

Efficiency Optimization in Ionically Self-Assembled Thin Film Polymer Light-Emitting Diodes

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ABSTRACT

We present detailed studies of polymer light emitting diodes fabricated from ionically self-assembled monolayer thin films. The ionically self-assembled monolayer (ISAM) films are created with a new thin film fabrication technique that allows detailed structural and thickness control at the molecular level. The ISAM fabrication method simply involves the dipping of a charged substrate alternately into polycationic and polyanionic aqueous solutions at room temperature. Importantly, the ISAM technique yields exceptionally homogeneous, large area films with excellent control of total film thickness. Our studies concentrate on improving the performance of ISAM light emitting diodes that include poly(para-phenylene vinylene) (PPV). The individual thickness of each monolayer and the interpenetration of adjacent layers can be precisely manipulated through the parameters of the electrolyte solutions. The effects of the pH and ionic strength of the immersion solutions, the total film thickness, and the PPV thermal conversion parameters on the photoluminescence and electroluminescence yields have been systematically studied. Through the ISAM process we can also deposit well-defined thicknesses of different polymers at the indium tin oxide and aluminum electrode interfaces. The interface layers are found to affect the electroluminescence efficiency.

Keywords: polyelectrolytes, ionically self-assembled monolayers, polymer light emitting diodes, poly(paraphenylene vinylene)

1. INTRODUCTION

The first demonstration of a light emitting diode fabricated from a conjugated polymer¹, has generated continued interest in developing new materials and improving the efficiency of the devices. Conjugated polymers are characterized by a delocalized π -electron system along the polymer backbone, which gives them the semiconducting properties. The advantages of using polymers for the fabrication of optoelectronic devices consist in their ease of fabrication, processability, and the possibility of designing new materials with various bandgaps and electron affinities. For display applications, the most heavily studied polymer has been poly(para-phenylene vinylene) (PPV)^{2,3} along with its derivatives^{4,5}. The typical process of forming thin films of these materials is the spin coating technique. Our approach is to fabricate homogeneous thin films through the ionically self-assembled monolayer (ISAM) technique, developed by Decher and coworkers^{6,7} and demonstrated for light emitting diodes (LED) applications by Rubner and coworkers^{8,9}. The technique allows for detailed structural control of materials at the molecular level combined with ease of fabrication and low cost. The ISAM method involves the alternate dipping of a charged substrate into an aqueous solution of a cation followed by dipping in an aqueous solution of an anion at room temperature. Since the adsorption is based on the electrostatic attraction of interlayer charges, each layer is self-limiting in thickness and uniform at the molecular level. This occurs because the film molecules are free to adjust their positions to improve the overall packing since they are not covalently bound to the substrate. Sequential layers are rapidly fixed by drying at room temperature and in air. The typical bilayer thickness is on the order of a nanometer and can be precisely controlled (0.5 to > 5.0 nm) by the parameters of the dipping solutions. Multilayer films several microns in thickness are easily

fabricated by repeating the dipping process with no practical limit to the number of layers that can be deposited. The resulting pliable films are mechanically very robust. The advantages afforded by molecular control on the subnanometer level provide opportunities for dramatically enhanced photonic¹⁰, electronic, and optoelectronic¹¹ devices.

2. EXPERIMENTAL DETAILS

The materials used for the fabrication of the emissive ISAM films were cationic precursor poly(para-phenylene vinylene) (PPVpc), prepared by the classic route^{8,12} and poly(methacrylic acid) (PMA) purchased from Polysciences. For the interface study we used several polymers. The polythiophene acetic acid (PTAA) was prepared according to Reference 13. Poly(allylamine hydrochloride) (PAH) was purchased from Aldrich, poly(sodium 4-styrenesulfonate) (PSS) was purchased from Polysciences, and the polymeric dyes poly S-119, and poly R-478 were purchased from Sigma. The pH and the ionic strength were adjusted accordingly for the different studies as described in the sections below. The films were prepared at room temperature and in air. After the deposition of the films on glass slides and indium tin oxide (ITO) coated glass slides, the films were thermally treated under dynamic vacuum at 300 °C for approximately 8 hours. Absorption spectra were taken with a Jasco spectrophotometer and fluorescence spectra were taken with a Perkin Elmer fluorescence spectrometer. For the electroluminescence spectra we used an Ocean Optics spectrometer. The I-V curves were obtained using a Keithley source unit, and the luminance values were read with a Minolta luminance meter. All measurements were carried in air at room temperature. Evaporated aluminum was used as the top electrode of the devices.

3. OPTIMIZATION OF THE ABSORPTION

In the initial study, we optimized the parameters of the dipping solutions for the absorbance of the films and thus, the thickness of the films. Two basic variables have been studied that control the amount of PPV precursor adsorbed into each monolayer: the presence of salt in the PPVpc solutions, and the pH of the PPVpc solution. The polyanion PMA dipping solution was adjusted to 10 mM concentration, pH=3.5 and salt concentration of 0.05 M. For the first series, the precursor PPV was 0.3 mM, 0.05 M salt, and the pH values were 3.5, 6.5, and 8.0. The films with the same number of bilayers were deposited on glass and we recorded the absorption spectra of the films for the three values of the pH, after the thermal conversion of the PPV. As seen in Figure 1 (left), the best (PPV/PMA)₂₀ (where the subscript indicates the number of bilayers deposited) film is obtained for pH=3.5. The high pH values of the PPVpc solution decreased the amount of PPVpc that adsorbed to the slides. In order to examine the light emission of the films, we also performed fluorescence measurements on the same films. The excitation wavelength was 360 nm. Figure 1 (right) shows the fluorescence spectra obtained for films made for the pH study, after the thermal conversion. The trends of the fluorescence spectra follow those of the absorption. The slide with the highest fluorescence intensity had the pH of 3.5, having the photoluminescence peak around 485 nm. These results indicate that the films fabricated from PPVpc solution with pH 3.5 had the largest amount of PPVpc adsorbed to the substrate.

