

# Photoluminescence Enhancement in MEH–PPV Polymer Thin Films by Surfactant Addition

Veronica Sholin, Enrique J. Lopez-Cabarcos, and Sue A. Carter\*

Physics Department, University of California, Santa Cruz, California 95064

Received November 9, 2005; Revised Manuscript Received April 26, 2006

**ABSTRACT:** We report on the enhancement of the photoluminescence (PL) of poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene] (MEH–PPV) by high concentrations of the surfactant tetra-*n*-octylammonium bromide (TOABr) in thin films. At constant absorbance intensity, enhancements in the PL of MEH–PPV of a factor of up to 22 were observed. Maximum PL enhancement was observed for thin films containing a molar ratio of 2 mol of TOABr per mole of MEH–PPV monomer units (2:1). In contrast, the absorbance and PL of MEH–PPV and TOABr liquid solutions showed no change as the molar concentration of TOABr changed over 5 orders of magnitude. By imaging the morphology and thickness of the films through confocal fluorescence microscopy and scanning electron microscopy, we observed that maximum PL enhancement was accompanied by the onset of the formation of a lamellar mesophase. Light-emitting devices fabricated from MEH–PPV/TOABr solutions in an ITO/PEDOT–PSS/polymer/Ca/Al architecture showed dramatic fall in the quantum efficiency and measured photocurrent as the amount of TOABr in the active layer increased. No electroluminescing activity was observed at molar ratios of 2:1, indicating that the addition of TOABr impedes charge recombination.

## Introduction

Conjugated polymers have received a great deal of attention because of their applications in photovoltaic devices,<sup>1</sup> light-emitting diodes,<sup>2</sup> transistors,<sup>3</sup> and chemical and biological sensors.<sup>4</sup> In particular, the versatility of phenylenevinylene (PPV) derivatives has made these polymers popular materials for research and applications. Among these, MEH–PPV and the water-soluble MPS–PPV have been extensively studied because of their good optical properties and applicability in the construction of devices for both the biological and nonbiological industries.<sup>5–8</sup>

Polymer–surfactant systems have also been the subject of extensive research because of their widespread appearance and many uses in the intensively studied areas of biotechnology and nanotechnology.<sup>9–13</sup> In particular, Chen et al.<sup>14</sup> found that the extension of the backbone of the polyelectrolyte MPS–PPV by the surfactant dodecyltrimethylammonium bromide (DTA) gave rise to enhanced photoluminescence of the polymer and proposed the use of polyelectrolyte/surfactant systems in biological and chemical sensors. This sparked great interest in the area of biotechnology since water-soluble polymers tend to have low PL quantum efficiencies. As a result of this, systems consisting of polyelectrolytes and surfactants in aqueous solutions have been widely studied.<sup>15–19</sup>

The interactions between polyelectrolytes and surfactants in water are driven by electrostatic forces between the ions in solution as well as by the hydrophobicity of the surfactant tails, causing the surfactant molecules to assemble into low-energy configurations such as micelles (see, for example, part 1 in ref 20). Because relatively weak dipole–dipole interactions drive surfactant micellization in organic solvents, leading to ordering at concentrations of surfactant as low as  $10^{-7}$  M,<sup>21</sup> interactions between surfactants and polymers, which are in general neutral, are not expected in organic solutions. Furthermore, polymers in organic solutions may have extremely high PL quantum efficiencies, lessening the interest in enhancing the PL of these

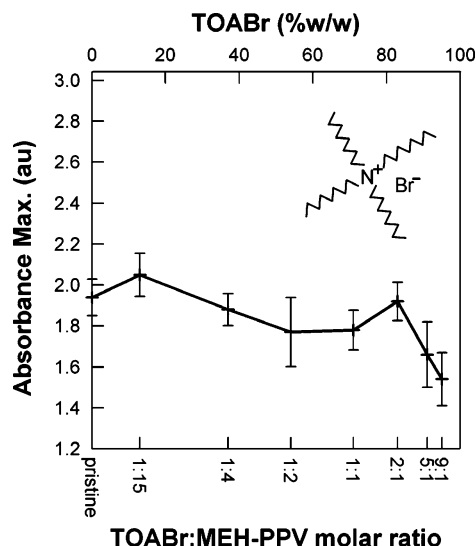
polymers through addition of surfactants in liquid media. Because polymer PL efficiencies are significantly lower in films due to a higher degree of interchain interactions (see, for example, ref 5), enhancing the PL in this case is a desirable effect. In the absence of a solvent, surfactant molecules and polymer chains will be more likely to interact; this may lead to changes of the optical properties of the polymer. Thünemann<sup>22</sup> found that the ionic complex formed by the polyelectrolyte poly-(1,4-phenyleneethynylene carboxylate acid) (PPE) and the surfactant dihexadecyldimethylammonium bromide prepared in stoichiometric proportions could form flexible mesomorphous films. He also found that the PL spectra of films of this complex were similar to the strong blue fluorescence of the complex solution and that light-emitting devices (LEDs) fabricated with a film of this complex exhibited low turn-on points. Thünemann and Ruppelt found that the optical properties of PPE could be changed when the polyelectrolyte was part of a complex with a surfactant<sup>23</sup> and that the fluorescence and electroluminescence properties of films of complexes of PPE with different surfactants depended on the nature of the ionic headgroup of the surfactant.<sup>24</sup>

