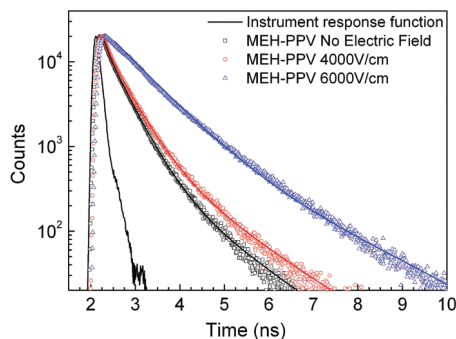
Figure 6. Time-resolved fluorescence decay for MEH-PPV thin films cast under different values of external electrical field (0, 4000, and 6000 V/cm). The solid lines are the fits using a multiexponential decay function.
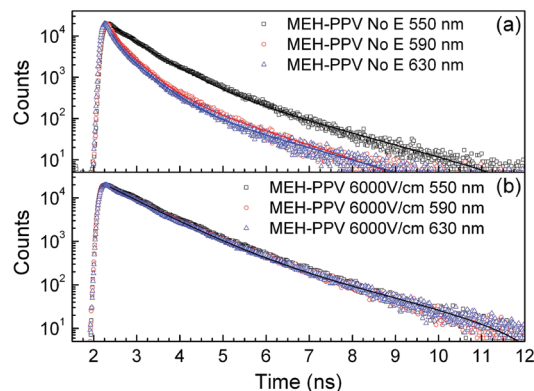

Figure 7. Fluorescence decay for MEH-PPV thin films cast under electrical field of (a) 0 and (b) 6000 V/cm detected at 550, 590, and 630 nm. The solid lines are the fits using a multiexponential decay function.

observed are less associated with a spectral shift, compared with Figure 5a, and are more based around changes in the intensity of certain bands. The peak red-shift in region I is similar (from 584 to 605 nm) with that in Figure 5a; however, the emission shoulder in region II becomes stronger with decreasing temperature, with no clear peak appearing even in the lowest temperature (78 K) (c.f. region II in Figure 5a). A significant peak arises and red-shifts in region III as the temperature is decreased. The red-shift of 6 nm of the peak maximum in region III is much smaller than the shift of 21 nm of that in region I, indicating that the emission segments with shorter conjugation length may have a more stable conformation than the emission segments with longer conjugation lengths, which contribute to the emission in region I. The electric-field-induced conformational changes and/or chromophore alignment may inhibit the energy migration from higher energy sites to lower energy sites and therefore more emission arises from the blue emitting chromophores.

Fluorescence decay measurements of the conjugated polymer thin films are illustrated in Figure 6 from which it is clearly seen that the fluorescence decays more slowly in the film cast under the applied electric field than that cast without the influence of the electric field. In addition, the higher the voltage applied to the thin films during the process of casting, the longer the fluorescence lifetime can be observed. The decay data for the thin film cast under no electric field can be fit by a triple-exponential function showing two major decay components (τ_3 = 104 ps and τ_2 = 393 ps) and a third residual component (τ_1 = 1191 ps). The decay for the film cast under an electric field of 4000 V/cm is also triple-exponential with two major components (τ_3 = 104 ps and τ_2 = 432 ps) and a third residual component (τ_1 = 1267 ps). However, the thin film cast under an electric field of 6000 V/cm is double-exponential with one major component (τ_2 = 780 ps) and a second residual component (τ_1 = 2102 ps). Time-resolved fluorescence decay profiles were also measured at three different characteristic emission wavelengths of 550, 590, and 630 nm (which are close to the peak maxima of the three main emission components) for MEH-PPV thin films cast under electrical field of 0 and 6000 V/cm, as illustrated in Figure 7. An obvious emission wavelength dependence can be observed for the fluorescence decay of the MEH-PPV thin film cast under the absence of the external electric field (Figure 7a). The dynamic behavior at short wavelengths (550 nm) is governed by a component with a decay time of 613 ps and a residual component of lifetime 1627 ps, while the decay at long wavelengths (590 nm) is faster and is triple-exponential, showing two major components (τ_3 = 104 ps and τ_2 = 393 ps) as mentioned relating to Figure 6. In the

