

Improving the performance of conjugated polymer-based devices by control of interchain interactions and polymer film morphology

Thuc-Quyen Nguyen

Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095-1569

Raymond C. Kwong and Mark E. Thompson

Department of Chemistry, University of Southern California, Los Angeles, California 90089

Benjamin J. Schwartz^{a)}

Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095-1569

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Interchain interactions in conjugated polymer films promote good carrier transport but also reduce the luminescence quantum yield, leading to a fundamental trade-off in optimizing film morphology for device performance. We present two methods to improve the efficiency of light-emitting diodes (LEDs) based on poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) by altering film morphology without changing device architecture. First, "trilayer" LEDs, which use a central MEH-PPV layer with reduced interchain interactions between layers of highly aggregated MEH-PPV near the electrodes, have a higher efficiency than single-layer devices. Second, device efficiency can be improved by annealing MEH-PPV films, so that the reduced emission upon increasing interchain interactions is overcome by more balanced charge injection. © 2000 American Institute of Physics. [S0003-6951(00)03817-1]

Conjugated polymers have received a great deal of attention due to their potential for applications in optoelectronic devices. Typical polymer-based devices, such as photovoltaic cells or light-emitting diodes (LEDs), are fabricated in a sandwich structure consisting of a conjugated polymer film spin coated onto one electrode with a second electrode evaporated on top. It is well known that the architecture of such devices affects their performance. Factors such as the presence of oxygen during electrode evaporation,¹ the distance the emissive region lies from the electrodes,² etc., control various aspects of device behavior. In addition to device architecture, the way in which conjugated polymer chains interact is important for optimizing the performance of devices based on these materials.³ Even though the presence of interchain electronic species has been a subject of debate,² it is becoming increasingly clear that the photophysical and electrical behavior of conjugated polymer films is highly sensitive to aggregation and chain morphology.³⁻⁶ Thus, the film morphology, and hence, the performance of conjugated polymer-based devices, can be controlled in a number of ways, which include: changing the solvent and polymer concentration of the solution from which the polymer film is cast,³ changing the spin speed,⁷ using Langmuir-Blodgett techniques to grow films layer by layer,⁸ or annealing.³

In previous work, we studied the photophysical and device behavior of poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) (see the inset to Fig. 1 for the chemical structure), as the polymer morphology was systematically varied.³ We found that aggregation of MEH-PPV chains is promoted in solvents such as chlorobenzene (CB), where the polymer has a more open conformation, and

is restricted in solvents such as tetrahydrofuran (THF), where the chains tend to form a tighter coil. Evidence from a variety of experiments suggests that the degree of aggregation in solution is largely preserved through the casting process and survives into the film.³ As a result, MEH-PPV LEDs based on films cast from THF, which have a lower degree of interchain interactions, have a higher turn-on voltage, lower injection current, but higher quantum efficiency (photons/electron) than corresponding devices based on films with a

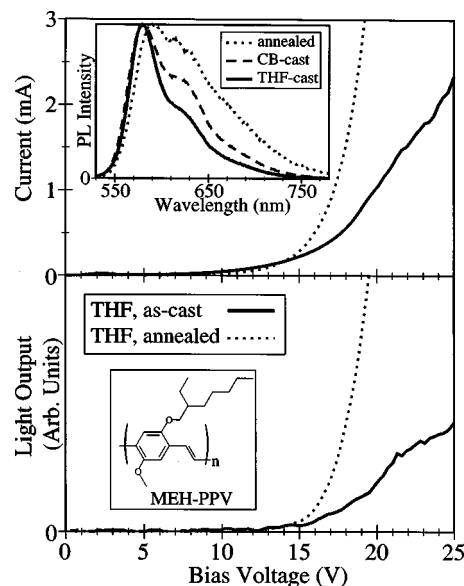


FIG. 1. Representative current-voltage (a) and brightness-voltage (b) curves for ITO/MEH-PPV/Mg:Ag LEDs, where the 200-nm-thick MEH-PPV active layer is used as cast from THF (solid curves) or has been annealed for several hours (dotted curves). Upper panel inset: normalized PL spectra of the MEH-PPV films. Lower panel inset: chemical structure of MEH-PPV.