The purpose of this work was to investigate possible PL enhancement in polymer solid films due to the presence of a surfactant. Solutions of MEH–PPV and the quaternary salt tetra-*n*-octylammonium bromide (TOABr) were spun-cast into solid thin films. The optical properties of the films were studied through steady-state spectroscopy. The morphology of the films was studied through scanning electron microscopy (SEM) and confocal fluorescent microscopy. For comparison, the behavior of the spectra of liquid solutions of MEH–PPV with varying amounts of TOABr was also investigated. Finally, light-emitting devices (LEDs) were fabricated to measure the effects of TOABr on the electroluminescence (EL) quantum efficiency of MEH–PPV and on charge transport across the film.

## Experimental Section

High molecular weight ( $>500\,000$  g/mol) MEH–PPV was purchased from American Dye Source and used without further purification. Tetra-*n*-octylammonium bromide (TOABr) was pur-

\* Corresponding author. E-mail: sacarter@ucsc.edu.



**Figure 1.** Maximum absorbance for a typical batch of samples of MEH-PPV/TOABr spun-cast films vs molar ratio (TOABr moles: moles of MEH-PPV monomer units). The top axis gives the percent per weight of TOABr in each film referred to the total weight of the TOABr/MEH-PPV system. The inset shows the structure of TOABr.

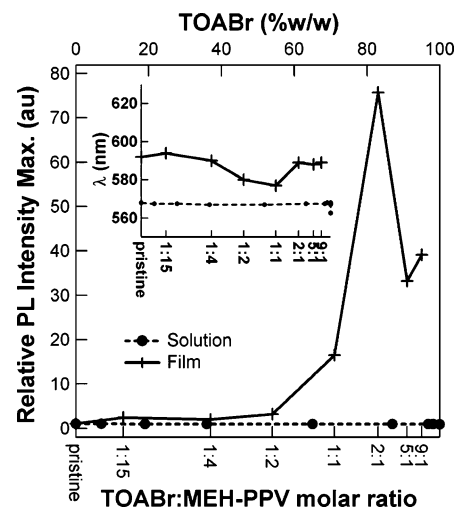
chased from Aldrich (see inset of Figure 1 for structure). For film fabrication, MEH-PPV solutions 0.4 wt % of polymer to weight of chlorobenzene were stirred for a minimum of 48 h at 50 °C. A TOABr/chlorobenzene stock solution was prepared separately, and lower concentration TOABr solutions were prepared by diluting the stock solution. TOABr readily dissolved in chlorobenzene because of the strong hydrophobic behavior imparted on the molecule by the four octyl chains. As a precaution toward the variability in results due to changes in the preparation conditions of the film, fixed amounts of MEH-PPV solution were added to TOABr solutions in the ratio 3:1, so that the amount of MEH-PPV in chlorobenzene was kept constant, while the ratio of TOABr to MEH-PPV decreased. The solutions, prepared in air, were kept in the dark under nitrogen to minimize photodegradation and were stirred for a minimum of 3 h at 50 °C to ensure mixing. Unless otherwise noted, concentrations reported in this paper are expressed in molar ratios, i.e., ratios of moles of TOABr to moles of MEH-PPV monomer units. Graphs also include TOABr percentages per weight referred to the total weight of the polymer/surfactant system.

Films were prepared by spin-casting 60  $\mu$ L of the polymer/surfactant solution onto quartz or glass substrates. To ensure that the PL enhancement observed in the films at high TOABr concentrations was independent of absorption, we monitored the absorbance of the films through steady-state spectroscopy. Experiments were repeated with films cast both at fixed speed for all concentrations (1000 rpm) and at increased speeds as TOABr concentration increased (from 850 rpm for pristine MEH-PPV films to 1550 rpm for highest concentration samples).

Absorbance and PL of film samples were measured immediately after spin-casting (as-cast) and after annealing at 110 °C for 1 h in a vacuum oven. Measurements of the spectra were repeated on samples that were annealed immediately after casting to check for photodegradation by exposure of the samples to air and light throughout the time of the experiment.

The effects of TOABr on the spectra of MEH-PPV were also monitored in liquid solutions. MEH-PPV was dissolved  $1.5 \times 10^{-4}$  M in chlorobenzene; TOABr was dissolved separately in chlorobenzene and then added as necessary to the MEH-PPV solution. The concentration of TOABr in the MEH-PPV solution was varied from  $4.7 \times 10^{-8}$  to  $1.2 \times 10^{-2}$  M.

