Effect of the layer thickness on the efficiency enhancement in bilayer polymer light-emitting diodes

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ABSTRACT

To eliminate quenching of excitons at the metallic cathode of a polymer light-emitting diode (PLED) the emitting layer is separated from the cathode by a hole-blocking layer (HBL). We investigate a wide range of single-layer and bilayer PLEDs with different thicknesses consisting of a poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) emitting layer and a 20 nm poly(9,9'-diocetylfluorene) (PFO) HBL. The highest efficiency for both single-layer and bilayer devices is achieved when the total polymer layer thickness is \(\sim 90\) nm. As a result, addition of an HBL to reduce cathode quenching is only effective when the luminescence enhancement due to microcavity effects in PLEDs is restored. The relative efficiency enhancement in bilayer devices as compared to single-layer devices varies from 283\% for a 30 nm active layer to 20\% for a 250 nm device.

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1. Introduction

In conventional polymer light-emitting diodes (PLEDs), the emissive layer is sandwiched between a PEDOT:PSS \(\text{poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid)}\) anode and a low work function metal cathode, like barium (Ba) or calcium (Ca), which is subsequently capped with aluminum (Al). Typically, charge transport is highly unbalanced in such devices, since in most polymers the electron transport is limited by the presence of electron traps, whereas hole transport shows trap-free behavior. Due to the unbalanced transport, excitons are mainly generated in a region close to the cathode \[1\]. It has been shown that a large fraction of generated excitons near the cathode is quenched by direct radiationless energy transfer to the metal and the quenching is further enhanced by diffusion of excitons into the depletion area of the excitation population at the polymer/metal interface \[2\]. For PPV derivatives as poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV), the width of the quenching area typically amounts to 10–15 nm \[2\]. From device simulations on a 75 nm MEH-PPV PLED, it was estimated that about 20\% of all generated excitons are quenched at the cathode \[1\]. Hence, to overcome this loss effect in PLEDs, a multilayer device structure was proposed in which exciton quenching at the cathode can be effectively suppressed upon the application of a hole blocking layer \[3\]. With a typical width of the quenching region of 10–15 nm, an HBL with a thickness of 20 nm should be sufficient to eliminate cathode quenching effects. Fabrication of such a multilayer device by solution processing is not straightforward, since a previously casted layer can dissolve while the subsequent layer is being deposited. A way to overcome this problem is to use polymers that dissolve in orthogonal solvents, i.e., the solvent of the subsequent layer cannot dissolve the previous layer, for instance by employing a difference in molecular weight \[4\].

In this paper, we investigate the efficiency enhancement in MEH-PPV/PFO bilayer devices. To eliminate cathode quenching and minimize the voltage loss across the PFO HBL, the thickness of the PFO HBL is kept fixed at 20 nm. The thickness of the MEH-PPV emitting layer is then systematically varied from 30 nm to 250 nm to investigate the effect of a HBL on the PLED efficiency as a function of device thickness. We observe that the maximum luminous efficiency increases from 4 cd/A to a bit over 5 cd/A by addition of a HBL under the condition that the total active layer thickness is kept constant at 90 nm, due to microcavity effects.
2. Experimental

To investigate the PLED performance in detail, three kinds of devices were fabricated: hole-only, electron-only and double carrier (or PLED) devices. Before spin-coating, the substrates (glass or indium-tin-oxide (ITO) patterned glass) were washed in soap solution, cleaned in an ultrasonic bath in acetone and propanol, consecutively, dried in an oven and treated in a UV-ozone photoreactor. For hole-only devices and PLEDs, poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonic acid) (PEDOT:PSS) was spin-coated on top of the cleaned ITO substrates and annealed at 140 °C. Subsequently, the active polymer layers were applied. For hole-only devices and PLEDs, MoO3/Al and Ba/Al top electrodes were thermally evaporated, respectively. Electron-only devices were prepared on glass substrates, with evaporated aluminum (30 nm) as a bottom electrode. After polymer deposition, Ba/Al was applied as a top electrode, being an Ohmic contact for electron injection. High molecular weight MEH-PPV (~603,000) was used for the emissive layers, making it insoluble in toluene but soluble in chlorobenzene. This enabled us to deposit PFO HBL blocking layers by spin coating from toluene solution without dissolving the underlying MEH-PPV emitting layer.

