Spatial Fluorescence Inhomogeneities in Light-Emitting Conjugated Polymer Films

3 AUTHORS, INCLUDING:

Xiao-Tao Hao
Shandong University

**69** PUBLICATIONS **1,303** CITATIONS

Spatial Fluorescence Inhomogeneities in Light-Emitting Conjugated Polymer Films

Xiao-Tao Hao, Lachlan J. McKimmie, and Trevor A. Smith*

School of Chemistry and ARC Centre of Excellence for Coherent X-ray Science, The University of Melbourne, Victoria 3010, Australia

ABSTRACT: Scanning confocal time-resolved fluorescence imaging measurements have been performed on light-emitting conjugated polymer thin films cast from a range of solvents. We have observed inhomogeneities in the emission spectra and fluorescence decay profiles at various micrometer-sized regions within these films. Some regions are observed to exhibit longer fluorescence decay times and emission at shorter wavelengths than typically reported for such films. These regions are associated with nonaggregated polymer structures. Solvent effects on the photophysical properties of conjugated polymer films were also investigated. The dissimilarity of fluorescence lifetime distributions and emission spectra for films deposited from different solvents shows the diversity of the configurations within films and a dependence/memory of the polymer conformation on the solvent from which the film was cast.

SECTION: Macromolecules, Soft Matter
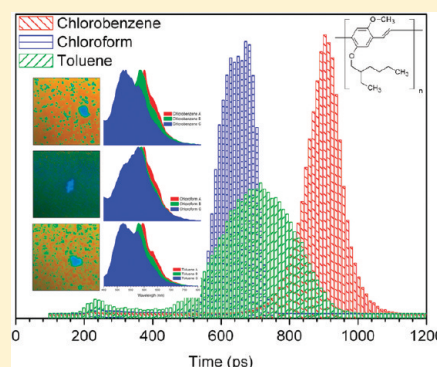
Successful applications of organic electronics including light-emitting diodes, organic photovoltaic cells, and lasers, rely on the fundamental and applied studies on conjugated polymers because of the outstanding electrical and optical properties, reasonable chemical stability, and processing ease of these materials.[1−7] In addition to the characteristics of these polymers in solution, the application of conjugated polymers in the above-mentioned solid-state devices requires the principle phenomena and mechanisms, such as morphological aggregates, chain—chain interactions, and charge transfer/transport, in solid-state thin films to be unraveled.[8−17] Aggregates are readily formed in most conjugated polymer films, resulting in good charge transport via strongly interacting π-electron systems, but these aggregates also likely induce inhomogeneous morphologies and emission quenching and thereby affect device efficiency.[18] Determining the spatial scale of these inhomogeneities in the coating of the conjugated polymer films to the substrate on different spatial scales from nanometers to many micrometers, and their effect on the dynamics of electron/hole transport is necessary to develop more efficient injection processes for high-performance devices. High-resolution optical microscopy methods are a useful tool to provide this spatial information. Coupling ultrafast spectroscopic methods with high spatial resolution optical techniques makes it possible to map the dynamics of the photoinduced charge transfer/transport processes as a function of location in the film. In this work, we observe inhomogeneities in the morphology and fluorescence dynamics of thin films of the light-emitting conjugated polymer, poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV, chemical structure shown in inset of Figure 1), on submicrometer spatial and picosecond temporal scales using time-resolved scanning confocal fluorescence imaging measurements.

The MEH-PPV polymer samples were purchased from Sigma Aldrich, with a reported molecular weight of 133 kg/mol and a polydispersity of 1.06, as determined by GPC-MALLS and used without further purification. The powder was dissolved into a solution of 3% (by weight) poly(methyl methacrylate) (PMMA, M_w = 96 700, Aldrich) in chlorobenzene, chloroform, or toluene with concentration of 0.1 mg/mL to minimize MEH-PPV aggregation during thin film formation. The solution was then drop cast onto 0.15 mm thick glass coverslips. No filtration of the solutions prior to film casting was performed. Absorption spectra were collected using a Varian Cary 50 Bio UV—vis spectrophotometer. A Varian Cary Eclipse fluorescence spectrophotometer was used to record the bulk fluorescence emission spectra of the conjugated polymer thin films. A Becker & Hickl SPC-830 FLIM module coupled to a modified Olympus confocal scanning microscope (FV300/IX71) was employed for the time-resolved fluorescence imaging measurements, and a high-resolution fiber-optic spectrophotometer (Ocean Optics HR2000) was adopted to collect the emission spectra for specific points in films by monitoring the emission immediately after the appropriate dichroic beamsplitter in the microscope filter cube. The pulsed excitation (400 nm) source was the frequency-doubled output of a mode-locked titanium sapphire laser (Coherent Mira 900f, ∼120 fs, ∼76 MHz) pumped by ∼9W from a DPSS laser (Coherent Verdi V10). This excitation source was delivered to the microscope via a single-mode optical fiber. Confocally isolated emission was acquired by an SPC-830 single photon-counting unit and controlled using the SPCM TCSPC operating

software. The fluorescence decay data were analyzed using "SPCImage" FLIM data analysis software. The time-resolved fluorescence images generated from this software displayed herein are plots of the amplitude-weighted mean lifetime, $\tau_m = \sum_{i=1}^{N} A_i \tau_i / \sum_{i=1}^{N} A_i$.