Steady-state absorption spectra were taken with a N&K UV-vis spectrometer. Steady-state PL spectra were measured with a LS-45 Perkin-Elmer spectrometer; all samples were excited at 505 nm. Polymer film morphology was studied with scanning electron microscopy (SEM) and a white light fluorescent confocal micro-



**Figure 2.** Profile of the maximum PL intensity vs molar ratio for a typical batch of films and for solution. The top axis gives the percent per weight of TOABr in each film referred to the total weight of the TOABr/MEH-PPV system. The inset shows the dependence of the wavelength of the peak PL with molar ratio.

scope (Nikon with a Technical Instrument confocal attachment). For SEM imaging, a thin layer of Au was sputtered onto the surface of the films. Lenses of 4 $\times$  and oil immersion 40 $\times$  with the confocal microscope allowed a maximum resolution of 250 nm horizontally and 250 nm vertically. For imaging with the oil immersion lens, film samples were prepared on thin glass substrates. The index-matching oil drop was placed on the glass rather than on the polymer film to avoid interaction between the oil and the TOABr. Thickness of the films was measured with a Park Scientific atomic force microscope.

Light-emitting devices (LEDs) were fabricated to monitor the EL of the films. Solutions of MEH-PPV/TOABr for the active layer of the devices were the same as those prepared for PL measurements. Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT/PSS) (Baytron from Bayer) was spun-cast onto thoroughly cleaned ITO-coated glass substrates. The samples were baked for 30 min at 110 °C in a vacuum oven and removed immediately from the hot oven so that the films reached room temperature rather quickly. Then MEH-PPV/TOABr solutions were spun-cast at speeds around 1250 rpm, and the samples were baked at 110 °C under vacuum for an additional 1 h. A layer of Ca, followed by a layer of Al, both deposited consecutively and without breaking the vacuum of around  $10^{-6}$  mbar, served as the top electrode. The current-voltage and quantum efficiency curves were obtained using a Keithley 2400 source meter, a Keithley 485 picoammeter, and a UV-100BQ (EG&E) calibrated silicon photodiode. All LED characterization was performed in a nitrogen drybox. Films spun-cast from identical solutions and under identical conditions as the active layers of the LEDs were fabricated to monitor the absorbance and PL of the LED films. All measurements were performed at room temperature.

## Results and Discussion

The absorption length of the films was calculated to be around 40 nm, and thicknesses of all films in this work were higher than 80 nm. Figure 1 shows the spread in average absorbance maxima vs concentration measured over several batches of samples. The curve is mostly featureless with a decrease in the absorbance for concentrations larger than 83%. We attribute this decrease in absorbance to the reduced amounts of MEH-PPV present in these films. The fluctuations in the absorbance intensity at each TOABr concentration did not affect the general behavior of the PL vs concentration reported in this paper.

Figure 2 illustrates the behavior of the maximum intensity of the PL spectra of MEH-PPV/TOABr in film and in solution

as the concentration of TOABr is increased. To appreciate the changes in PL intensity maximum with TOABr concentration, the curves were normalized so that the intensity of the pristine solution and the pristine film were equal to 1. In solution, no changes were observed in either the shape or the peak intensity wavelength of the absorbance or the PL spectra (see inset of Figure 2 for dependence of peak PL wavelength with TOABr concentration). Furthermore, a decrease in PL intensity with addition of TOABr was accompanied by a similar decrease in absorbance, showing that the polymer and surfactant did not interact in solution. These results indicate that, in addition to the large mean separation between polymer and surfactant molecules in liquid, the organic solvent and the polymer compete to interact with the surfactant.

In contrast, an enhancement in the PL at high concentrations of TOABr was observed in solid films (Figure 2). The enhancement for different batches of samples varied between factors of 6 and 22. Although the factor varied from batch to batch, the visible increase in PL at high concentrations of TOABr was reproducible through measurements of several batches of samples on both quartz and glass substrates, with maximum enhancement occurring at a molar ratio of around 2:1 TOABr:MEH-PPV (about 80% w/w). The intensity of the PL, although still high, decreases for ratios of around 5:1 and higher; this is partly due to the reduced absorption of films of high concentration of TOABr. We attribute the variability in the amount of enhancement to sensitivity of the polymer/surfactant interaction to film preparation conditions. It is well-known that systems that can form reverse micelles, such as the polymer/surfactant system in this work, may have considerably complex phase diagrams.<sup>21,25–27</sup> Previous work by Thünemann,<sup>22</sup> in which a 1:1 polyelectrolyte/surfactant complex is examined, finds that the spectra of the complex in solution and film are similar in shape and intensity. This similarity between solution and film is striking, and although a large enhancement in the PL of films was observed in our study, the intensity of the signal in this case was lower than that of solution.

The inset of Figure 2 shows the dependence of the peak PL wavelength with TOABr concentration. Films exhibited a blue shift of about 10 nm for spectra of molar ratios between 1:4 and 1:1 TOABr:MEH-PPV. In contrast, films of ratios of 2:1 and higher showed no shift in PL peak wavelength with respect to that of the pristine MEH-PPV film. Two competing mechanisms may be determining this behavior. At low concentrations, larger separation between polymers strands due to the presence of increasing amounts of TOABr leads to a decrease in the number of interchain interactions and thus a blue shift in the spectra. At high concentrations, the large amounts of TOABr render the film softer, allowing for easier relaxation of the Franck-Condon states and thus an increase in the Stokes shift.

