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Synthetic Metals 111–112 (2000) 159–163

SYNTHETIC METALS

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Bright and efficient blue and green light-emitting diodes based on conjugated polymer blends

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Abstract

We report the use of green and blue fluorene conjugated polymers doped with hole transport materials consisting of triarylamine copolymers to fabricate bright and efficient blue and green single-layer light-emitting diodes (LEDs). These blends show enhanced quantum and power efficiency, much higher brightness and current densities and lower turn on and operating voltages compared with undoped devices. Optimised blue emission devices exhibited a maximum brightness of 1550 cd/m^2, a maximum external electroluminescence quantum efficiency of 0.9 cd/A or 0.4% and a maximum power efficiency of 0.3 lm/W. Optimised green emission devices showed a maximum brightness of 7400 cd/m^2, a maximum external electroluminescence quantum yield of 0.9% or 2.75 cd/A and a maximum power efficiency of 0.64 lm/W at high brightness.

Keywords: Electroluminescence; Blends; Fluorene copolymers; Triarylamine copolymers

1. Introduction

Polymer based light-emitting diodes (PLEDs) have been the subject of intense research effort in the last few years due to their potential use for full-colour display applications. They are now approaching commercial requirements in terms of high efficiency, high brightness, low operating voltage and long lifetimes [1–4]. The ease of fabrication based on solution processing techniques offers a significant advantage over their inorganic counterparts. Many different electroluminescent conjugated polymers have been reported in literature that emit colours that cover the whole of the visible spectrum. However, most of them have the characteristic that one charge carrier is preferentially injected and/or transported. This generally results in low efficiencies and brightnesses when these polymers are used to fabricate single-layer LEDs. Therefore, multilayer structures are often employed in order to improve the device performance. With polymers, however, the construction of multilayer structures is in general problematic due to the fact that many polymers are soluble in a wide range of solvents making it difficult to avoid significant interpenetration between different layers that are deposited on top of one another.

A different approach is to incorporate the functions of different materials into a single film in the form of a blend [5,6]. Mixing an emissive and a transport material together in a single solvent and then spin-coating the mixture in a single step allows simplification of the device fabrication. Both the emissive and the transport properties of the different materials in the blend can be preserved by appropriate choice of blend composition. As in multilayer devices, polymer blends can allow charge carrier injection from both contacts to be optimised and charge carrier transport to be controlled so that a high device performance can be achieved.

Here, we report the use of green and blue emission fluorene conjugated polymers doped with hole transport materials consisting of triarylamine copolymers to fabricate bright and efficient blue and green single-layer light-emitting diodes (LEDs). These blends show enhanced quantum and power efficiency, higher brightness and current densities and lower turn on and operating voltages compared with undoped devices.

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0379-6779/00/$ - see front matter
PII: S0379-6779(99)00337-9

2. Experimental

In order to compare directly the effect of blending the emissive polymer with a hole transport material, we fabricated two different kinds of devices: ‘conventional’ devices which have an active single layer of the emissive material between the electrodes, and ‘doped’ devices which have a single layer of the emissive polymer doped with an amount of the hole transport material between the electrodes. Conventional and doped LEDs comprise an indium tin oxide (ITO) anode, a single layer of the emissive polymer or the blend spin cast from a solution in toluene with a concentration of 20 mg/ml and a metal top cathode. A stable alloy comprising magnesium (Mg), aluminium (Al) and traces of Zn, known as Dow metal, was vapour-deposited through a shadow mask to form the cathode for blue devices. This alloy has the work function of Mg (3.7 eV) and the environmental stability of Al. A bilayer cathode consisting of LiF(1 nm)–Al was used as the top electrode in the case of green devices. All devices had an active area of 4.5 mm^2. The base pressure in the evaporation chamber was approximately 4×10^{-6} mbar. The typical deposition rate was between 0.1 and 0.3 nm/s for the Al, 0.5–1 nm/s for the Dow metal and 0.01 nm/s for the inorganic LiF layer. All device measurements were carried out at room temperature under a dynamic vacuum of 10^{-1} mbar. Current–voltage characteristics were measured with a Keithley 237 Source Meter. The brightness was measured with a Topcon™ BM-8 Luminance meter. Electroluminescence (EL) and photoluminescence (PL) spectra were measured with an Oriel Instaspec™ 4 CCD multichannel analyser. The 354 nm line of an HeCd laser was used as the excitation source for the PL measurements. The external EL quantum efficiency was calculated by comparing the absolute luminance of the device in e forward direction to the current density flowing through the device, taking into account the spectral characteristics of the emitted light and the photopic efficiency of the detector.