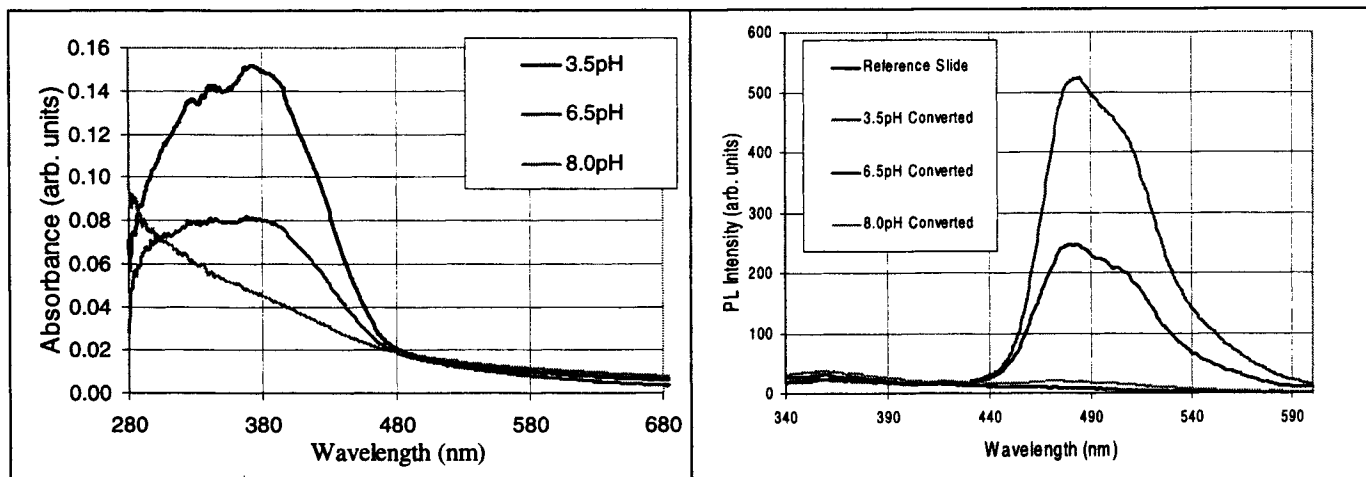


Figure 1. Results of the effects of pH on absorbance (left) and photoluminescence (right) of (PPV/PMA)₂₀ films on glass substrate. The absorption spectra (left) from bottom to top are for pH values of 8.0, 6.5, and 3.5. The post-conversion photoluminescence spectra (right) from bottom to top are for pH values of 8.0, 6.5, and 3.5.

The next study examined the adsorption of the $(PPV/PMA)_{20}$ films on glass as a function of the ionic strength of the PPVpc dipping solution. All solutions had pH adjusted to 3.5, and the salt content for the PPV varied as shown in Figure 2 where the absorption spectra were taken after the thermal conversion of the PPVpc. The absorbance of the films increases with increased ionic strength of the solution, up to 0.5 M, after which the absorbance decreases with increased ionic strength. However, the salt concentration does not seem to affect the position of the peaks, as all are at approximately 370 nm. This indicates that the conjugation length distribution of the PPV is unchanged. The fluorescence measurements (Figure 3) for this series also follow the trend observed in the absorption. The excitation wavelength was 360 nm. The spectra show increasing luminescence up to 0.5 M and decreasing luminescence beyond that point, similar with the absorbance results. The fixed position of the peak for all spectra confirms that the conjugation length distribution of the PPV is unchanged.

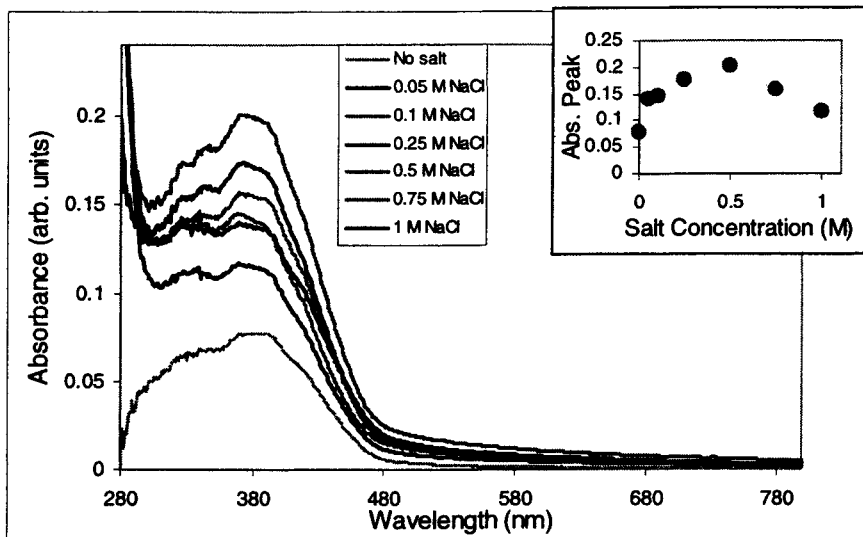


Figure 2. Absorption spectra of $(PPV/PMA)_{20}$ films with different salt content. The spectra from bottom to top are for salt concentrations of 0.0 M, 1.0 M, 0.05 M, 0.1 M, 0.75 M, 0.25 M, and 0.5 M. The curve with highest absorbance was obtained for 0.5 M salt. The inset shows the absorption peak (at 370 nm) vs. the salt content.