Photobleaching was not observed to be a major problem in these experiments because the use of the scanning confocal technique with photon-counting detection minimizes the laser power required and time the laser resides on a given pixel. Repeated scans produced similar photon count rates. We did not see any spectral changes from the films before and after the experiments, suggesting that no conjugated length changes corresponding to chemical change occurred during the measurements.

Conformational structure of conjugated polymer thin films can be revealed from steady-state absorption and fluorescence emission spectra.[13] Absorption spectra of MEH-PPV thin films cast from different solvents and emission spectra for solutions and films are shown in Figure 1. These ensemble-averaged spectra, recorded from a bulk area of the sample in conventional spectrometers, are in general agreement with the spectra reported elsewhere for MEH-PPV.[19] In solutions of good solvents such as chlorobenzene, MEH-PPV is generally thought to form an "unfolded" structure, thereby maximizing favorable $\pi-\pi$ interactions between the polymer and solvent molecules and therefore absorbing and emitting toward the red. In contrast, a tighter coil conformation of the polymer chains is expected in poorer solvents such as THF to minimize the number of aromatic repeat units interacting with the nonaromatic solvent molecules, thus pushing the absorption and emission spectra toward the blue.[19] It is recognized that polymer chains in solid-state films have "memory" retaining, at least to some degree, the conformation they adopt in the solution from which they are cast.[9] However, slight changes could occur during the process of self-assembly in the film formation during the period of solvent evaporation. This is observed through differences in the shape and spectral shift behavior of the emission spectra for the solutions compared with films (Figure 1). The absorption maximum of the film cast from chlorobenzene is slightly blue-shifted (496 nm) relative to the λ_{max} of the films cast from chloroform (500 nm) and toluene (509 nm) — the opposite behavior to the polymer in solution. This may be construed to be indicative of a larger population of shorter conjugation length segments, which might arise from tighter packing in the film cast from chlorobenzene compared with the other solvents. However, the broad and unstructured nature of the absorption spectrum of the film is suggestive of a wide distribution of conjugation lengths and the possibility of aggregates of MEH-PPV.[18]

The emission spectral maxima in these films show the same trend as the absorption maxima with solvent (chlorobenzene 599 nm, chloroform 603 nm, and toluene 605 nm) — the opposite behavior to the polymer in solution. The emission spectra are uniformly far more structured than the absorption spectra, both in solution and in films, indicating that the broad distribution of absorbing species gives rise to emission from a significantly narrower distribution of emitting species. The emission spectra are also generally somewhat broader in the films compared with the solution, again suggesting that there is a broader distribution of emitting species in the films compared with in solution. These results suggest that the shift to more red-dominated emission as the solvent from which the film is cast is varied reflects the ability of the excitation energy to migrate to the lower energy segments through increasingly tighter packing rather than an increase in the average conjugation length adopted
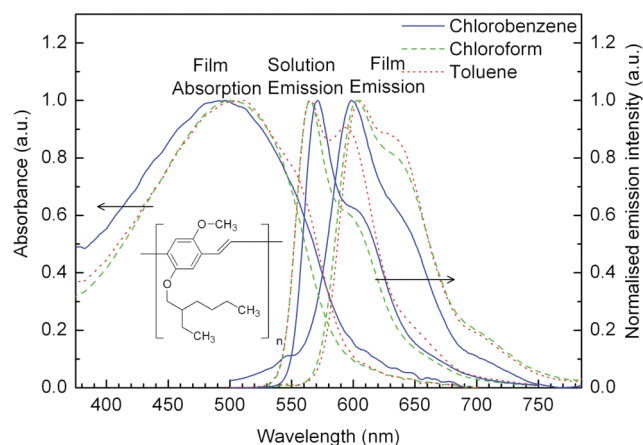

Figure 1. Absorption and fluorescence emission (excited at 400 nm) spectra of the MEH-PPV drop cast thin films originating from different solvents: chlorobenzene, chloroform, and toluene.

by the polymer chains. This is in agreement with the single-molecule studies of Huser et al.[20] that show that this polymer adopts a tightly coiled conformation when prepared from toluene and a more expanded conformation when prepared from chloroform.