3. Results and discussion

The blue emitting conjugated polymer poly(9,9-dioctylfluorene) (PFO) is used as the host material in the blend. It possesses a large room temperature hole mobility of the order 10^{-4} to 10^{-3} $cm^2\ V^{-1}\ s^{-1}$ with a rather weak field dependence [7]. A hole transport material consisting of a triarylamine copolymer, namely poly(9,9-dioctylfluorene-co-bis-N,N'-(4-methylphenyl)-bis-N,N'-phenyl-1,4 phenylenediamine) (PFM) is used as the guest material in the blend. Both polymers were synthesised via a Suzuki coupling reaction [8] and were carefully purified to remove catalyst residues and ionic impurities. The arylamine donor functionality leads to a significant reduction in the ionisation potential from the 5.8 eV value for the polyfluorene homopolymer. PFM has an ionisation potential of 5.04 eV allowing for an efficient hole injection from an ITO transparent anode. It also possesses a large room temperature hole mobility [9] (of the order 7×10^{-4} $cm^2\ V^{-1}\ s^{-1}$). Three different concentrations of the PFM guest in the blend have been examined, namely 5%, 20% and 33%.

The typical room temperature absorption and PL spectra of PFO along with its chemical structure are shown in Fig. 1. The absorption spectrum consists of a strong featureless peak at 385 nm. The PL spectrum shows a maximum that corresponds to the 0–0 transition at 422 nm with a well defined vibronic feature at 447 nm (the 0–1 transition) and a shoulder at 473 nm. The EL spectrum of PFO (not shown) very closely resembles the PL spectrum [10]. The PL and the absorption spectra of the hole transport material PFM are also shown in Fig. 1 (the inset shows the PFM chemical structure). The absorption peaks at 390 nm and the PL spectrum is dominated by a rather broad featureless peak at 445 nm. Due to the spectral overlap between the PL spectrum of the host (PFO) and the absorption spectrum of the guest (PFM), excitation energy transfer of excitons from the host to the guest is energetically favourable and a direct dipole–dipole interaction (i.e., a Forster type energy transfer [11]) can occur between the two polymers. The normalised PL spectra of the different PFO/PFM blends are depicted in Fig. 2. When the concentration of the guest in the blend increases, the relative contribution of the dominant peak at 446 nm in the emission spectrum increases. However, the energy transfer is not complete even at the maximum concentration of 33% guest in the blend. Using active layers of PFO doped with different amounts of PFM causes the deep blue emission of pure PFO to be converted into blue emission originating substantially from the PFM molecules.

Fig. 3 shows the EL spectra of the polymer blend LEDs with an emissive layer thickness of 110 nm for different concentrations of PFM in the host–guest system. The EL

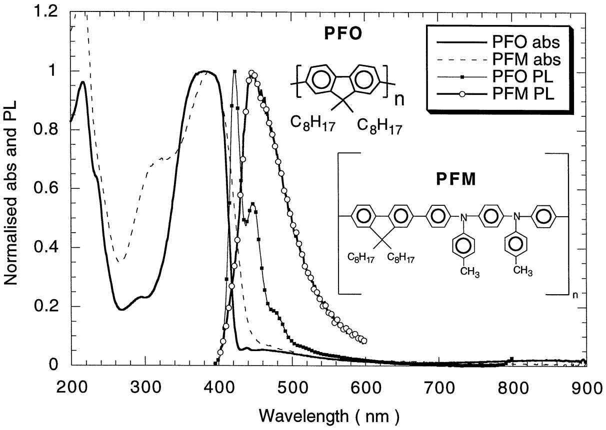

Fig. 1. The optical absorption and photoluminescence spectra of PFO and PFM films on quartz substrates. The chemical structures of PFO and PFM are shown as insets.