Figure 3 shows images of annealed films examined using a transmission microscope, a fluorescence microscope, and a SEM. To show the phase change occurring at the concentration at which PL enhancement is observed (2:1), the images shown are those of a pristine MEH-PPV film and of the films of ratios 1:1, 2:1, and 5:1 TOABr:MEH-PPV. Column A shows images taken under 4× magnification through transmission microscopy. Films with increasing amount of TOABr up to 1:1 TOABr:MEH-PPV were featureless; a phase change is observed for samples of ratio 2:1 and higher. Films of 5:1 TOABr:MEH-PPV displayed spherulitic formations of up to 0.5 cm in diameter, although no spherulites were observed in either the 2:1 or higher TOABr concentration films. Domidontova and

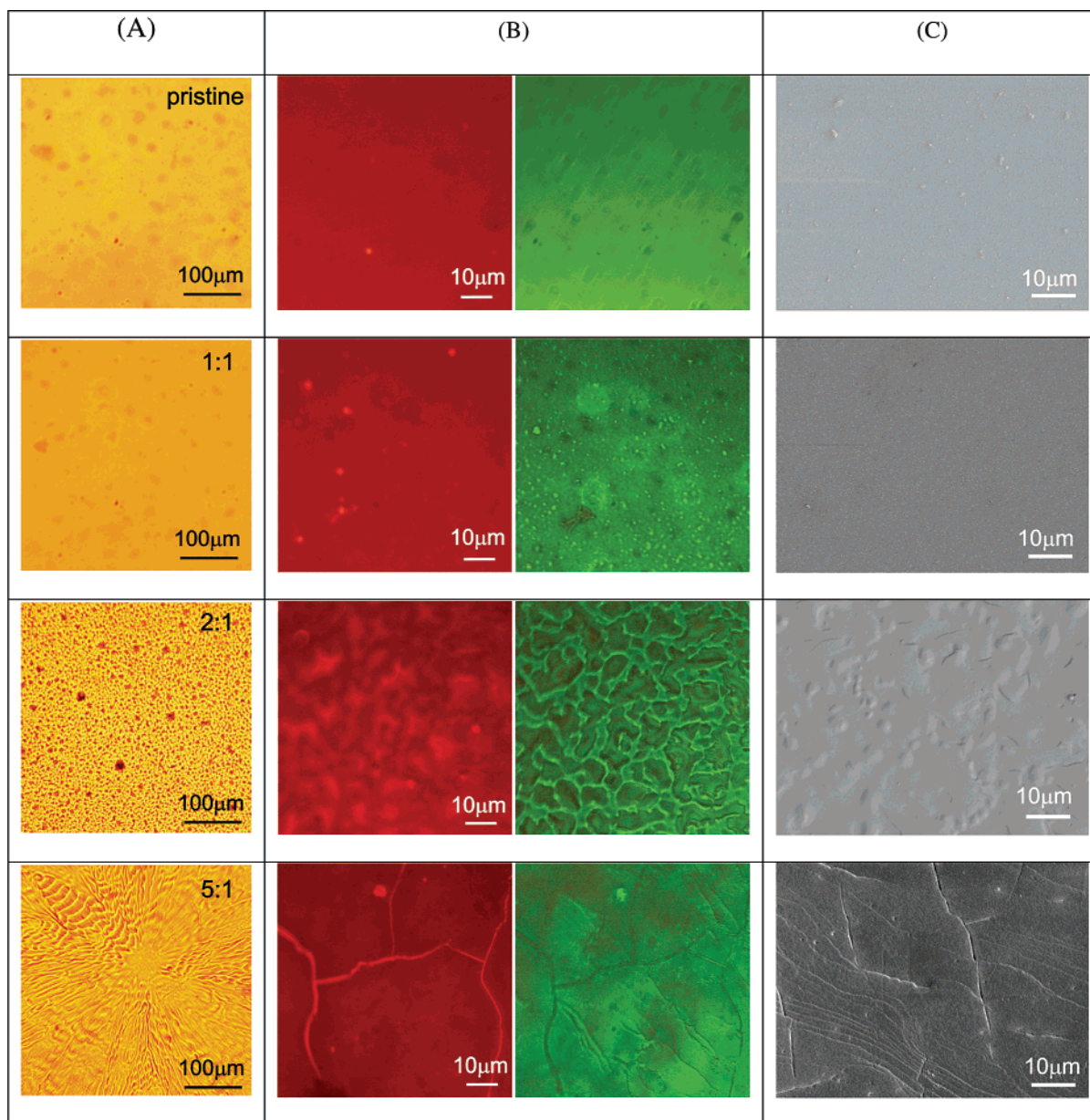
ten Brinke<sup>25</sup> and Tanaka and Ishida<sup>27</sup> study the phase diagrams of systems of polymers and single-chain surfactants and show that, at a given temperature, a system may pass through alternating homogeneous and micro- and macrophase-separated regions as the fraction of surfactant to polymer is varied. We anticipate that the phase diagram for the system studied in this work is even more complex, since each surfactant molecule can interact with any of four octyl chains per surfactant molecule. It should be noted that this work includes the study of films in which there is stoichiometric proportion (1:1) as well as films in which the molar ratio is 1:4 TOABr:MEH-PPV. The large enhancement of the PL is not occurring at these limit case ratios at which interesting behavior could have been expected.