This spectral behavior is similar to that we have reported for MEH-PPV films cast under the influence of the electric field, where the red-shifted spectral feature with strong vibronic structure was attributed to the existence of the aggregates.[13] Barbara et al.[21,22] pointed out that in a good solvent the polymer conformation should be extended without chain—chain contacts and, as a result, lacks low-energy trap sites for singlet excitons. The presence of aggregated species and the inhomogeneous distribution within the films will be further confirmed by the following fluorescence lifetime imaging measurements.

Conventional fluorescence imaging methods merely map the emission intensity as a function of location in the film, but many factors can contribute to the fluorescence intensity recorded, such as fluorophore concentration, variations in film thickness or surface properties (e.g., roughness) resulting in collection efficiency variability, etc. Alternatively, time-resolved fluorescence imaging is less susceptible to such influences and maps the variations in the fluorescence decay characteristics (rather than intensity) as a function of location. Changes in fluorescence decay behavior are indicative of variations in emitting species, their molecular environment, or both.

Time-resolved scanning confocal fluorescence imaging measurements were performed on these MEH-PPV films deposited from solutions of various solvents. For each solvent-cast film, we show a fluorescence lifetime map and fluorescence decay profiles corresponding to three representative locations on the map (Figure 2a,d) chlorobenzene, (Figure 2b,e) chloroform, and (Figure 2c,f) toluene. The morphology of the films, in particular, the presence of inhomogeneities in fluorescence decay behavior on micro- and submicro-meter scales, is clear. These inhomogeneites are attributed to regions of various degrees of polymer aggregation that contribute to, but are unresolvable in, the overall bulk spectral properties of the films shown in Figure 1. The images were collected from typical regions in films containing what appear to be distributions of larger aggregates, smaller aggregates, and largely nonaggregated (or uniformly coated) regions, and the decay profiles shown are from points that
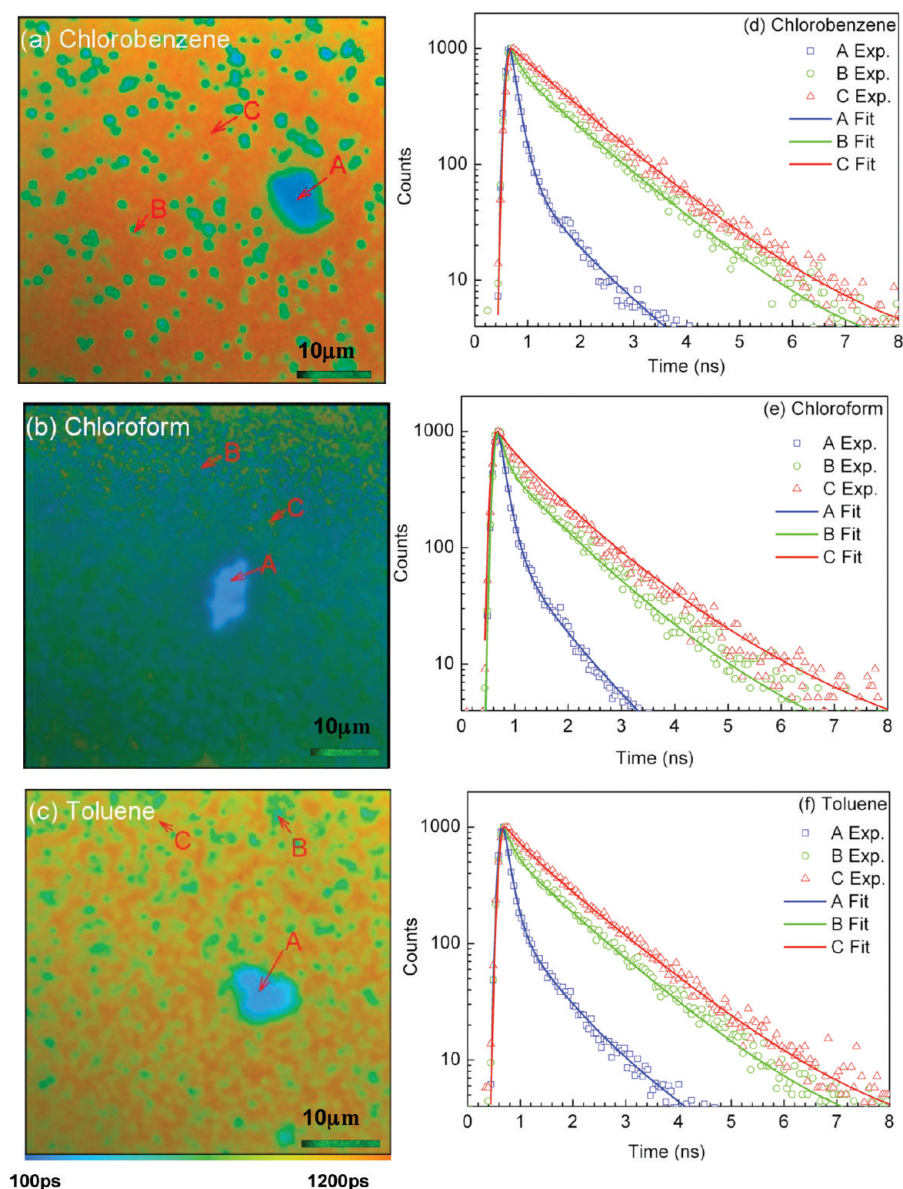
Figure 2. Fluorescence lifetime images (left panel) for MEH-PPV thin films cast from various solvents (a) chlorobenzene, (b) chloroform, and (c) toluene and the fluorescence decay profiles (right panel) recovered from the lifetime images (d) chlorobenzene, (e) chloroform, and (f) toluene.

