Poly(*p*-phenylene vinylene)/*tris*(8-hydroxy) quinoline aluminum heterostructure light emitting diode

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Results are presented from polymer/molecular organic heterostructure light emitting diodes composed of a layer of the conjugated conducting polymer poly(*p*-phenylene vinylene) (PPV), and a layer of fluorescent molecular compound *tris*(8-hydroxy) quinoline aluminum (Alq). The external quantum efficiency of these heterostructure LEDs is ~0.1%, which is over one order of magnitude higher than that of simple PPV LEDs. The electroluminescence (EL) spectra indicate that both materials in the device emit comparable amounts of light. The dependence of the EL spectra on the layer thicknesses and its independence on bias suggest that neutral excitons are formed in the Alq, far from the PPV/Alq interface, and subsequently diffuse into the PPV layer. © *1995 American Institute of Physics.*

Since the first report of efficient electroluminescence (EL) from an organic heterojunction device using *tris*(8-hydroxy)quinoline aluminum (Alq) as the emissive material,[1,2] organic light emitting diodes (OLEDs) utilizing fluorescent molecules have attracted considerable interest for display applications.[3–7] Due to some distinctive advantages of organic polymers, recent research efforts have increasingly focused on the investigation of polymer LEDs.[8–11] Currently, poly(*p*-phenylene vinylene) (PPV) and its derivatives are the most widely studied EL polymers. Since neither PPV nor Alq forms an efficient bipolar charge transport layer, efficient OLEDs typically incorporate separate carrier transport and emission layers. PPV LEDs are known to suffer from inefficient electron injection due to the relatively large difference between the electron affinity of PPV[11] (~2.6 eV) and the work function of common metals[7] (e.g., 3.7 eV for Mg:Ag, 4.2 eV for Al) used as the cathode contact. Conversely, Alq is known to be a better electron transport material because of its larger electron affinity[5–7] (3.1±0.1 eV) compared to that of PPV. In this letter, we investigate the use of Alq as a cathode material for PPV LEDs. Furthermore, because PPV is generally acknowledged to be a good hole transport material, one might expect light emission from both the Alq and PPV layers in such structures. Therefore, we examine the EL spectra of PPV/Alq heterostructure LEDs and fit them to a model to better understand the mechanisms for light emission and carrier transport.

The devices were built on indium tin oxide (ITO) coated glass slides, which were cleaned by sequential ultrasonication in 1,1,1-trichloroethane, acetone, and methanol, and dried in a stream of nitrogen between each step. The PPV films were deposited on the ITO by spin-coating an aqueous solution of the nonconjugated PPV precursor[8] and then thermally converting the precursor into the final conjugated PPV at 300 °C for 12 h in a vacuum oven. The final thicknesses of the PPV films were measured by a stylus profilometer to be

500 Å. The samples were then loaded into a vacuum chamber, with a base pressure of 10^{-6} Torr. The deposition of 150 or 300 Å thick Alq films was carried out by thermal evaporation from a baffled Mo crucible at a nominal deposition rate of 2–4 Å/s, as measured by a quartz crystal thickness monitor placed near the substrate. During Alq growth, half of each sample was masked to prevent the deposition of the prepurified Alq. Electrodes consisting of Mg:Ag in a 10:1 atomic ratio, patterned by a shadow mask, were subsequently deposited on the whole sample by coevaporation from two separate Mo boats under a vacuum of 10^{-5} Torr. Without breaking the vacuum, a 200 Å layer of Ag was then deposited to retard oxidation of the electrode. All measurements of the PPV, PPV/150 Å Alq and PPV/300 Å Alq devices were then carried out in air at room temperature without any subsequent processing.

Figure 1 shows the forward-biased (i.e., positive on the ITO electrode) current-voltage (*I-V*) characteristics of bare PPV and PPV/Alq devices in both linear and log–log plots. The voltage dependence of current appears to follow the
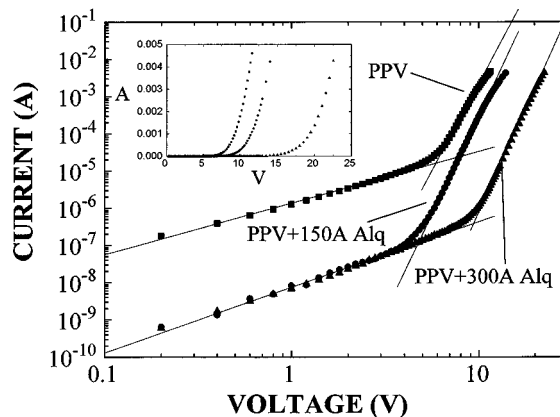

FIG. 1. Log–log plots of forward-biased *I-V* characteristics for bare PPV (500 Å), PPV (500 Å)/Alq (150 Å), and PPV (500 Å)/Alq (300 Å) devices. The inset shows the linear plot of the same *I-V* curves.