Column B of Figure 3 shows pairs of images of films examined through a 40× oil immersion lens by reflection mode. In each pair, the leftmost image was taken by exciting the sample with a Rhodamine filter (excitation wavelength around 530 nm); the rightmost image was taken under full spectrum illumination. Images within each pair were taken on the same location of the film so there is point-to-point correspondence between the images. Brighter regions in images taken using the Rhodamine filter indicate PL activity at those locations. Pristine MEH-PPV films display few photoluminescent centers; the number and density of these centers become greater as the amount of TOABr in the film is increased (1:1). At 2:1, the films experienced phase separation, and this phenomenon persisted when increasing the concentration. The patterns formed in the phase-separated films were different in aspect for each of the ratios 2:1, 5:1, and 9:1, although the appearance of the films at each of these concentrations was consistent from batch to batch.

Column C of Figure 3 shows scanning electron micrographs of the films. The phase change is evident when the pristine MEH-PPV and 1:1 films are compared to the 2:1 and 5:1 films. The 2:1 image shows lamellar domains of around 10 μm in size; lamellae in the 5:1 film are larger in size than those in the 2:1 films and are stacked in a terrace-like fashion. With the use of wide- and small-angle X-ray scattering (WAXS and SAXS, respectively), Antonietti et al.<sup>12</sup> suggested that polyelectrolyte/single-chain surfactant complexes could be assembling in an alternating bilayer structure of polyelectrolyte and surfactant. WAXS, SAXS, and X-ray reflectivity measurements performed on different polymer/surfactant complexes by Thünemann and Ruppelt<sup>23</sup> yielded results that confirmed this hypothesis. These films were also inspected by atomic force microscopy, and lamellae such as those seen in the column C of Figure 3 were observed. In our films, large amounts of TOABr seem to drive the MEH-PPV into a lamellar mesophase. Although X-ray scattering experiments are necessary in order to verify whether a bilayer structure is forming in the films, we believe it is safe to assume that the lamellae are formed by pure MEH-PPV and that TOABr domains are located between these layers in a fashion that may or may not be ordered.

An analysis of the spectral profiles for films of different amounts of TOABr before and after annealing reflects the high degree of order in the films with large amounts of surfactant. Nguyen et al.<sup>5</sup> have reported in detail on the effects of annealing on the absorption and PL spectra of MEH-PPV films. Annealing allows polymer chains to reorder into lower energy conformations. In general, this results in a higher degree of interchain interactions, which are characterized by red-shifted, broadened, and lower quantum yield PL spectra compared to the spectra of as-cast films. Figure 4 shows the effects of TOABr on the absorbance spectra of films as-cast and after annealing



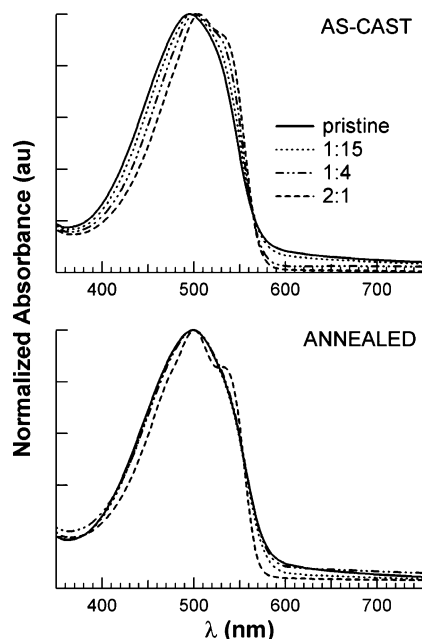


**Figure 3.** Images of MEH-PPV/TOABr films as viewed by transmission microscopy (column A), fluorescence microscopy (from left to right, Rhodamine filter excitation  $\sim 530$  nm and full spectrum illumination, corresponding to same area on the film) (column B), and SEM (column C). Each row shows a different surfactant concentration: pristine, 1:1, 2:1, and 5:1 TOABr:MEH-PPV (from top to bottom). A phase change is observed for TOABr concentrations of 2:1 TOABr:MEH-PPV and higher. Spherulites as large as 0.5 cm in diameter, as well as lamellae, are observed in 5:1 films. Lamellae of smaller domain size are also observed in 2:1 films.