correspond to these differently sized aggregates (points A−C, respectively). The decays are clearly nonexponential, and we have analyzed them in terms of multiexponential decay functions, although we do not intend to attribute specific decay components to individual species. The decay times, relative intensities and amplitude weighted-average lifetimes for three representative points in each of the three solvent-cast films are tabulated in Table 1.

In each case, the regions representing the larger aggregated areas (A) show the shortest emission decay compared with regions B and C, and regions C are generally dominated by a decay component in the nanosecond regime. The contribution of the slower decay component increases as the aggregate size decreases for all films cast from different solvents, consistent with the findings of Sherwood et al.[18] The films cast from chloroform and toluene show similar fluorescence decay behavior for the respective regions in the emission image, whereas in the case of

chlorobenzene, there is little evidence of the short-lived (∼few hundred picosecond) component at all in the largely nonaggregated region C. The shortest of the decay times we observed are in general agreement with those typically reported for MEH-PPV solutions and films recorded in large area illumination (ensemble averaged) measurements.[19,23,24] The components with decay times in the nanosecond regime resemble those reported by Rothberg et al.[25] for PPV that were attributed to relaxed intrachain excitons formed via interchain excitons, with the more usually observed picosecond range fluorescence decay resulting from the rapid diffusion by Förster transfer from short to long conjugation segments. Sherwood et al.[18] used time-resolved fluorescence measurements to study the aggregate size and dynamics of MEH-PPV using model oligomers of various lengths. They discuss several explanations for their observations but found the most consistent was the formation of a "core-shell" structure in which "there are areas of the aggregate core that are

1522

dx.doi.org/10.1021/jz200540j |*J. Phys. Chem. Lett.* 2011, 2, 1520–1525

Table 1. Peak Emission Wavelength (λ_{max}^{em}, see Figure 4), Fluorescence Decay Times, Relative Intensities (in Brackets) and Amplitude Weighted Mean Lifetime Lifetimes, τ_m, for Three Representative Points in Each of the Three Solvent-Cast Films

		peak emission wavelength	fitted decay times (ps) and relative intensities			
			τ_1 (nm)	τ_2	τ_3	τ_m
chlorobenzene film	A	597	130 (90.5%)	301 (5.4%)	975 (4.1%)	174
	B	582	178 (44%)	1062 (49%)	1443 (7%)	699
	C	575 and 530	946 (56%)	1208 (37%)	1852 (7%)	1110
toluene film	A	595	122 (89%)	480 (7%)	1070 (4%)	188
	B	580	156 (50%)	911 (34%)	1378 (16%)	606
	C	575 and 525	330 (22%)	1078 (68%)	1726 (10%)	974
chloroform film	A	596	125 (88%)	290 (7%)	836 (5%)	171
	B	587	131 (63%)	816 (29%)	1502 (8%)	423
	C	575 and 530	240 (18%)	842 (65%)	1688 (17%)	879
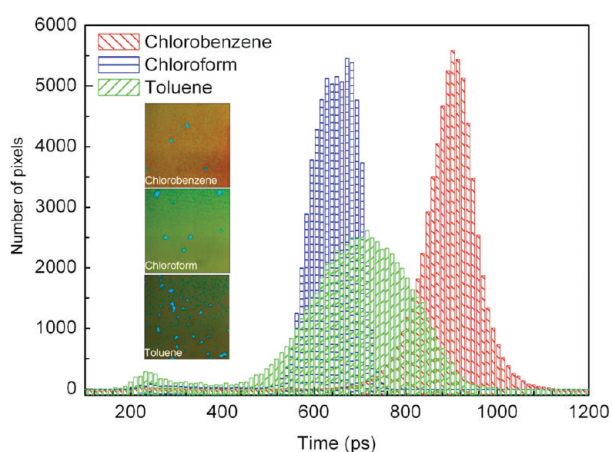
Figure 3. Distribution histogram deduced from fluorescence lifetime images of the MEH-PPV films cast from various solvents scanning over an area of 375 μm × 375 μm. The lifetime images are shown in the insets.