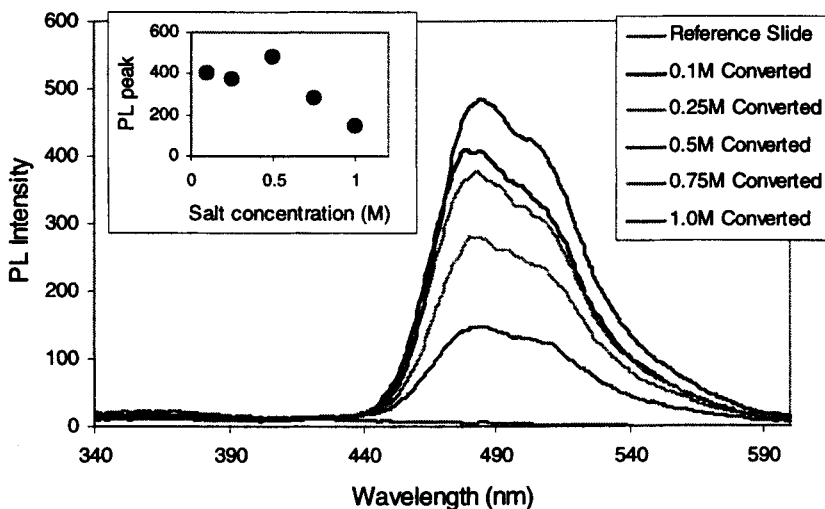


Figure 3. Photoluminescence spectra for post-conversion slides with a pH of 3.5 and varying salt molarity. The spectra from bottom to top are for salt concentrations of 1.0 M, 0.75 M, 0.25 M, 0.1 M, and 0.5 M. The highest intensity in the photoluminescence was obtained for 0.5 M salt. The inset shows the PL peak intensity at 485 nm vs. salt concentration.

4. PPV/PMA LED DEVICES

The device configuration is typical for a polymer LED device. On top of an indium tin oxide (ITO) coated glass slide we deposited the ISAM (PPV/PMA)_x film, where x denotes the number of bilayers, and on top of the film we deposited the aluminum electrodes by resistive evaporation. Figure 4 contains the absorbance, photoluminescence, and electroluminescence spectra for typical ISAM (PPV/PMA)_x device. The photoluminescence spectrum was obtained using the excitation wavelength of 440 nm and has similar features with the photoluminescence spectrum, as expected for a good thermal conversion of the PPVpc to the fully conjugated form. Typical current-voltage and light-voltage curves for the films are presented in Figure 5. The low luminance values are due to the fact that we used a low concentration for the PPVpc dipping solution and therefore obtained very thin films. More recent results from devices prepared with more concentrated solutions, yielding thicker films, showed an increased value for the luminance.

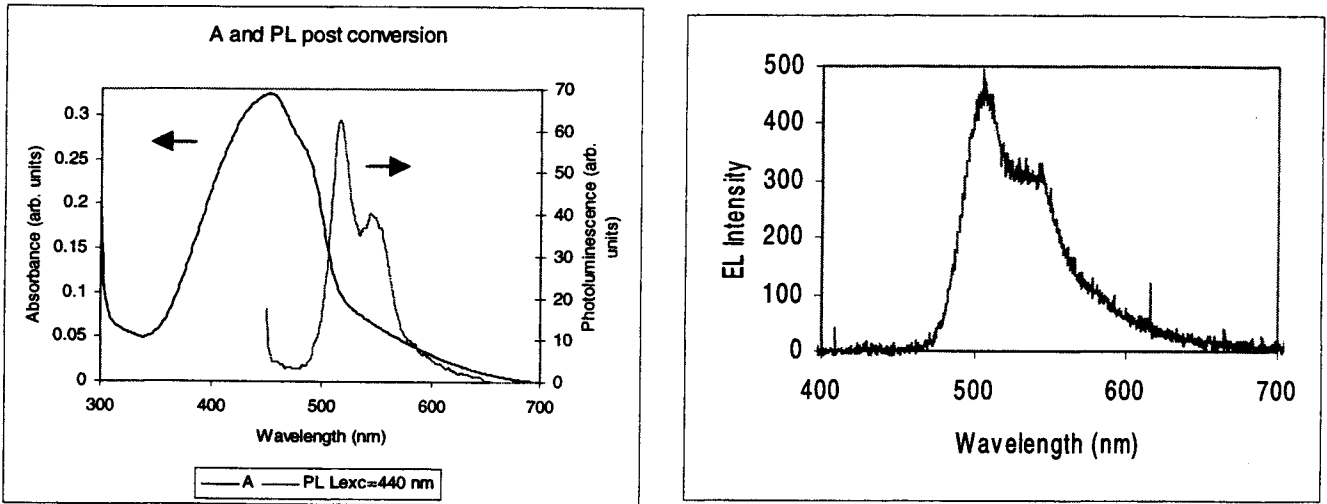


Figure 4. Absorbance, photoluminescence, and electroluminescence spectra for a typical ISAM (PPV/PMA)₂₀ LED device.