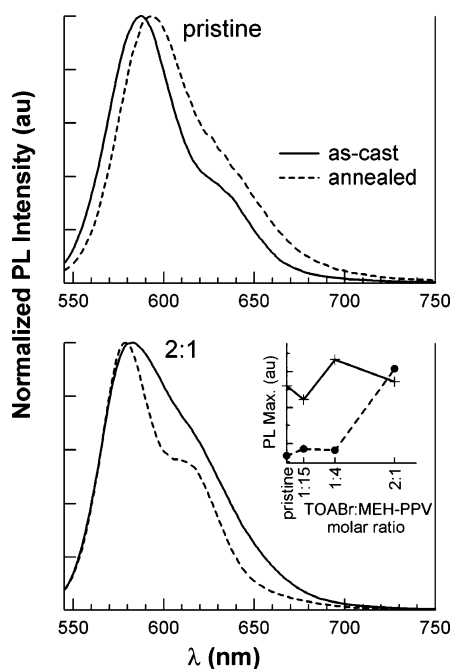
for a pristine sample as well as samples of 1:15, 1:4, and 2:1 TOABr:MEH-PPV. In as-cast films, the addition of surfactant results in spectra that are more narrow and exhibit some vibronic structure. Since these characteristics become more pronounced as larger amounts of TOABr are added to the film, we suggest that larger amounts of TOABr that lay “interstitially” between polymer strands are reducing the number of interchain interactions. Annealing produces broadening of the absorbance spectra and loss of vibronic detail for all samples except the 2:1 film, which instead exhibits a well-defined vibronic peak. This confirms that, while samples with low concentrations of TOABr are behaving as prescribed with annealing, large amounts of TOABr in the film produce an ordered phase.

Figure 5 shows the effects of TOABr on the PL spectra of MEH-PPV films as-cast and after annealing for a pristine sample and a 2:1 TOABr:MEH-PPV sample. Similar conclusions to those made for the behavior of absorbance before and after annealing apply to this case. In as-cast films, the pristine

film exhibits vibronic structure in the PL spectrum; the PL spectra of films with concentrations of TOABr lower than 2:1 TOABr:MEH-PPV behave similarly and are not shown. Vibronic structure is not present in the as-cast 2:1 film, suggesting that in this phase of this high TOABr concentration as-cast sample the polymer strands might be extended and interacting strongly with each other. After annealing, the spectra of the pristine films as well as those of TOABr concentrations lower than 2:1 are broadened and visibly red-shifted, indicating that interchain interactions are playing a larger role than before annealing. In contrast, the 2:1 sample displays higher vibronic definition and a high PL. This is consistent with the formation of lamellae, since in this phase the polymer strands are folded on themselves and interact less with each other. Earlier, we proposed that the red shift of the 2:1 film PL spectrum relative to the spectra of 1:4 to 1:1 films was due to the increased softness of the film. Increased flexibility of the polymer chains should then lead to a broadening of the spectrum, in contrast to



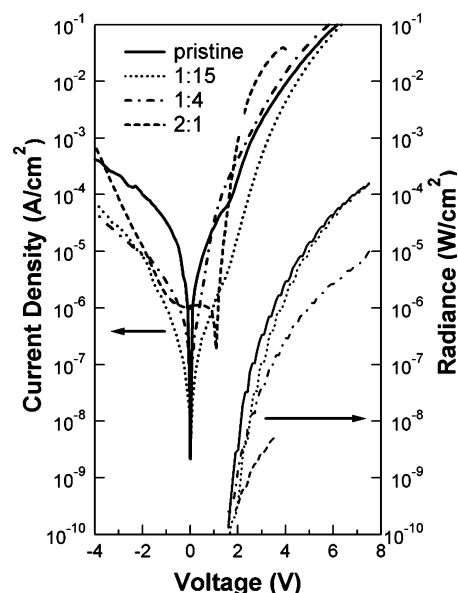
**Figure 4.** Absorbance spectra for as-cast and annealed films. Concentrations are expressed in ratios of TOABr moles to moles of MEH-PPV monomer units.



**Figure 5.** PL spectra for a pristine film and a 2:1 TOABr:MEH-PPV film as-cast and after annealing at 110 °C for 1 h. The inset shows the PL peak intensity as a function of TOABr concentration.

what is observed. If we assume that the lamellae are formed by MEH-PPV and that the TOABr lays between lamellae “interstitially”, then TOABr domains may be acting as a buffer making the film softer overall, while allowing the MEH-PPV to luminesce more efficiently. In this way, high quantum yields and vibronic structure observed in the PL can be consistent with the red shift, measured relative to that of lower TOABr concentration films, observed for 2:1 TOABr:MEH-PPV films.

The inset in Figure 5 shows that annealing the samples causes a decrease of the peak PL intensity for all samples except the 2:1 film. We believe the high PL of low-concentration as-cast films is due to the presence of solvent remnants, and it should be noted that, in the majority of cases, 2:1 samples displayed a

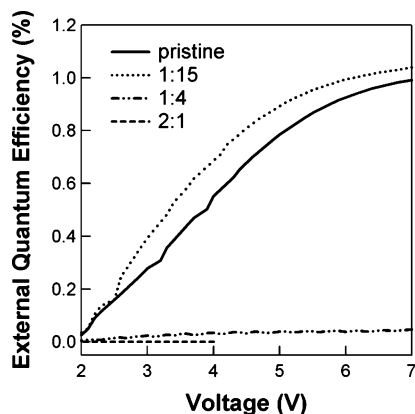


**Figure 6.** Current density (thick lines, left axis) and radiance (thin lines, right axis) vs voltage for TOABr:MEH-PPV LEDs.

significantly larger PL intensity than lower concentration samples even immediately after casting. Also, films in general displayed a smooth glassy surface immediately after casting, whereas only films of ratio of 1:1 or lower amounts of TOABr preserved this aspect after annealing. Films of 2:1 TOABr:MEH-PPV became cloudy, 5:1 samples displayed spherulitic formations, and 9:1 films showed a beady surface after annealing.