"monomer-like" and contain weakly interacting chains and those that are "aggregate-like" and contain strongly interacting chains".[18] Collison et al.[26] also reported time-resolved emission studies of MEH-PPV in solutions of different solvent quality suggesting that isolated segments with shorter conjugation lengths existed in good solvents. The long-lived fluorescence decay was attributed to the singlet state following back-transfer from nonemissive interchain excited states to intrachain excited states. It is worth noting that the decay times reported here are shorter than those that have been attributed elsewhere to excited state complexes[27,28] with "excimer-like" species having emission lifetimes significantly longer than the ~0.8 to 1 ns radiative lifetime of the monomer.[18] The diverse fluorescence decay behaviors in micrometer regions of films cast from all solutions show the inhomogeneous structures existing on microscopic scales depending on chain conformation and packing configuration of conjugated polymers.

This suggests that the "uniformly coated" and small regions (e.g., points B and C) correspond to areas in which any aggregates formed are small, whereas the large regions (e.g., region A) correspond to larger aggregates with correspondingly shorter fluorescence decay times. In most work on bulk films (i.e., the functional form of conjugated polymer[21]), the measurements reflect films that consist largely of highly aggregated forms

of the polymer. The current work identifies inhomogeneities in the monomer/aggregate populations in the films, which will affect the overall photophysical properties of the film.

The inherent aggregation characteristics of conjugated polymers due to the $\pi-\pi$ electronic interaction among polymer chains impose the existence of the spatial photophysical inhomogeneities in solid state films. The distribution histograms of average fluorescence lifetime in the MEH-PPV films cast from various solvents are depicted in Figure 3. The samples were scanned over an area of 375 μm × 375 μm selected from the representative regions of the films. The experiments were carried out on three to five samples for polymers cast from each solvent. Average fluorescence lifetimes from pixels shown in the lifetime image recorded from the film cast from chlorobenzene solution concentrate around 800 to 1000 ps with a peak at 905 ps, whereas the average lifetime of the toluene film is rather more dispersed, mainly in the range 450−950 ps with a peak at 715 ps and some pixels in the 200 ps region. The longer average lifetimes, being concentrated in a relatively small range of the chlorobenzene-cast films, demonstrate the higher degree of uniformity of this film compared with the broader lifetime distribution in toluene-cast films. More aggregated clusters also can be seen in the inset lifetime image of the film cast from toluene. The distribution histogram of the chloroform-cast film is uniformly distributed in a shorter lifetime range from 530 to 750 ps with a peak around 670 ps. The existence of a higher propensity for aggregate formation is therefore inferred in the chloroform film.