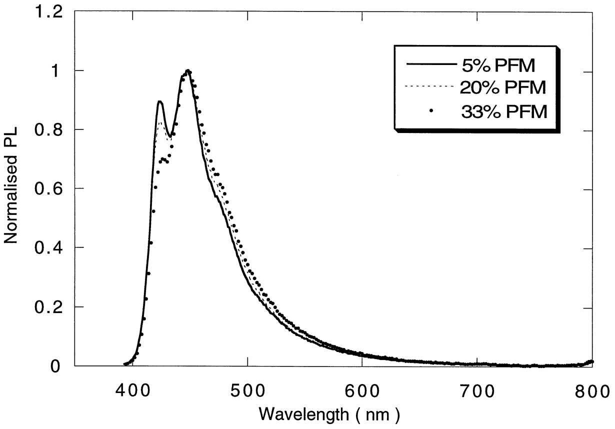

Fig. 2. The photoluminescence spectra of PFO/PFM polymer blend with different PFM wt.% concentrations.

spectra for all three concentrations show a broad rather structureless peak at 480–485 nm. The EL spectra of these devices resemble the PL spectra of PFM but they are red shifted and broader with a tail appearing at longer wavelengths. Charge carrier trapping may play an important role in the emission process. The EL spectra are similar in shape to the PL spectrum of PFM, which may indicate that PFM molecules act as the dominant recombination centres. Recombination on the guest molecules may become more favourable due to the dual action of PFM molecules as deep hole traps in the host PFO and as electron hopping sites. Electron transport can take place by hopping between the host and guest molecules. As the concentration of the guest is increased, the distance between the PFM molecules becomes shorter and the electrons may be shared more equally between the host and the guest molecules. Evidence for the role of PFM molecules as hole traps is obtained from time of flight mobility measurements on the blend samples. The shape of the transient photo current signal changes from nondispersive to fully dispersive. Non dispersive hole transport is seen in both PFO [7] and PFM [9] polymers. The formation of deep traps is also consistent with the large difference in the ionisation potential between the host and the guest and can lead to a reduction in the hole mobility of the blend compared to the hole mobilities of the two individual polymers.

The J–V and L–V characteristics of PLEDs fabricated with an active layer containing 20% of PFM are presented in Fig. 4. The optimised thickness of the active layer in terms of maximum external EL quantum efficiency at high brightness is 110 nm. The device turns on at 6.5 V (defined as the voltage required to give a luminance of 5 cd/m^2). The device shows a maximum luminance of 1550 cd/m^2 at a drive voltage of 22 V and a current density of 620 mA/cm^2. The maximum external EL quantum efficiency is 0.4% or 0.8 cd/A and the corresponding maximum power efficiency is 0.3 lm/W at a brightness of 40 cd/m^2. The fact that the EL efficiency is strongly voltage dependent points to an unbalanced electron and hole injection and transport even in the blend. The maximum efficiency is achieved when the balance between the charge carriers reaches its optimum. However, more than a two orders of magnitude improvement in the maximum luminance and efficiency is achieved in the blend compared to the undoped device due to a better balance between the charge carriers which leads to a more efficient exciton formation and recombination. The trapping of holes on the guest reduces their discharge at the cathode and may increase the probability for encountering an oppositely charged carrier and thus forming an exciton. A redistribution of the internal electric field due to the formation of a hole space charge near the anode can also enhance the electron injection from the cathode and block the excessive hole current that does not contribute to the emission. This would result in more efficient recombination and a higher rate of exciton formation. Significantly lower turn on and operating voltage is also achieved in the blend due to the reduced barrier for the injection of the majority carriers (holes) from the ITO anode to the guest molecules. In the absence of the hole transport material in the blend, hole

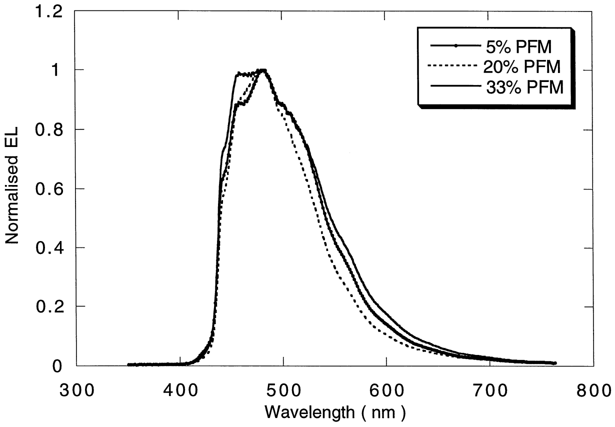

Fig. 3. The electroluminescence spectra of LEDs based on PFO/PFM blend with different PFM wt.% concentrations.