case of the applied electric field, the decay is virtually emission wavelength independent and nearly monoexponential with a decay time of 780 ps for the major component. Emission quantum yield measurements using a fluorimeter coupled with an integrating sphere show that the quantum yield increases by a factor of about 3.3 times for the films prepared under electric field of 6000 V/cm compared to that prepared without the electric field. The enhancement of the quantum yield is consistent with the increased emission lifetime observed from the films, and is probably due to reduced fluorescence quenching in the more aligned, nonaggregated, polymer chains. In related work on MEH-PPV in solution, it has been shown that the degree of packing, on a microscopic level, reduces the quantum efficiency by as much as 2/3.[20]

In association with the spectral results discussed above, this time-resolved behavior can be interpreted in terms of changes in the level of aggregate formation with the application of an electric field, if the red emission of the aggregates exhibit shorter emission decay times compared with the individual chromophores. We attribute the long decay component, dominant at the short wavelengths in Figure 7a, to the fluorescence decay of isolated chromophores.[28] In the case when the electric field has been applied (Figure 7b) and aggregate formation has apparently been suppressed, the emission decays uniformly across the emission bands. When no electric field has been applied, aggregation is more favored (as evidenced by the red-emission) and the emission decays over shorter time-scales. This interpretation is somewhat different to the behavior reported from MEH-PPV in solutions of varying solvent quality in which no significant change in singlet decay time was observed despite chain packing.[20] This apparent discrepancy may relate to the differences between solution and thin film behavior. Emission decay times in films are often significantly shorter than for the same fluorophore in the corresponding solution phase.

4. Conclusions

We have demonstrated that the electric field induced conformational changes in thin films of the conjugated polymer MEH-PPV can be observed from their photophysical behavior from steady-state, temperature-dependent and time-resolved fluorescence measurements. A change in the emission spectrum biased toward the blue (as distinct from a blue-shift) was seen in fluorescence spectra for the films cast under the external electric field compared to the films cast in the absence of electric field. We attribute this to decreased aggregate formation due to conformational changes induced in the polymer as the film forms

under the influence of the electric field. Polarized emission spectra indicate that an increased level of chromophoric alignment is achieved in films cast under an electric field. Time-resolved emission measurements indicated that the emission decay time of the aggregate species in these films is shorter than the "isolated" chromophores. The observations regarding the longer lifetime and blue shift of the spectra of the films cast under electric field are in excellent agreement with the previously reported behavior of MEH-PPV at the single molecule level which was interpreted in a similar fashion in terms of the blue emission dominating at low concentrations.[26,29] The casting of MEH-PPV films under the influence of the electric field therefore seems to induce behavior, which mimics that induced by the environment of the polymer chains formed by being spin-cast at very low concentration. While these measurements were performed under DC electric field conditions, further experiments using AC electric fields during deposition of the films would also promote a deeper understanding of the behavior of the conjugated polymer chains and their interactions with strong electric fields.

References and Notes

(1) Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. *Adv. Mater.* **2000**, *12*, 1737.

(2) Hoppe, H.; Sariciftci, N. S. *J. Mater. Res.* **2004**, *19*, 1924.

(3) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature* **1999**, *401*, 685.

(4) Hao, X. T.; Hosokai, T.; Mitsuo, N.; Kera, S.; Mase, K.; Okudaira, K. K.; Ueno, N. *Appl. Phys. Lett.* **2006**, *89*.

(5) Hao, X. T.; Hosokai, T.; Mitsuo, N.; Kera, S.; Okudaira, K. K.; Mase, K.; Ueno, N. *J. Phys. Chem. B* **2007**, *111*, 10365.

(6) Kim, J.; Swager, T. M. *Nature* **2001**, *411*, 1030.

(7) Leclere, P.; Surin, M.; Brocorens, P.; Cavallini, M.; Biscarini, F.; Lazzaroni, R. *Mater. Sci. Eng. R* **2006**, *55*, 1.