Because the fluorescence decay profiles at different points of the films are distinct from each other, they may also be expected to exhibit diverse fluorescence spectral behaviors. The confocal microscope coupled to a high-resolution Ocean Optics spectrometer allows us to record the emission spectra of specific points by holding the excitation laser beam stationary at those points. The sampled volume is significantly smaller than the colored areas in the emission images of Figure 2. Fluorescence emission spectra at different points of the film cast from various solvents are illustrated in Figure 4 ((a) chlorobenzene, (b) chloroform, and (c) toluene). It is clear that these spectra are significantly different from those recorded from bulk areas of the film in the conventional fluorimeter. For point A, which is considered as a highly aggregated region in the chlorobenzene-cast film, the peak position of the emission spectrum is located at 597 nm, and the shape closely resembles that of the corresponding (bulk film) spectrum in Figure 1. The spectrum is blue-shifted with the band
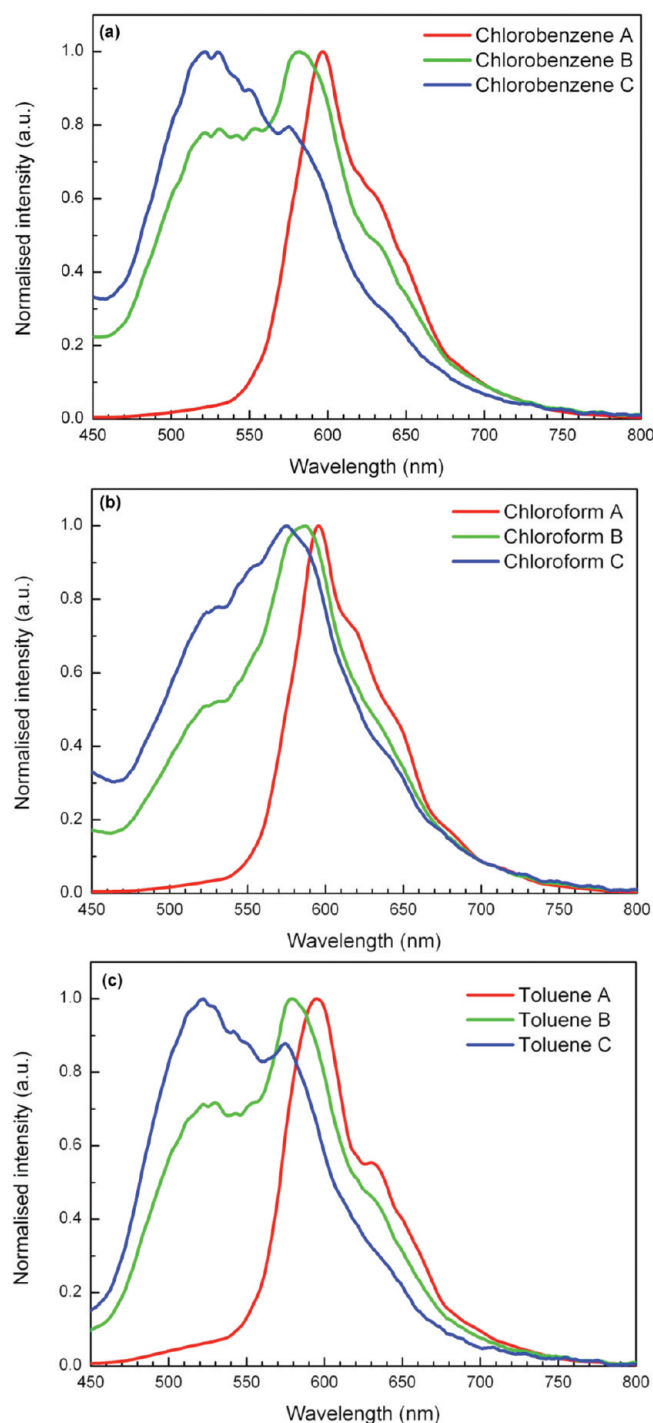
1523

dx.doi.org/10.1021/jz200540j |*J. Phys. Chem. Lett.* 2011, 2, 1520–1525

Figure 4. Intensity normalized emission spectra at different points of the films cast from various solvents (a) chlorobenzene, (b) chloroform, and (c) toluene.

maximum at 582 nm and a strong shoulder at 530 nm for the smaller aggregate region around point B. However, the vibronic shape of the emission spectra for a nonaggregated region (C) is totally changed with its peak position at 530 nm and an emission shoulder at 575 nm. Similar variations of emission spectra are observed as shown in Figure 4c for films cast from toluene solution. For the film cast from chloroform, the spectrum from the large aggregated region (A) is again similar to the films cast

from the other solvents, but the peak position appears to shift from 596 to 575 nm in going from region A to C. The 525 nm shoulder is far less pronounced for region A than for the other solvents. These observations suggest that aggregation is more prevalent across the film, and the aggregates are on average smaller when the film is cast from chloroform compared with the other solvents.

These spectral features are somewhat different from those observed in single-molecule experiments by Huser et al.[20,29] The spectrum of the aggregated regions centered around 600 nm is significantly to the red of the emission maxima reported by Huser et al. for the longest (lowest energy) segments (from either chloroform or toluene). The spectral behavior observed is, however, similar to that reported by Sherwood et al.[18] for small aggregates. The emission band from regions C at ∼525 nm, which corresponds closely to the 0−0 band of MEH-PPV oligomers,[18] is not often observed in MEH-PPV films, and its presence is indicative of either (i) reduced energy migration from high energy, short segments to lower energy, longer conjugation length segments (or aggregates), resulting in more emission from the blue emitting chromophores,[13,18] or (ii) a preponderance of shorter conjugation length polymer segments in regions C. Either of these explanations is consistent with shorter conjugated segments exhibiting longer emission lifetimes and higher quantum yields than the longer, lower energy segments[30] or aggregates, but the observed spectral behavior is more indicative of variability in interchain interactions than individual chain conformation (conjugation length) differences.