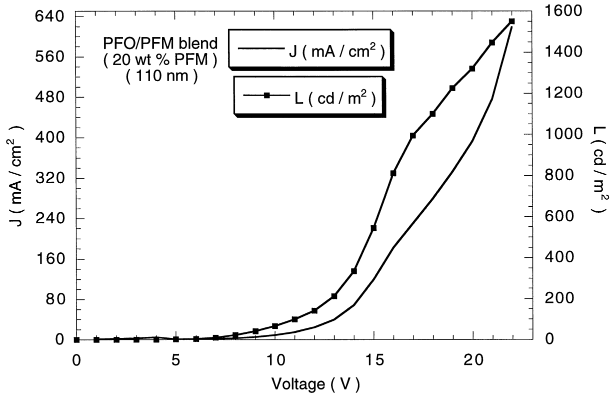

Fig. 4. Current density vs. voltage and luminance vs. voltage characteristics for an ITO/PFO + PFM(4/1) (110 nm)/Dow metal device.

injection is difficult due to the high ionisation potential of PFO, namely 5.8 eV.

We also fabricated green single-layer LEDs using a green emitting conjugated polymer (a proprietary material of the Dow Chemical) as the host material in the blend and a hole transport material consisting of a triarylamine copolymer, namely poly(9,9-dioctylfluorene-co-bis-*N*,*N*′-(4-butylphenyl)-bis-*N*,*N*′-phenylbenzidine) (BFB) as the guest. BFB has an ionisation potential of 5.26 eV, which facilitates hole [9] injection from the ITO and also possess a large room temperature TOF hole mobility (of the order 3×10^{-4} cm^2 V^{-1} s^{-1}). A bilayer cathode consisting of LiF(1 nm)–Al was used as the top metal electrode. Poor electron injection at the cathode is the limiting factor in efficiency in many cases and the insertion of a dielectric layer between the cathode (Al) and the active polymer layer has been shown to enhance the device performance significantly [12].

The absorption and the PL spectra of the host polymer are shown in Fig. 5. The absorption spectrum exhibits a featureless peak at 384 nm and has a relatively narrow line width with a full width at half maximum of 68 nm. The emission is in the green region of the spectrum with a peak position at 536 nm and a shoulder at 564 nm. The absorption and the PL spectra of the hole transport material BFB along with its chemical structure are also presented in Fig. 5. The absorption spectrum shows a broad featureless peak at 386 nm. The PL spectrum peaks at 433 nm (0–0 transition) with a shoulder at 457 nm. The PL and the EL spectra of the blend at a guest concentration of 20% are presented in Fig. 6. The EL spectrum peaks at 535 nm and very closely resembles the PL spectrum. Both spectra are identical to the emission spectrum of the green host polymer and this confirms that emission solely originates from the radiative charge carrier recombination of singlet excitons within the host.

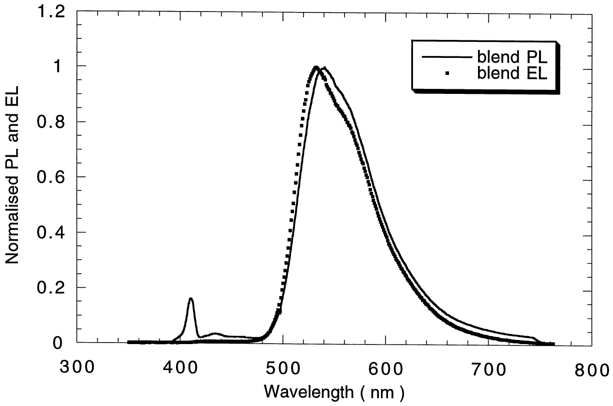

Fig. 6. The photoluminescence and electroluminescence spectra of the green emitting host/BFB blend for a 20 wt.% BFB concentration. (The small peak at 400 nm in the PL spectrum is due to the excitation source.)