Optoelectronic devices such as LEDs benefit from high PL yield of their active layer, since this may provide grounds for efficient electroluminescence. For this reason, LEDs of MEH-PPV/TOABr active layers were fabricated. The current density (IV) and radiance curves for LEDs with pristine MEH-PPV and 1:15, 1:4, and 2:1 TOABr:MEH-PPV active regions are shown in Figure 6. While the IV curves of the pristine MEH-PPV and 1:15 samples exhibit normal LED behavior, the IV for the 1:4 sample is missing the characteristic kink signaling the turn-on voltage. At 2:1, the shape of the IV curve is characteristic of an LEC, and the high currents seen around 2 V indicate there may be unipolar drift. We suggest this current consists predominantly of  $\text{Br}^-$ , since interaction of the four octyl chains with the polymer may be hindering  $\text{N}^+$  drift. Also, the radiance at 4 V decreases by 3 orders of magnitude as the amount of TOABr is increased from none to 2:1 TOABr:MEH-PPV. As mentioned above, Thünemann<sup>22</sup> fabricated LEDs with 1:1 polymer/surfactant complexes in a similar architecture of those in this work. Thünemann and Ruppelt<sup>24</sup> fabricated LEDs using complexes of a different polymer and several surfactants. Although the performance of the complex layer LEDs is not compared to that of a pure polymer LED in these reports, the authors do not observe poor device behavior in 1:1 complexes. In our work, the performance of the devices deteriorates as the amount of surfactant in the film increases. Poor behavior is observed for surfactant amounts below (1:4) and above (2:1) stoichiometric proportions. In the works mentioned previously, excess salt was removed from the complex solutions that were used to fabricate the LEDs. Here  $\text{Br}^-$  ions are still present in the solution and may be the cause of the poor LED performance for high concentrations of surfactant.

As shown in Figure 7, the external quantum efficiency (QE) of the pristine and 1:15 devices are similar. At 1:4, the QE has decreased by an order of magnitude, and at 2:1 the device shows



**Figure 7.** External quantum efficiency vs voltage for MEH-PPV/TOABr LEDs. Corresponding IV and radiance curves are presented in Figure 6.

no charge-to-photon conversion. A dim flash that quickly faded was observed when a voltage was applied across the 1:4 device, and no light was produced on 2:1 samples, except at few micron-sized points along the device. The reason for this poor performance is not yet fully understood in view of the results shown previously. Holt et al.<sup>28</sup> have observed PL quenching in MEH-PPV/salt thin films at nonzero voltages due to electrochemical doping of the polymer. As mentioned, Br<sup>-</sup> ions are still present in MEH-PPV/TOABr films, and they may be doping the polymer and quenching the PL in the presence of an applied bias. In the majority of cases, 2:1 samples were not conducting when a voltage was applied across them. This could be due to an increasing number of fractures in the film as the amount of TOABr increases. At 2:1 TOABr:MEH-PPV, the number of ruptures is sufficiently high to change the appearance of the film, and a percolation path for charge transport may no longer exist.

The PL quantum efficiency in MEH-PPV films has been reported to be 12%.<sup>29</sup> At constant absorption, an enhancement in the PL of a film would have to be attributed to an increase of the PL quantum efficiency. In this work, we observe an enhancement of the PL of a factor of up to 22, which would violate the physical requirement that the PL quantum efficiency be less than 100%. One mechanism that may be leading to an apparent violation of this requirement is an improvement in the out-coupling efficiency, which is well-known to be low (<12.5%).<sup>30,31</sup> The high degree of order observed in the films can be contributing to the enhancement of the PL through, for example, ordering of the dipoles of the polymer. Such ordering leads to increased out-coupling efficiency.<sup>32</sup> Furthermore, the corrugation of the film surface, evident in Figure 3C (2:1), may be allowing the escape of trapped waveguide modes. Finally, we consider the possibility that bilayers of polymer and surfactant may be assembling into a photonic structure that allows emission enhancement (such as a dielectric mirror) or amplified spontaneous emission, although the mechanisms for these to occur in our films are unclear at this stage.

## Conclusions

We have shown an enhancement of the PL intensity of MEH-PPV/TOABr films of a factor of up to 22 for samples of molar ratio 2:1 TOABr:MEH-PPV. The enhancement followed a phase change at the 2:1 ratio, since increases in the PL with respect to that of the pristine MEH-PPV film were rarely observed for ratios of 1:1 or less. The morphology of the films as studied through SEM and confocal fluorescent microscopy showed the formation of lamellae at ratios of 2:1 and

higher. Quantum efficiency curves for LEDs showed that TOABr is effectively quenching the electroluminescence in these devices. The cause of the enhancement of the PL remains unclear, and the resolution of this question may lead to interesting physics. X-ray scattering techniques should provide revealing information about the mechanisms leading to this effect.