In summary, this work illustrates the power of time-resolved emission imaging to identify regions of varying degrees of aggregation, whether pre-existing aggregates or those formed during film formation, in MEH-PPV/PMMA films cast from a range of solvents, and that these differences correlate to some extent with the solvent from which the films are cast. The spatiotemporal spectral behavior observed resembles that of varying degrees of aggregation, from a level of "single-chain like" regions (emitting to the blue with approximately nanosecond emission decay components) to highly aggregated (short-lived, red emitting) regions, within the film morphology. The overall time-resolved behavior was sensitive to the degree of aggregation, which in turn was dependent on the solvent from which the film was cast. This spectral behavior is indicative of reduced interchain energy migration. Overall, the chlorobenzene-cast film showed the least aggregated behavior, whereas the film cast from chloroform showed the shortest-lived, more red emission corresponding to a higher degree of aggregation. In much of the relevant work to date (e.g., ref 20), variations in polymer conformational and spectral behavior as a function of solvent have been interpreted in terms of solvent "quality", which is an unquantifiable parameter. The ET(30) polarity values for the solvents used here do not differ enormously.[31] The solvatochromism-derived parameters (e.g., polarizability, hydrogen bonding acidity, and basicity) for the solvents used[32,33] may shed more light on the energetics of the interactions between the solvent molecules and the side chains of the polymer (because it is the pendant groups that afford solubility of PPV polymers). This is clearly an area requiring further research. Further work investigating any differences in spatiotemporal behavior between spin coating and films formed by the slow evaporation process, which allows polymer chains to achieve equilibrium thermodynamics in the solid state, will also be informative.

The range of emission and decay behavior and the concomitant spatial variations in emission quantum yield will ultimately affect the efficiency of organic electronics devices based on such films for use in organic opto-electronic applications such as OLEDs, organic photovoltaics, and so on and may be of importance in single-molecule studies in which conjugated polymers are immobilized in inert polymer matrices.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: trevoras@unimelb.edu.au.

■ REFERENCES

(1) Brabec, C. J.; Gowrisanker, S.; Halls, J. J. M.; Laird, D.; Jia, S. J.; Williams, S. P. Polymer-Fullerene Bulk-Heterojunction Solar Cells. *Adv. Mater.* **2010**, *22*, 3839–3856.

(2) Calzado, E. M.; Boj, P. G.; Diaz-Garcia, M. A. Amplified Spontaneous Emission Properties of Semiconducting Organic Materials. *Int. J. Mol. Sci.* **2010**, *11*, 2546–2565.

(3) Chen, S. A.; Jen, T. H.; Lu, H. H. A Review on the Emitting Species in Conjugated Polymers for Photo- and Electro-Luminescence. *J. Chinese Chem. Soc.* **2010**, *57*, 439–458.

(4) McMahon, D. P.; Troisi, A. Organic Semiconductors: Impact of Disorder at Different Timescales. *ChemPhysChem* **2010**, *11*, 2067–2074.

(5) Scherf, U.; Riechel, S.; Lemmer, U.; Mahrt, R. F. Conjugated Polymers: Lasing and Stimulated Emission. *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 143–154.

(6) Slota, J. E.; He, X. M.; Huck, W. T. S. Controlling Nanoscale Morphology in Polymer Photovoltaic Devices. *Nano Today* **2010**, *5*, 231–242.

(7) So, F.; Krummacher, B.; Mathai, M. K.; Poplavskyy, D.; Choulis, S. A.; Choong, V. E. Recent Progress in Solution Processable Organic Light Emitting Devices. *J. Appl. Phys.* **2007**, *102*, 21.

(8) Lee, S. S.; Loo, Y. L. Structural Complexities in the Active Layers of Organic Electronics. *Ann. Rev. Chem. Biomol. Eng.* **2010**, *1*, 59–78.

(9) Schwartz, B. J. Conjugated Polymers as Molecular Materials: How Chain Conformation and Film Morphology Influence Energy Transfer and Interchain Interactions. *Annu. Rev. Phys. Chem.* **2003**, *54*, 141–172.

(10) Ravindranath, R.; Ajikumar, P. K.; Bahulayan, S.; Hanafiah, N. B. M.; Baba, A.; Advincula, R. C.; Knoll, W.; Valiyaveettil, S. Ultrathin Conjugated Polymer Network Films of Carbazole Functionalized Poly(*p*-phenylenes) via Electropolymerization. *J. Phys. Chem. B* **2007**, *111*, 6336–6343.

(11) Chabinyc, M. L. X-ray Scattering From Films of Semiconducting Polymers. *Polym. Rev.* **2008**, *48*, 463–492.

(12) Chabinyc, M. L. Characterization of Semiconducting Polymers for Thin Film Transistors. *J. Vac. Sci. Technol., B* **2008**, *26*, 445–457.

(13) Hao, X. T.; Chan, N. Y.; Dunstan, D. E.; Smith, T. A. Conformational Changes and Photophysical Behavior in Poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] Thin Films Cast under an Electric Field. *J. Phys. Chem. C* **2009**, *113*, 11657–11661.

(14) Hao, X. T.; Hosokai, T.; Mitsuo, N.; Kera, S.; Mase, K.; Okudaira, K. K.; Ueno, N. Electronic Density Tailing Outside Pi-Conjugated Polymer Surface. *Appl. Phys. Lett.* **2006**, *89*, 182113.