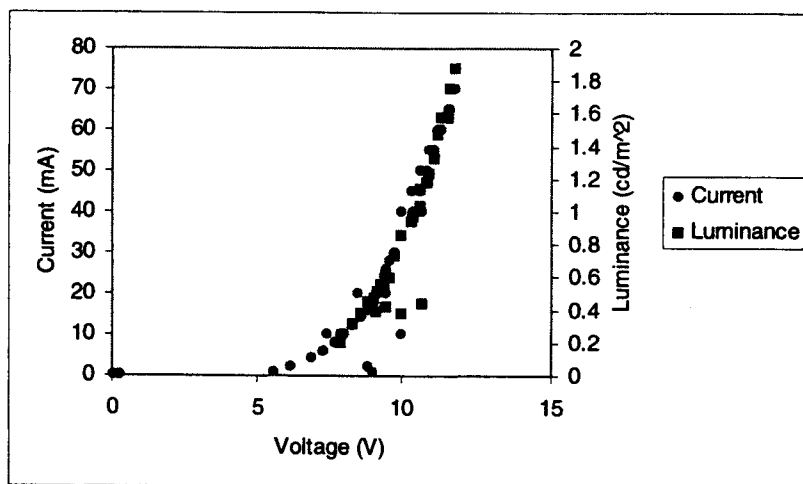


Figure 5. Current and luminance vs. voltage for ITO/(SPS/PPV)₇/(PMA/PPV)₃₀/Al₂O₃/Al.

Interesting results were obtained from the measurements of small (0.6 cm x 0.3 cm) and large (0.6 cm x 0.7 cm) area devices, which were fabricated on the same ITO coated glass slide. The device size is determined by the size of the deposited Al electrodes. The films had 20 bilayers of (PPV/PMA). Figure 6 (left) shows that the small devices had a higher current density for the same applied voltage, and both types of devices had the threshold voltage at around 3.5 V. Figure 6 (right) shows that the luminance values of the devices are similar for current densities below 200 mA/cm². Beyond this value, the large area device failed during testing, while the small device sustained much higher current densities. The higher heat generation combined with the larger number of defects present in the large area devices may cause the device failure. Our smallest devices are still much larger than the typical devices described by other groups⁸, which used 0.2 cm x 0.2 cm polymer LEDs that yielded higher luminances.

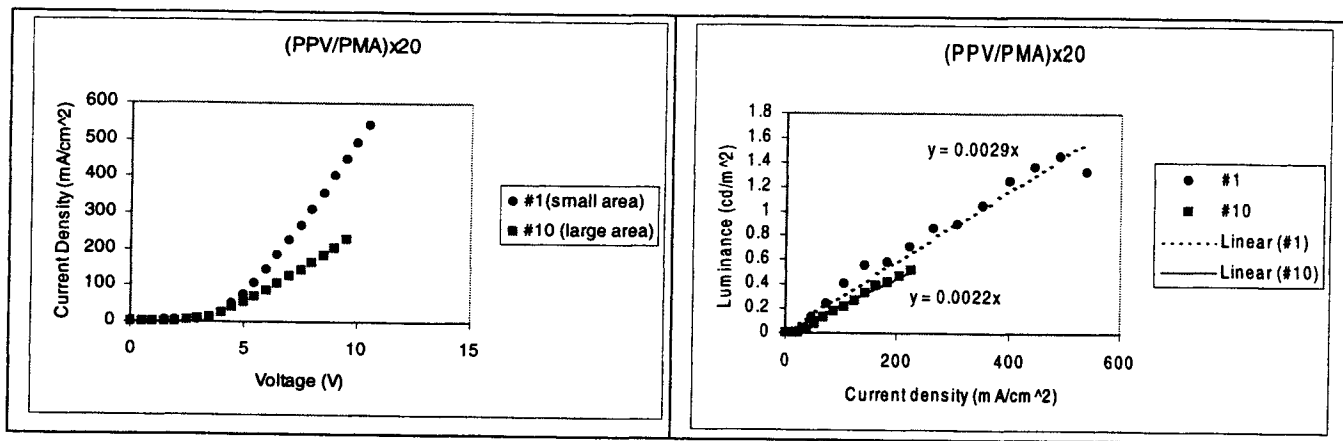


Figure 6. Current density vs. voltage (left) and luminance curves (right) for the small (#1) and large (#10) are devices made with (PPV/PMA)₂₀.

5. CONTROL OF POLYMER-ELECTRODE INTERFACES

The interface study was aimed at finding ways to improve the ISAM thin film (PPV/PMA)_x device performance by inserting different layers between the emissive ISAM film and the anode (ITO) or the cathode (aluminum). By manipulating the interface layers it is possible to modify the injection of the carriers at the electrodes, and ultimately to control the efficiency of the devices. It has been shown previously¹⁴ for MEH-PPV spin coated devices that the efficiency can be controlled by inserting conducting, semiconducting or insulating polymer self-assembled layers between the organic emissive layer and the anode. Onitsuka et al.¹⁵ also demonstrated that the efficiency of the self-assembled light emitting diodes could be influenced through manipulation of the thin film/electrode interface and through use of various polyanions in combination with the PPV.