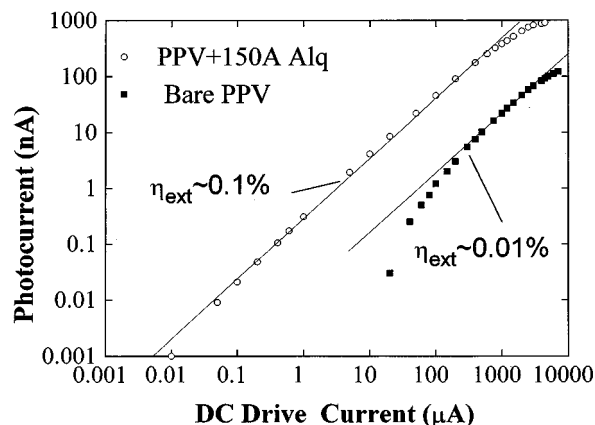[a] Present address: i-Stat Corp., 303 College Rd. East, Princeton, NJ 08540.

FIG. 2. Light intensity vs drive current for bare PPV and PPV/150 Å Alq devices.
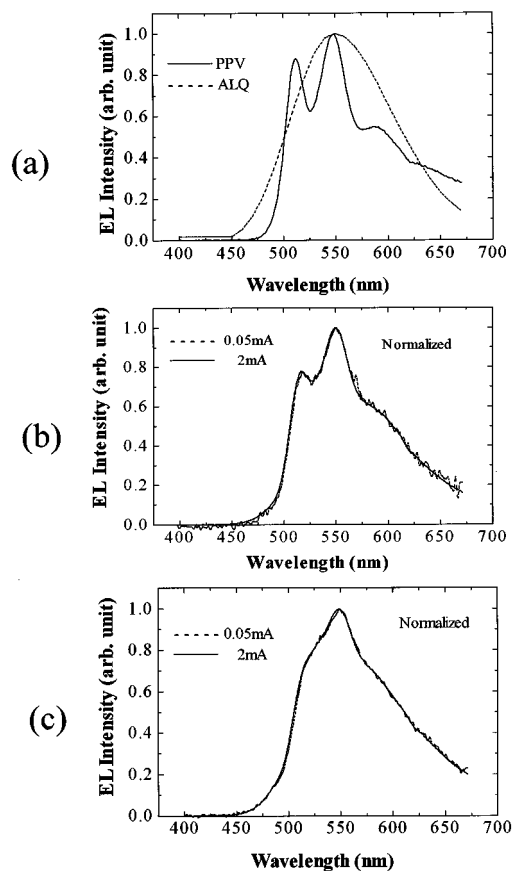

FIG. 3. Normalized electroluminescence spectra of (a) the bare PPV and the Alq/TPD LEDs (TPD as the nonemissive hole transport layer) (b) the PPV/150 Å Alq LED for different drive currents (c) the PPV/300 Å Alq LED for different drive currents.

power law: $I \propto V^m$, with m varying from 1 to 2 at low voltage and from 9 to 11 at high voltage. These results for the PPV and PPV/Alq devices are similar to those previously reported for Alq heterostructure devices,[5] where the I-V dependence was attributed to a combination of Ohmic and trap-limited space charge effects.

Figure 2 shows the emission intensity versus drive current (L-I) curves for the devices in Fig. 1. The light intensity is linear with drive current for the PPV/Alq heterostructure devices over four orders of magnitude. The L-I characteristics were measured through the bottom of the glass slide by using a broad area silicon photodiode. No correction was made for losses due to absorption, reflections, or waveguiding effects of the glass slide. This measurement, therefore, represents a lower limit of the emission intensity, but accurately measures the relative power of different devices. The uncorrected external quantum efficiency measured in this way is ~0.1% for the PPV/150 Å Alq heterostructure LED, which is more than one order of magnitude higher than that of the PPV homostructure LED. The quantum efficiency of the PPV 300 Å Alq device is similar to that of the PPV/150 Å Alq device. Taking into account the difference between internal and external efficiencies,[12] these results are comparable to the best results reported for PPV-based LEDs.[10]

Figure 3 shows the EL spectra of the PPV, PPV/150 Å Alq, and PPV/300 Å Alq OLEDs fabricated as above, and a standard Alq/TPD[1,2,5] OLED, where TPD [N,N'-diphenyl-N,N'-bis(3-methylphenyl)1-1'biphenyl-4,4'diamine] is used as the nonemissive hole transport layer. Therefore, the Alq/TPD device gives emission characteristic of Alq alone. The spectra for the PPV/Alq OLEDs were measured over two orders of magnitude of current, and are plotted normalized to their peak values in Fig. 3. Note that the shape of the spectra of the heterostructure devices, each of which is a superposition of both Alq and PPV components, is independent of bias. In contrast, in previous work on heterostructure LEDs made from cadmium selenide nanocrystals and PPV,[13] or Alq and a derivative of PPV, poly(2,5-dioctyloxy-p-phenylene vinylene) (ROPPV-8),[14] the El spectra were observed to be bias dependent.