^{a)}Corresponding author; electronic mail: schwartz@chem.ucla.edu

larger number of aggregates cast from CB.³ This illustrates an apparently fundamental trade-off when trying to optimize conjugated polymer films for maximum device performance: the same interchain interactions which promote charge transport are detrimental to luminescence efficiency.³

In this letter, we will show that it is possible to exploit the ability to control the morphology of conjugated polymer films to fabricate LEDs with better performance than devices prepared using conventional spin coating of the active polymer layer. We will focus on the properties of two sets of devices. First, we explore the behavior of “annealed” LEDs, in which the morphology of the active MEH-PPV layer is altered by heating the films at the glass-transition temperature for several hours in an inert environment. The idea is to examine how the trade off between favorable current injection and lower emission quantum yield changes by packing the polymer chains into lower-energy structures with a greatly increased degree of interchain contact. Second, we investigate the performance of “heterostructure” LEDs, composed of a layer of MEH-PPV cast from THF sandwiched between MEH-PPV layers spin coated from CB (“trilayer” device). Here, the idea is that highly aggregated CB-cast layers will allow for good current transport near the electrodes, while the low-mobility THF-cast layer will trap carriers and promote recombination in a region with lower interchain interactions, and thus higher luminescence quantum yield. We find that both the trilayer and the annealed devices have higher efficiency than comparable devices based on single-layer films cast directly from either CB or THF solutions. Since the device architecture is the same for all the LEDs in our study, the improvements in performance are the direct result of changes in polymer morphology, which as we will argue below, result primarily from changes in morphology at the polymer/electrode interface.

To explore the effects of polymer morphology on device performance, we constructed the two sets of LEDs by spin coating 1% (w/v) solutions of MEH-PPV in either CB or THF directly onto indium–tin–oxide (ITO)-coated glass substrates; the resultant films were heated at 50 °C for 2 h to evaporate the solvent. Prior to polymer deposition, the ITO substrates were washed with tetrachloroethylene, acetone, and isopropanol followed by oxygen plasma cleaning. For both sets of devices, metal cathodes consisting of 1-mm-diam. spots of 10:1 Mg:Ag alloy (80 nm thick), capped with 100 nm of Ag, were thermally evaporated at $\sim 10^{-6}$ Torr. Device current–voltage–brightness was measured using a Keithley 2400 source meter/2000 multimeter coupled to a Newport 1834-C optical meter; the system has been calibrated to measure absolute external electroluminescence (EL) quantum efficiencies. All device processing steps were carried out in an inert environment. For the first set of devices, four LEDs were fabricated, two each from MEH-PPV films cast from CB and THF, with spin speeds chosen to ensure that the thickness was 200 ± 10 nm. One film cast from each solvent was annealed at the glass transition temperature (210 °C) (Ref. 3) for several hours prior to deposition of the cathode; annealing had little effect on the thickness of the films. For the second set of devices, three LEDs were constructed: one with a single MEH-PPV layer cast from THF, one with a single layer cast from CB, and a

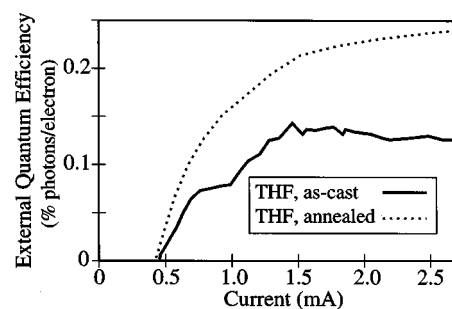


FIG. 2. External EL quantum efficiency (% photons/electron) for the same MEH-PPV-based LEDs shown in Fig. 1.

trilayer device. The trilayer device was made by first spin casting a thin film of MEH-PPV from CB solution onto the ITO substrate, allowing the solvent to dry, and then casting another layer of polymer from THF solution over the CB-cast layer. Finally, a third layer of MEH-PPV was cast from CB solution on top of the other two layers. Spin speeds were chosen so that the total thickness of the MEH-PPV active layer was 400 ± 20 nm for all three devices. The three layers in the trilayer device were of roughly equal thickness. For both sets of devices, we verified reproducibility by fabricating at least four of each kind of device; typical results are presented below.

The photoluminescence (PL) spectra of the MEH-PPV films used as the active layer in the first set of devices are shown in the inset to Fig. 1. The spectra have been normalized to the same maximum intensity, but the absolute PL intensity decreases in the order THF cast (solid curve), CB cast (dashed curve), and annealed (dotted curve). This drop in PL quantum yield, combined with the redshift of the PL spectrum, shows that the degree of interchain interactions in the films increases as the solvent is changed from THF to CB, and increases further upon annealing.³

The main part of Fig. 1 shows typical current–voltage (upper panel) and brightness–voltage (lower panel) curves for MEH-PPV LEDs constructed from as-cast THF films (solid curve) and from annealed films (dotted curve). The annealed devices have a lower turn-on voltage and higher light output than devices constructed from as-cast films, consistent with the idea that increased interchain interactions facilitate charge transport.³ The fact that the increased interchain interactions in the annealed devices lower the PL quantum yield leads us to expect a lower EL efficiency than in the as-cast devices. Surprisingly, Fig. 2 shows that the opposite is observed: at a given current, the external EL quantum efficiency is $\sim 50\%$ higher for the devices based on annealed films. This result leads us to conclude that there is another morphology-dependent factor that also plays an important role in device performance: the structure of the interface between the polymer and the electrodes. In a previous paper, we used scanning force microscopy to show that annealed MEH-PPV films have a much smoother surface than the as-cast films.³ As a result of the better interfacial contact, we believe carrier injection from the cathode improves upon annealing. This leads to a more balanced injection of electrons and holes, an improvement that more than compensates for the loss in PL efficiency. Annealing films cast from CB solution leads to a similar enhancement in efficiency. We note