The materials that we used for the interface study were polyallylamine hydrochloride (PAH) as the polycation, and for polyanions several polymers were employed: poly(sodium 4-styrenesulfonate) (PSS), polythiophene acetic acid (PT), poly S-119, and poly R-478. The two polymeric dyes, poly S-119 and poly R-478 are water soluble polymeric dyes and are compatible with the ISAM technique. All ISAM interface layers were made of three bilayers, using the same polycation, PAH. The parameters, (concentration, pH, and ionic strength) of the dipping solutions are listed in Table 1. The films were deposited on ITO coated glass slides, in the combinations shown in Table 2. Aluminum electrodes were then deposited on top of the ISAM layer.

Table 1 Polymers and the solutions parameters used the interface study of ISAM LEDs

	Concentration	pH	Salt
PPV	1.8 mM	4.5	0.3M
PMA	10 mM	2.5	0.1M
PAH	1 mM	3.0	0.1M
PSS	10 mM	3.0	0.1M
PT	6.6 mM	5.5	No NaCl
R478	1 mM	3.0	0.1M
PS119	1 mM	3.0	0.1 M

Table 2. ISAM films used for the LED interface measurements

$(\text{PAH/PT})_3(\text{PPV/PMA})_{20}$	$(\text{PPV/PMA})_{20}(\text{PAH/PT})_3$
$(\text{PAH/PSS})_3(\text{PPV/PMA})_{20}$	$(\text{PPV/PMA})_{20}(\text{PAH/PSS})_3$
$(\text{PAH/R478})_3(\text{PPV/PMA})_{20}$	$(\text{PPV/PMA})_{20}(\text{PAH/R478})_3$
$(\text{PAH/PS119})_3(\text{PPV/PMA})_{20}$	$(\text{PPV/PMA})_{20}(\text{PAH/PS119})_3$
$(\text{PPV/PMA})_{20}$	

In previous work, we have studied these polymeric dyes for nonlinear optical applications and demonstrated that they exhibit reasonably large second order nonlinear susceptibility values, comparable to that of quartz^{10,16}. The chromophore is attached to the polymer backbone and the resulting ISAM film has the dipole moments aligned perpendicular to the film substrate. Depending on the chromophore incorporated into the polymer, the dipole moments can point towards or away from the substrate. Using this property of the film, we investigated the possibility of modifying the work function of the ITO and/or of the top electrode, respectively, by inserting a thin ISAM layer between the PPV containing layer and one of the electrodes. Initially, we measured the work function of the two polymeric dyes using a Kelvin probe experiment¹⁷. The resulting value is reported with respect to a gold electrode. The ISAM polymeric dyes were deposited on a 200 nm vacuum-deposited aluminum layer. The results indicated that when bare aluminum was measured against the gold, the difference in the work functions was 0.8 eV, in agreement with the difference between the known work functions values for the Al (4.25 eV) and Au (5.10 eV). When the polymeric dyes were deposited on top of the aluminum, the Kelvin probe measurements yielded 0.67 eV for poly R-478 and 0.82 eV for poly S-119, indicating that the resulting “work function” of the aluminum/dye film was changed to 4.38 eV and 4.23 eV, respectively, from the initial value of 4.25 eV. We thus expected to be able to tailor the injection of either carrier from its respective electrode by using an appropriate material between the organic layer and the electrode. We present here preliminary results of the interface study, with the specification that there is work in progress in synthesizing new polymeric dyes specifically designed for the efficiency control of the devices.

For an accurate comparison of the data, the entire set of films for the interface study was prepared from the same batch of PPVpc solution, which was more concentrated than the films described in the previous sections. The pH of the PPVpc solution was adjusted to 4.5 and the ionic strength to 0.3 M. For the polyanion, we used PMA with 10 mM concentration, pH=2.5 and 0.1 M NaCl. The absorption spectra of the films are similar, indicating that the introduction of the interface layers did not modify the position of the absorption peak. In Figure 7 we present the absorption spectra of all slides, after the thermal conversion of the PPVpc. The peak of the absorption is around 450 nm, demonstrating a good conversion of the PPVpc to the conjugated form. As observed from these absorption spectra the absorption peak of the polymeric dyes does not show in these curves, since we only deposited 3 bilayers, compared to the 20 bilayers of (PPV/PMA) film. Poly S-119 has maximum absorption at wavelength 475 nm and poly R-478 has the maximum absorption at 519 nm.