**Acknowledgment.** V.S. acknowledges support from GAANN. E.L.-C. acknowledges support from "Fundación del Amo" of the Complutense University, "Secretaría de Estado de Educación y Universidades" (Salvador de Madariga Program), and DGI (MAT2003-03051-C03-03) of the Spanish Science and Technology Ministry. S.A.C. acknowledges NSF-ECS for support. The authors also thank the Palo Alto Research Center for allowing use of the SEM.

## References and Notes

- (1) Tang, C. W. *Appl. Phys. Lett.* **1986**, *48*, 183–185.
- (2) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913–915.
- (3) Burroughes, J. H.; Jones, C. A.; Friend, R. H. *Nature (London)* **1988**, *335*, 137–141.
- (4) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537–2574.
- (5) Nguyen, T. Q.; Martini, I. B.; Liu, J.; Schwartz, B. J. *J. Phys. Chem. B* **2000**, *104*, 237–255.
- (6) Chen, L.; McBranch, D.; Wang, H.-L.; Helgeson, R.; Wudl, F.; Whitten, D. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 12287–12292.
- (7) Yan, M.; Rothberg, L. J.; Kwock, E. W.; Miller, T. M. *Phys. Rev. Lett.* **1995**, *75*, 1992–1995.
- (8) Wang, J.; Wang, D.; Miller, E. K.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Macromolecules* **2000**, *33*, 5153–5158.
- (9) Goddard, E. D.; Ananthapadmanabhan, K. P., Eds. *Interaction of Surfactants with Polymers and Proteins*; CRC Press: Boca Raton, FL, 1993.
- (10) Kwak, J. C. T., Ed.; *Polymer-Surfactant Systems*; Dekker: New York, 1998.
- (11) Pileni, M. P., Ed.; *Structure and Reactivity in Reverse Micelles*; Elsevier: Dordrecht, The Netherlands, 1989.
- (12) Antonietti, M.; Conrad, J.; Thünemann, A. *Macromolecules* **1994**, *27*, 6007–6011.
- (13) Fendler, J. H. *Chem. Rev.* **1987**, *87*, 877–899.
- (14) Chen, L.; Xu, S.; McBranch, D.; Whitten, D. *J. Am. Chem. Soc.* **2000**, *122*, 9302–9303.
- (15) Chen, L.; McBranch, D.; Wong, R.; Whitten, D. *Chem. Phys. Lett.* **2000**, *330*, 27–33.
- (16) Wang, X.; Li, Y.; Li, J.; Wang, J.; Wang, Y.; Guo, Z.; Yan, H. *J. Phys. Chem. B* **2005**, *109*, 10807–10812.
- (17) MacKnight, W. J.; Ponomarenko, E. A.; Tirrell, D. A. *Acc. Chem. Res.* **1998**, *31*, 781–788.
- (18) Lavigne, J. J.; Broughton, D. L.; Wilson, J. N.; Erdogan, B.; Bunz, U. H. F. *Macromolecules* **2003**, *36*, 7409–7412.
- (19) Yan, P.; Jin, C.; Wang, C.; Ye, J.; Xiao, J.-X. *J. Colloid Interface Sci.* **2005**, *282*, 188–192.
- (20) Mittal, K. L., Ed. *Micellization, Solubilization, and Microemulsions*; Plenum Press: New York, 1977; Vol. 1.
- (21) Kertes, A. S. In *Micellization, Solubilization, and Microemulsions*; Mittal, K. L., Ed.; Plenum Press: New York, 1977; Vol. 1.
- (22) Thünemann, A. F. *Adv. Mater.* **1999**, *11*, 127–130.
- (23) Thünemann, A. F.; Ruppelt, D. *Langmuir* **2000**, *16*, 3221–3226.
- (24) Thünemann, A. F.; Ruppelt, D. *Langmuir* **2001**, *17*, 5098–5102.
- (25) Dormidontova, E.; ten Brinke, G. *Colloids Surf., A* **1999**, *147*, 249–262.
- (26) Roukolainen, J.; Torkkeli, M.; Serimaa, R.; Komanshek, B. E.; Ikkala, O.; ten Brinke, G. *Phys. Rev. E* **1996**, *54*, 6646–6649.
- (27) Tanaka, F.; Ishida, M. *Macromolecules* **1997**, *30*, 1836–1844.
- (28) Holt, A. L.; Leger, J. M.; Carter, S. A. *J. Chem. Phys.* **2005**, *123*, 044704.
- (29) Samuel, I. D. W.; Rumbles, G.; Collison, C. J.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Synth. Met.* **1997**, *84*, 497–500.
- (30) Greenham, N. C.; Friend, R. H.; Bradley, D. D. C. *Adv. Mater.* **1994**, *6*, 491–494.
- (31) Benisty, H.; De Neve, H.; Weisbuch, C. *IEEE J. Quantum Electron.* **1998**, *34*, 1612–1631.
- (32) Wasey, J. A. E.; Barnes, W. L. *J. Mod. Opt.* **2000**, *47*, 725–741.