The current–voltage and the luminance–voltage characteristics for a device with an active layer of the blend are given in Fig. 7. The best EL performance is achieved for an optimised thickness of the emitting layer of approximately 70 nm. The luminance reaches a maximum of 7400 cd/m^2 at 22 V and for a current density of 940 mA/cm^2. The maximum external EL quantum efficiency is 0.9% or 2.75 cd/A and the corresponding maximum power efficiency is 0.64 lm/W at a brightness of 260 cd/m^2. As in the case of blue devices, the unbalanced injection of the charge carriers gives rise to a bias dependent efficiency with the maximum efficiency achieved when the carrier balance reaches its optimum. The turn on voltage (defined as the bias required to give a luminance of 5 cd/m^2) is 6.5 V and is significantly lower than in the undoped device due to the reduced barrier for hole injection from the ITO to the highest occupied molecular orbital (HOMO) of the guest in the blend. More than an order of magnitude enhancement in the maximum brightness and efficiency is found in the blend compared to the standard device without the dopant. The improved hole injection and transport leads to an increased current flow through the device and a corresponding increase in the brightness. However, the

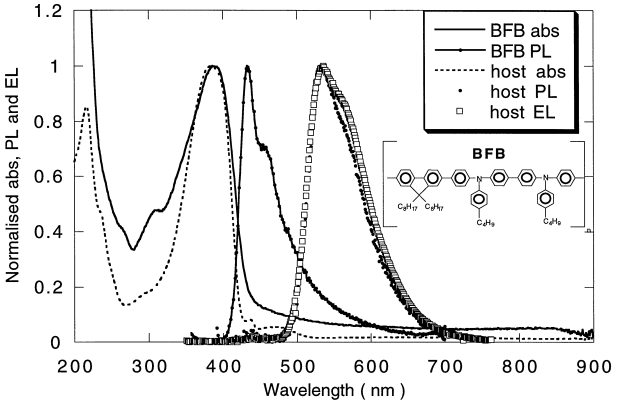

Fig. 5. The optical absorption and photoluminescence spectra of the green emitting host and the hole transport material BFB. Also shown is the chemical structure of BFB.

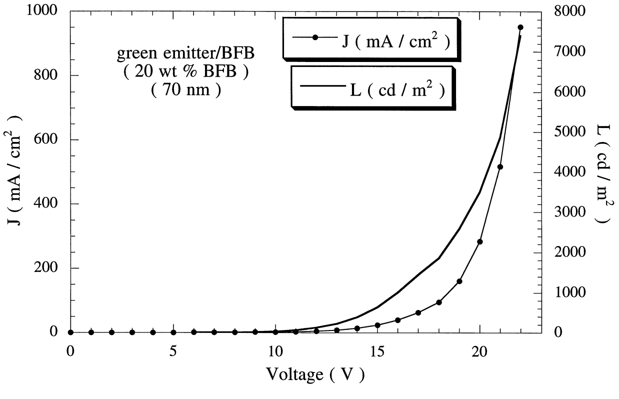

Fig. 7. Current density vs. voltage and luminance vs. voltage characteristics for an ITO/green emitter + BFB (4/1) (70 nm)/ LiF(1 nm)–Al device.

efficiency is much higher due to an improvement of the current balance factor that results in an increased exciton formation rate and more efficient recombination. An increased electron injection from the bilayer cathode is expected as a result of the presence of the LiF layer, which is thought to decrease the effective work function of the cathode. Some redistribution of the internal electric field due to hole space charge formation can also result in enhanced electron injection from the cathode by increasing the effective electric field close to the cathode. The electric field-induced dissociation of excitons at high field strengths is considered to be a possible factor in luminescence quenching so the decreased operating voltage due to the enhanced electron injection [12] will result in a decreased electric field strength within the emissive layer and therefore in reduced exciton quenching.

In summary, we have demonstrated that by using blends of suitable emissive and hole transport materials a significant improvement of the device performance can be achieved in terms of higher efficiency and brightness, lower operating voltage and better stability compared with undoped devices. Devices showing green emission exhibited a maximum external quantum efficiency of 0.9% and a maximum luminance of 7400 cd/m^2. Blue devices showed a maximum luminance of 1550 cd/m^2 and a maximum external quantum efficiency of 0.4%. The improvement of the device performance in the blend is mainly due to improved hole injection and transport in the presence of the guest hole transporting material. Energy transfer from the host to the guest has also been exploited in the case of blue devices to account for the different emission properties of the blend compared to that of the host material. Work is currently in progress to further optimise these blends.

Acknowledgements

The Sheffield group gratefully acknowledges The Dow Chemical and the Commission of the European Community (TMR Network EUROLED contract ERBFMRX-CT970106) for their support of this work. L.P. thanks the University of Sheffield for provision of a White Rose Studentship. D.G.L. thanks the Lloyds of London Tercentary Fund for a Fellowship.

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