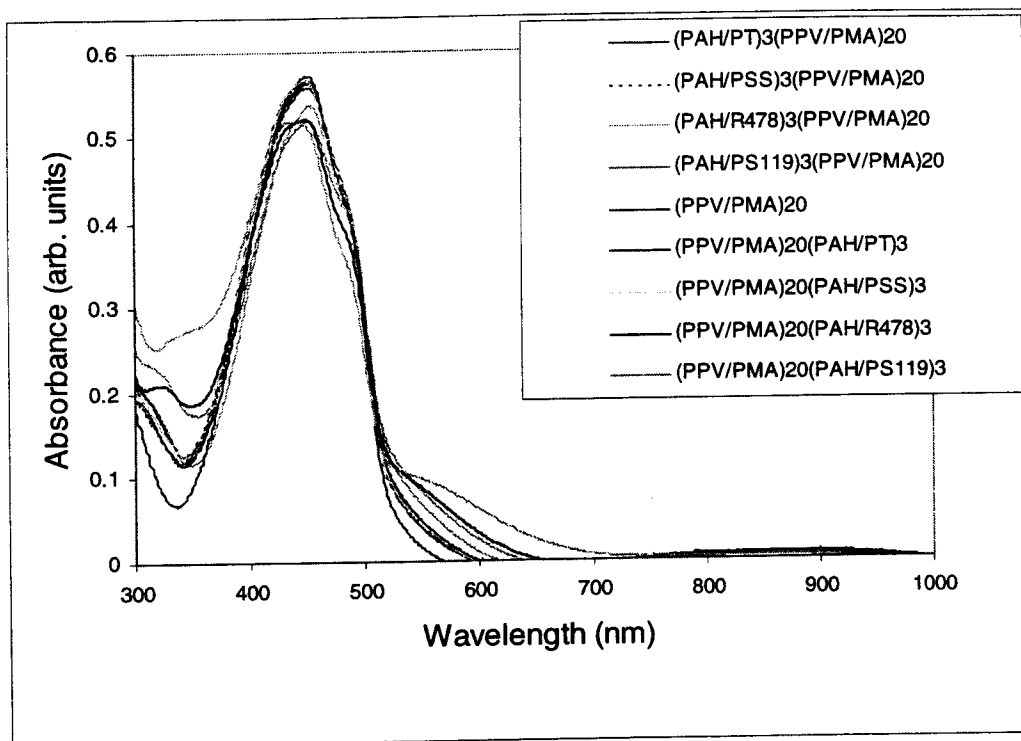


Figure 7. Absorption spectra for the films used in the interface study.

The current-voltage, luminance-current, and power conversion efficiency curves for the devices prepared for the interface study are presented in Figures 8-13. All devices have an active area of approximately 0.6 cm x 0.3 cm. As it can be seen from these graphs, when (PAH/PT)₃ is deposited between the ITO and the (PPV/PMA)₂₀ layer, the device has similar performance as the device with (PPV/PMA)₂₀ only. For the device configuration with the interface layer between (PPV/PMA)₂₀ and the aluminum electrode (Figure 9), the (PAH/PT)₃ layer appears as a wide band gap insulator, and we observe a much higher turn-on voltage of approximately 13 V. Figure 9 shows that all devices that had the interface layer between the organic and the aluminum electrode had the turn-on voltage at higher values (around 13 V) than the device with (PPV/PMA)₂₀ only (approximately 7 V). It should also be noted that the current observed at 2-4 V in the film with no interface layers is due to a short-circuit defect that burnt out at 4 V. The luminance-current plots for both cases are shown in Figure 10 and Figure 12. The device with the (PAH/PT)₃ layer between the ITO and (PPV/PMA)₂₀ indicates improvement in the efficiency of the LED, compared to the device where there is no interface layer towards the ITO. Similar improvement in the device efficiency can be noticed for the (PAH/PSS)₃ layer placed on the ITO side. The devices with the polymeric dyes incorporated in the ITO interface layer have poorer performance than (PPV/PMA)₂₀.

In the case when the interface layer was placed between (PPV/PMA)₂₀ and aluminum, the devices sustained larger current densities than in the case where the interface layer was between ITO and (PPV/PMA)₂₀, although the luminance values were significantly lower than the luminance values for the devices with the interface layer towards ITO. This indicates that the presence of the layer at the aluminum side increases even further the energy gap between aluminum and the (PPV/PMA)₂₀ layer, thus blocking the electron injection from the aluminum. This assumption is confirmed by the sharp rise in the current density for the devices with the interface layer at the aluminum. The improvement in the luminance for the devices with the (PAH/PT)₃ and (PAH/PSS)₃ layers at the ITO suggests that the presence of these layers improves the device efficiency, as can be seen from the slopes of the luminance-current curves.

The power conversion efficiency curves (Figure 11 and Figure 13) indicate that the efficiency of the devices reaches a maximum around 6 V when the interface layer is placed on the ITO, similar to the (PPV/PMA)₂₀ device with no interface layer (Figure 11). When the interface layer is placed towards the aluminum (Figure 13), the maximum power conversion efficiency varies from device to device, from 6 V for the (PPV/PMA)₂₀ to 15 V for (PPV/PMA)₂₀(PAH/PSS)₃, and 16 V for

(PPV/PMA)₂₀(PAH/PT)₃. The devices with the polymeric dyes included in the interface towards aluminum do not show decrease in the power conversion efficiency, although the performance of these devices was not as good as of the other devices. In general, the power conversion efficiencies are larger when the interface layer is placed at the ITO rather than aluminum electrode. Although the luminance values are relatively large at high values of the applied voltage, the power conversion efficiencies of many of these devices are already reduced in the high voltage regime.