To determine the origin of the EL emission, the EL spec-

tra of the heterostructure devices are fitted by assuming a simple superposition of light emission from the PPV and Alq layers. By using this method, we can determine the fraction of light emission from each material at a particular current level. In the insets of Fig. 4, example fits are given for two PPV/Alq OLEDs at a fixed current level, 800 μA. We observe that the fit is quite good over a broad wavelength range. Using this procedure, we then plot in Fig. 4 the relative light output from the two materials for all three experimental devices. In the homostructure device (no Alq), all light is generated in the PPV. With 150 Å Alq, the total EL intensity is about 13 times greater, composed of 40% of total emission from the Alq region and 60% from the PPV region of this device. The PPV emission alone from this heterostructure device is eight times higher than that from the simple PPV device. When the Alq thickness is increased to 300 Å, the total EL intensity is similar to that of the 150 Å Alq device, but the contributions from PPV and Alq emission are different. The emission from Alq region increased by nearly a factor of two, to 76% of the total output power, while the emission from the PPV region decreases substantially, to only 40% of that for the 150 Å Alq device.

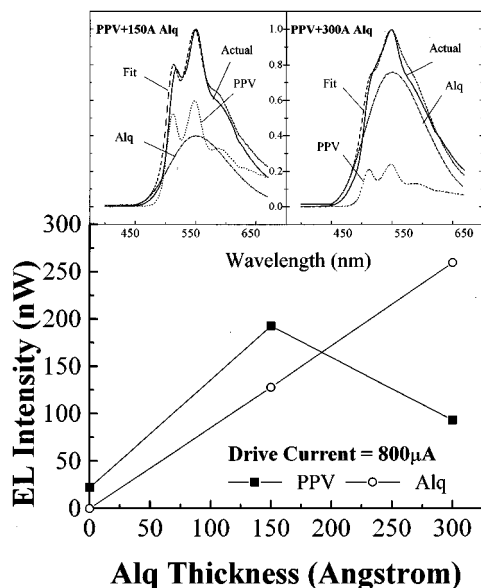If one were to assume that light emission in each mate-

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FIG. 4. Light output from the PPV and Alq layers for all three experimental devices, at 800 μA drive current. The insets show the fits to the EL spectra of the PPV/150 Å Alq LED and the PPV/300 Å Alq LED. Individual PPV and Alq emission are shown as well.

rial is due to exciton formation in that material and that no exciton transport occurs between layers, our results imply that the Alq layer improves the electron injection into PPV, while holes reach the Alq from the PPV. The decrease in PPV emission and the increase in Alq emission in going from 150 to 300 Å Alq is then explained by a reduction in the number of electrons reaching the PPV, leading to less exciton recombination in PPV, while enhancing that in Alq. This model requires that the electron flux decay with distance from the metal/Alq interface, with a decay length of a few hundred angstroms.[5] However, the independence of the spectral shape on bias would imply that the relative injection of electrons from Alq into PPV and holes from PPV into Alq is independent of bias. This is quite remarkable, given that different materials and energy barriers control the transport of electrons versus holes, and suggests that this model is unsatisfactory.

The structure of our devices is very similar to that investigated by Tang et al.,[1,2] except that we have replaced the aromatic diamine with PPV as the hole transport layer. In their work, they concluded that exciton formation occurs as soon as holes are injected into Alq, and that the diffusion length of neutral excitons in Alq is estimated to be about 200 Å. Exciton formation in Alq only near the PPV/Alq interface and subsequent diffusion in both directions is inconsistent with our results, as it does not explain why the total emission intensity remains nearly unchanged while the emission from the PPV region decreases as the thickness of Alq increases. On the other hand, our results suggest that most excitons are formed far from the PPV/Alq interface (i.e., most electrons form excitons before they reach PPV), and subsequently diffuse towards the PPV. PPV emission would thus be due to exciton diffusion through the Alq into PPV before exciton recombination, explaining the increase in Alq emission and

the decrease in PPV emission as the thickness of Alq increases. An exciton diffusion length of 200 Å is qualitatively consistent with our results. The diffusion of neutral excitons across the PPV/Alq interface would also be consistent with the observation that the spectra of PPV/Alq devices are bias independent. That the exciton formation in these PPV/Alq devices appears to occur far from PPV/Alq interface, as opposed to that observed for the aromatic diamine/Alq interface, may suggest that PPV is a more efficient hole injector into the Alq than the diamine. While the transport properties of Alq are not well understood, an abundance of holes (rather than electrons) could lead to electrons forming excitons soon after they are injected from the metal and before they reach PPV.

In conclusion, we have demonstrated high efficiency PPV/Alq heterostructure OLEDs. Both Alq and PPV in the heterostructure emit light. The presence of the Alq increases the PPV emission by about one order of magnitude above that observed for devices without Alq. The total external quantum efficiency is ~0.1% and the light intensity is linear with current over four orders of magnitude. The spectral shape is independent of bias over two orders of magnitude of current, and is dependent on the layer thicknesses. These results are consistent with formation of excitons in the Alq far from the PPV/Alq interface, followed by exciton diffusion across the PPV/Alq interface. At present, further experiments are needed to determine optimum thicknesses of the two materials for the maximal external quantum efficiency. Further understanding of the nature of the excitons in these devices will also help the design of the most efficient devices.

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