(15) Hao, X. T.; Hosokai, T.; Mitsuo, N.; Kera, S.; Okudaira, K. K.; Mase, K.; Ueno, N. Control of the Interchain Pi-Pi Interaction and Electron Density Distribution at the Surface of Conjugated Poly(3-hexylthiophene) Thin Films. *J. Phys. Chem. B* **2007**, *111*, 10365–10372.

(16) Hao, X. T.; Ryan, T.; Bailey, M. F.; Smith, T. A. Molar Mass Determination of Water-Soluble Light-Emitting Conjugated Polymers by Fluorescence-Based Analytical Ultracentrifugation. *Macromolecules* **2009**, *42*, 2737–2740.

(17) Hao, X. T.; Zhu, F. R.; Ong, K. S.; Tan, L. W. Top Emitting Poly(*p*-phenylene vinylene) Light-Emitting Diodes on Metal Sandwiched Polyethylene Terephthalate Substrates. *Appl. Phys. B: Lasers Opt.* **2006**, *83*, 67–74.

(18) Sherwood, G. A.; Cheng, R.; Smith, T. M.; Werner, J. H.; Shreve, A. P.; Peteanu, L. A.; Wildeman, J. Aggregation Effects on the Emission Spectra and Dynamics of Model Oligomers of MEH-PPV. *J. Phys. Chem. C* **2009**, *113*, 18851–18862.

(19) Nguyen, T. Q.; Doan, V.; Schwartz, B. J. Conjugated Polymer Aggregates in Solution: Control of Interchain Interactions. *J. Chem. Phys.* **1999**, *110*, 4068–4078.

(20) Huser, T.; Yan, M.; Rothberg, L. J. Single Chain Spectroscopy of Conformational Dependence of Conjugated Polymer Photophysics. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 11187–11191.

(21) Grey, J. K.; Kim, D. Y.; Norris, B. C.; Miller, W. L.; Barbara, P. F. Size-Dependent Spectroscopic Properties of Conjugated Polymer Nanoparticles. *J. Phys. Chem. B* **2006**, *110*, 25568–25572.

(22) Yu, J.; Hu, D. H.; Barbara, P. F. Unmasking Electronic Energy Transfer of Conjugated Polymers by Suppression Of O_2 Quenching. *Science* **2000**, *289*.

(23) Samuel, I. D. W.; Rumbles, G.; Collison, C. Efficient Interchain Photoluminescence in a High-Electron-Affinity Conjugated Polymer. *J. Phys. Rev. B* **1995**, *52*, 11573–11576.

(24) Samuel, I. D. W.; Rumbles, G.; Collison, C. J.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. Picosecond Time-Resolved Photoluminescence of PPV Derivatives. *Synth. Met.* **1997**, *84*, 497–500.

(25) Yan, M.; Rothberg, L. J.; Papadimitrakopoulos, F.; Galvin, M. E.; Miller, T. M. Defect Quenching of Conjugated Polymer Luminescence. *Phys. Rev. Lett.* **1994**, *73*, 744–747.

(26) Collison, C. J.; Rothberg, L. J.; Treemaneekarn, V.; Li, Y. Conformational Effects on the Photophysics of Conjugated Polymers: A Two Species Model for MEH-PPV Spectroscopy and Dynamics. *Macromolecules* **2001**, *34*, 2346–2352.

(27) Cronwell, E. Excimer Formation in Conducting Polymers. *Trends Polym. Sci.* **1997**, *5*, 218–222.

(28) Rothberg, L. J.; Yan, M.; Papadimitrakopoulos, F.; Galvin, M. E.; Kwock, E. W.; Miller, T. M. Photophysics of Phenylenevinylene Polymers. *Synth. Met.* **1996**, *80*, 41–58.

(29) Huser, T.; Yan, M. Solvent-Related Conformational Changes and Aggregation of Conjugated Polymers Studied by Single Molecule Fluorescence Spectroscopy. *J. Photochem. Photobiol., A* **2001**, *144*, 43–51.

(30) Tilley, A. J.; Danczak, S. M.; Browne, C.; Young, T.; Tan, T.; Ghiggino, K. P.; Smith, T. A.; White, J. Synthesis and Fluorescence Characterization of MEHPPV Oligomers. *J. Org. Chem.* **2011**, *76*, 3372–3380.

(31) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, Germany, 1988.

(32) Paley, M. S.; McGill, R. A.; Howard, S. C.; Wallace, S. E.; Harris, J. M. Solvatochromism - A New Method for Polymer Characterization. *Macromolecules* **1990**, *23*, 4557–4564.

(33) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. Linear Solvation Energy Relationships. 23. A Comprehensive Collection of the Solvatochromic Parameters, π^*, α, and β, and Some Methods for Simplifying the Generalized Solvatochromic Equation. *J. Org. Chem.* **1983**, *48*, 2877–2887.