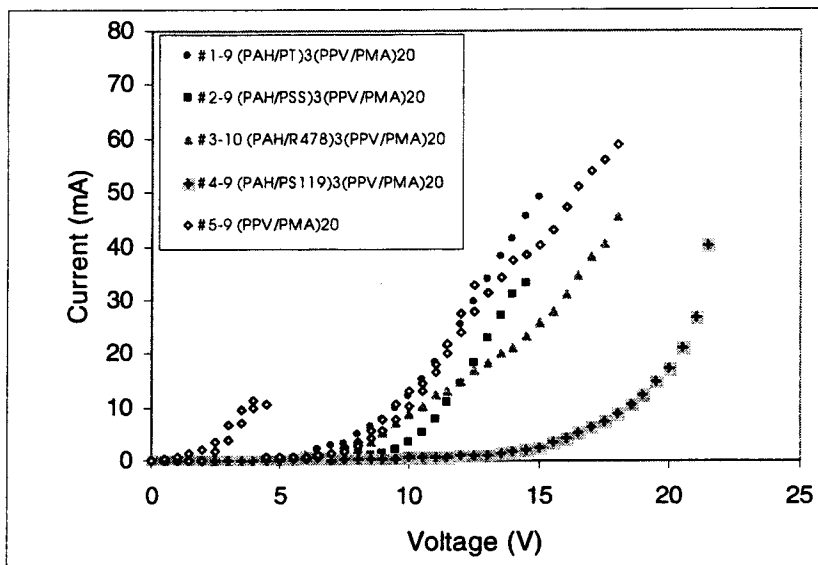


Figure 8. Current-voltage characteristics for the devices with the interface layer placed between the ITO and (PPV/PMA)₂₀.

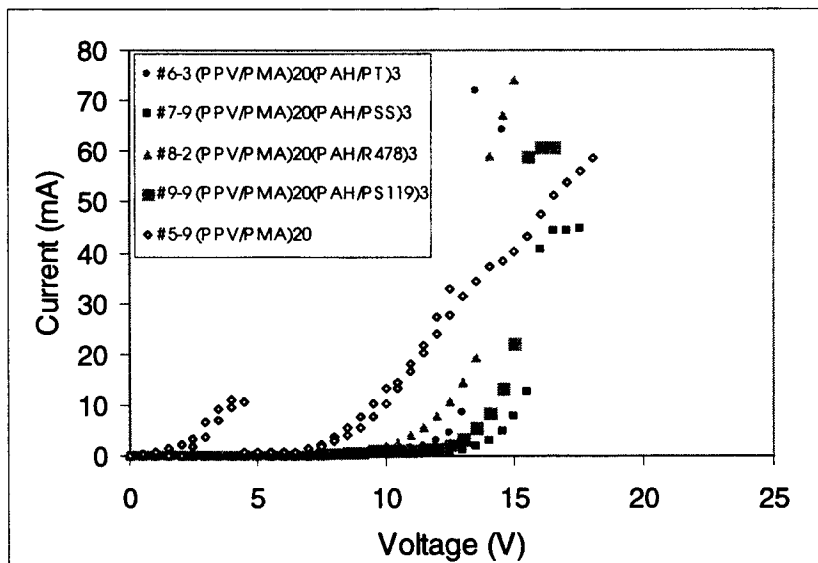


Figure 9. Current-voltage characteristics for the ISAM LED devices with the interface layer placed between (PPV/PMA)₂₀ and the aluminum electrode.

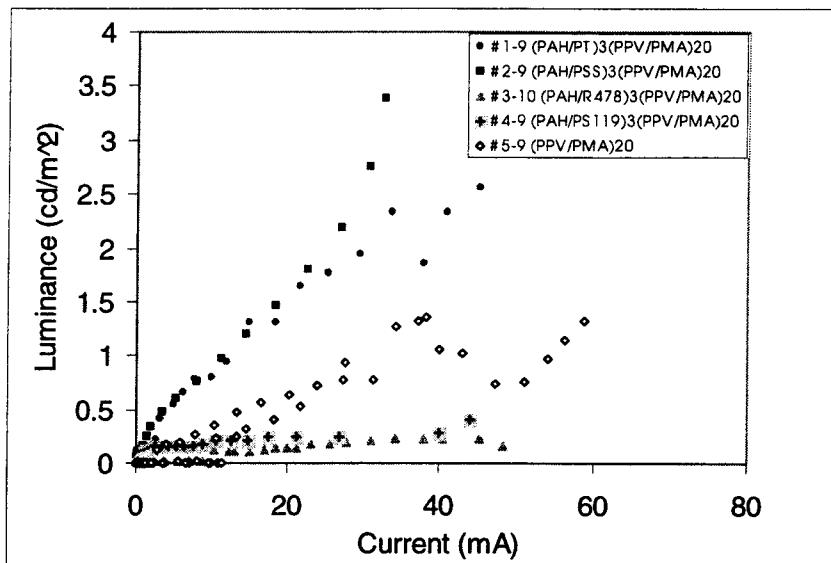


Figure 10. Device efficiencies for the interface placed between ITO and emissive (PPV/PMA)₂₀ layer.