(8) Marletta, A.; Goncalves, D.; Oliveira, O. N.; Faria, R. M.; Guimaraes, F. E. G. *Macromolecules* **2000**, *33*, 5886.

(9) Decher, G. *Science* **1997**, *277*, 1232.

(10) Chang, W. S.; Link, S.; Yethiraj, A.; Barbara, P. F. *J. Phys. Chem. B* **2008**, *112*, 448.

(11) Lammi, R. K.; Fritz, K. P.; Scholes, G. D.; Barbara, P. F. *J. Phys. Chem. B* **2004**, *108*, 4593.

(12) Link, S.; Hu, D.; Chang, W. S.; Scholes, G. D.; Barbara, P. F. *Nano Lett.* **2005**, *5*, 1757.

(13) Nagamatsu, S.; Misaki, M.; Chikamatsu, M.; Kimura, T.; Yoshida, Y.; Azumi, R.; Tanigaki, N.; Yase, K. *J. Phys. Chem. B* **2007**, *111*, 4349.

(14) Yang, G.; Li, Y.; Zhu, A.; White, J. O.; Drickamer, H. G. *Macromolecules* **2000**, *33*, 3173.

(15) Oikawa, H.; Nakanishi, H., Particle-Based Optical Devices, In *Single Organic Nanoparticles*; Masuhara, H., Nakanishi, H., Sasaki, K., Eds.; Springer-Verlag: New York, 2003; p 382.

(16) Schindler, F.; Lupton, J. M.; Müller, J.; Feldmann, J.; Scherf, U. *Nat. Mater.* **2006**, *5*, 141.

(17) Jin, H.; Hou, Y. B.; Meng, X. G.; Teng, F. *Chem. Phys. Lett.* **2007**, *443*, 374.

(18) Jin, H.; Hou, Y. B.; Shi, Q. M.; Meng, X. G.; Teng, F. *Solid State Commun.* **2006**, *140*, 555.

(19) Scheblykin, I.; Zoriniants, G.; Hofkens, J.; De Feyter, S.; Van der Auweraer, M.; De Schryver, F. C. *ChemPhysChem* **2003**, *4*, 260.

(20) Collison, C. J.; Rothberg, L. J.; Treemaneekarn, V.; Li, Y. *Macromolecules* **2001**, *34*, 2346.

(21) Masuo, S.; Yoshikawa, H.; Asahi, T.; Masuhara, H.; Sato, T.; Jiang, D.-L.; Aida, T. *J. Phys. Chem. B* **2003**, *107*, 2471.

(22) Feist, F. A.; Basche, T. *J. Phys. Chem. B* **2008**, *112*, 9700.

(23) Grey, J. K.; Kim, D. Y.; Donley, C. L.; Miller, W. L.; Kim, J. S.; Silva, C.; Friend, R. H.; Barbara, P. F. *J. Phys. Chem. B* **2006**, *110*, 18898.

(24) Huang, Y. F.; Shiu, Y. J.; Hsu, J. H.; Lin, S. H.; Su, A. C.; Peng, K. Y.; Chen, S. A.; Fann, W. S. *J. Phys. Chem. C* **2007**, *111*, 5533.

(25) Fritz, K. P.; Scholes, G. D. *J. Phys. Chem. B* **2003**, *107*, 10141.

(26) Mirzov, O.; Scheblykin, I. G. *Phys. Chem. Chem. Phys.* **2006**, *8*, 5569.

(27) Yu, Z. H.; Barbara, P. F. *J. Phys. Chem. B* **2004**, *108*, 11321.

(28) Fakis, M.; Anestopoulos, D.; Giannetas, V.; Persephonis, P.; Mikroyannidis, J. *J. Phys. Chem. B* **2006**, *110*, 12926.

(29) Lin, H. Z.; Tabei, S. R.; Thomsson, D.; Mirzov, O.; Larsson, P. O.; Scheblykin, I. G. *J. Am. Chem. Soc.* **2008**, *130*, 7042.