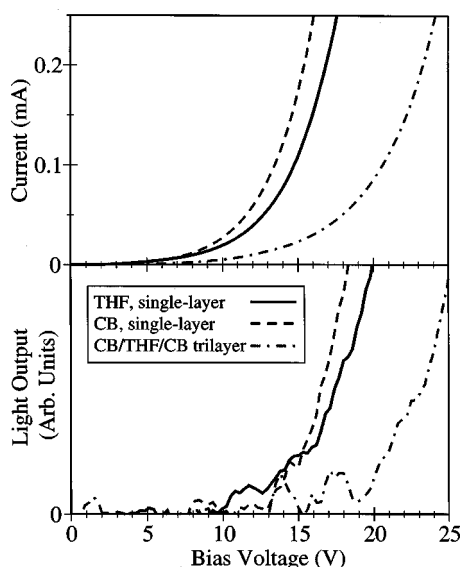


FIG. 3. Current–voltage (a) and brightness–voltage (b) curves for ITO/MEH-PPV/Mg:Ag LEDs where the 400-nm-thick MEH-PPV layer is fabricated in a CB-cast/THF-cast/CB-cast trilayer structure (dot-dashed curves) or is used as-cast from THF (solid curves) or CB (dashed curves).

that this idea of controlling carrier injection by varying the polymer surface morphology is also consistent with recent work exploring the behavior of MEH-PPV LEDs as the spin-casting speed is varied.⁷

Figure 3 shows typical current–voltage (upper panel) and brightness–voltage (lower panel) curves for single-layer MEH-PPV LEDs cast from CB (dashed curve) or THF (dotted curve) and for CB/THF/CB trilayer devices (dot-dashed curve). Consistent with our previous report,³ devices based on single-layer CB-cast MEH-PPV films show higher current and a lower EL efficiency than devices based on THF-cast films. The trilayer films have a lower working current than the single-layer films, the result of poor charge transport across the internal interfaces. Despite the low current, the EL efficiency of the trilayer devices is noticeably better than the single-layer devices, as illustrated in Fig. 4. The enhanced efficiency of the trilayer LEDs results from a combination of factors. First, the trilayer devices have higher EL efficiency than single-layer THF-cast devices because charge injection in the trilayer devices is more balanced due to the larger number of aggregates present in the CB-cast layers near the electrodes. Second, the trilayer devices have a higher EL efficiency than single-layer CB-cast devices because recombination in the trilayer device is largely confined to the central THF layer where weaker interchain interactions lead to

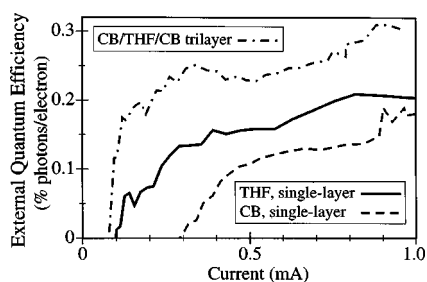


FIG. 4. External EL quantum efficiency (% photons/electron) for the same MEH-PPV-based LEDs shown in Fig. 3.

higher overall luminescence quantum yield. Finally, because carriers tend to recombine in the low-mobility THF layer in the center of the trilayer device, quenching interactions with the electrodes² are reduced relative to either the CB- or THF-cast single-layer devices. Therefore, the efficiency of the three-layer devices is higher than for either type of single-layer device at the same overall thickness.

In summary, we have shown that controlling the degree of interchain interactions in conjugated polymer films can enhance the performance of conjugated polymer-based LEDs by balancing factors such as the ability to inject current across the interface and the quenching of luminescence by aggregation. In the data presented here, the architecture of the device was held constant while only the morphology of the conjugated polymer chains was varied. Since the device architecture used here is not optimal (devices too thick, no hole or electron transport layers, etc.), it should be possible to combine design innovations with control over the morphology of the active layer to greatly improve the absolute efficiency of conjugated polymer devices. The methods for controlling morphology proposed here, annealing the active layer and casting multiple layers from different solvents, represent straightforward extensions of traditional polymer device fabrication: neither new materials nor significant complexity in processing are required. Finally, the failure mechanisms that ultimately limit the useful lifetime of conjugated polymer-based devices also depend on how the polymer chains in the active layer are packed. Changes in film morphology resulting from device operation lead to the need for increased drive voltage to maintain a constant current, and ultimately result in lower EL efficiency and device failure.⁹ Overall, understanding the interactions between chains of conjugated polymers and learning to control them will be critical to the commercialization of devices based on these materials.

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