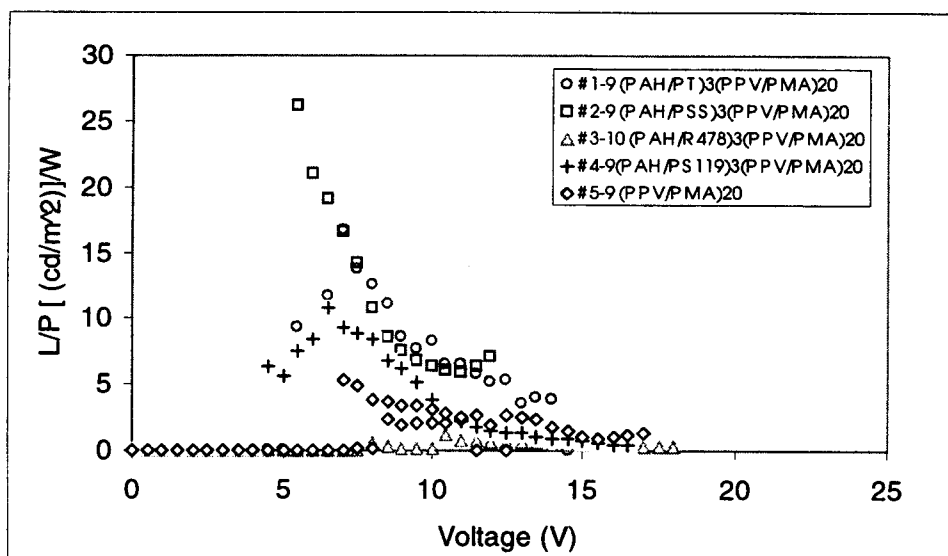


Figure 11. Power efficiency conversion for the devices with the interface placed between ITO and emissive (PPV/PMA)₂₀ layer.

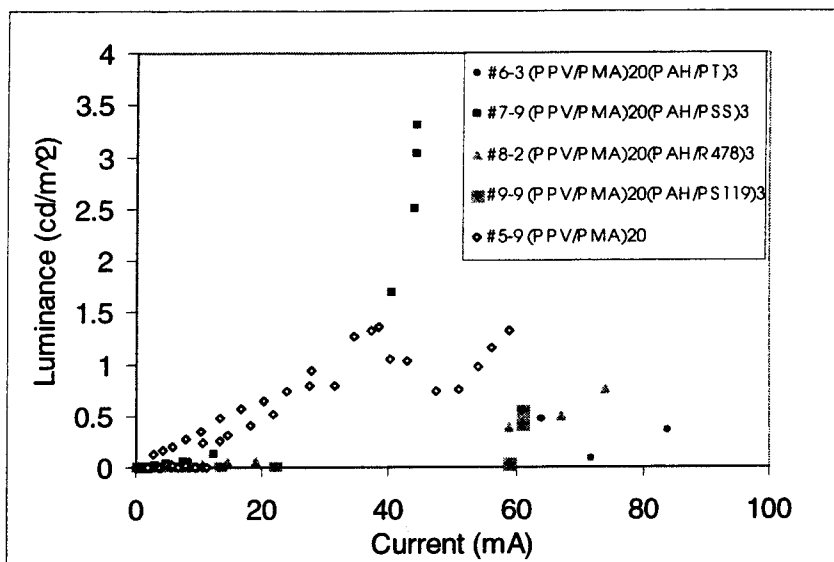


Figure 12. Device efficiencies for the interface placed between the emissive (PPV/PMA)₂₀ layer and aluminum electrode.

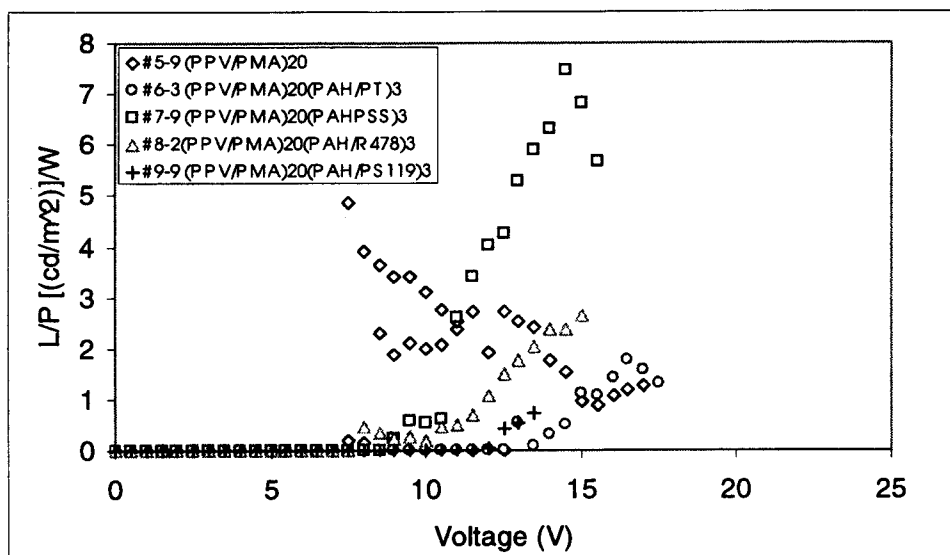


Figure 13. Power conversion efficiency for devices with the interface layer placed between the emissive (PPV/PMA)₂₀ layer and aluminum electrode.

CONCLUSIONS

The ionically self-assembled monolayer (ISAM) technique can successfully be used for the fabrication of polymer light emitting diodes, yielding homogeneous deposition and buildup of monolayers. The amount of deposited PPV can be controlled through pH and salt concentration. Lastly, the efficiency of the devices can be improved through manipulation of the interface layers. The ISAM technique is appropriate for this procedure, allowing for detailed structural and thickness control at the molecular level.

ACKNOWLEDGMENTS

The authors would like to thank Winston Matthews for the help in the preparation of the samples. This research was supported by the U. S. Navy under contract no. N00014-98-C-0161 and in part by the U. S. Department of Energy under contract No. DE-FG02-99ER86091, whose support does not constitute an endorsement by DOE of the views expressed in the article.

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