3. Results and discussions

As mentioned in the introduction, in many semiconducting polymers electron transport is severely trap-limited. The resulting unbalanced transport in PLEDs confines the recombination zone near to the metallic cathode. Recent model calculations showed that exciton quenching by the metallic cathode reduces the efficiency of a PLED with typically 20% [1]. Addition of a HBL moves the recombination zone away from the cathode and is therefore expected to enhance the PLED efficiency. In this study, we use MEH-PPV (E_HOMO = -5.2 eV) as emitting layer and PFO as hole blocking layer (E_LUMO = -5.8 eV). The energy diagrams of single-layer and bilayer PLEDs are schematically indicated in Fig. 1. To test if applying PFO from toluene does not wash off the MEH-PPV layer, we first spin-coated pure toluene on top of MEH-PPV. We found that after applying toluene, the thickness of the MEH-PPV layer was decreased by only a few nm. Furthermore, after spin coating a 20 nm PFO HBL on top of MEH-PPV, we found that the total layer thickness increased by 20 nm, as expected when no intermixing takes place between the layers.

As a further check we verified that the hole current in a MEH-PPV/PFO bilayer is indeed reduced, as expected from the offset in HOMO-levels of ~0.5–0.6 eV. Fig. 2 shows both electron and hole transport in the bilayer devices as compared to the reference single layer. We observe that the electron current does not change upon addition of a thin PFO hole-blocking layer, as expected from the LUMO alignment. The hole current, on the other hand, drops more than an order of magnitude. In case of strong intermixing between the MEH-PPV and PFO, the holes would still be able to pass through such an intermixed top-layer via the MEH-PPV-rich phase and hole blocking would not be observed. The occurrence of hole blocking confirms that our bilayer devices consist of two separated layers, allowing us to do a comparative study of the performance of bilayer and conventional single-layer PLED devices.

As a first step, we fabricated a single-layer MEH-PPV PLED with a thickness of 98 nm. As shown in Fig. 3, for this layer thickness a maximum luminous efficiency of 4 cd/A can be reached. As a next step, a bilayer device is made with a 20 nm PFO layer on top of MEH-PPV (95 nm), resulting in a total thickness of 115 nm. Although the cathode quenching should be eliminated by this additional PFO layer, the efficiency of the PLED is unchanged and not enhanced by 20% as was expected.

To address this unexpected behavior, we systematically varied the thickness of the MEH-PPV layer, while keeping the PFO layer thickness fixed at 20 nm. Fig. 4(a) and (b) compares the current and light output of single-layer (symbols) and bilayer PLEDs (lines) for a range of thicknesses. It is observed that the current of the bilayer PLED is slightly reduced as compared to the single-layer PLED with nearly equal thickness. In the bilayer PLED, the current is mainly carried by holes (trap-free) across the MEH-PPV layer and electrons (trap-limited) across the PFO layer, due to the blocking of holes at the MEH-PPV/PFO interface. The total current is reduced due to the slow electron transport through PFO, whereas the holes in a single layer device can travel closer to the cathode and do not have to wait for the slower electrons. The accumulated holes in a bilayer device, however, increase the electric field across the PFO layer, enhancing the electron transport through PFO and making the current reduction less severe. From Fig. 4(b), it is already qualitatively observed that the PLED light intensity does not drop as much as the current for bilayer devices. This indicates that with the insertion of
the hole blocking layer the efficiency gets improved. Fig. 5(a) shows the luminous efficiency for single-layer devices compared to the luminous efficiencies of bilayer devices in Fig. 5(b). From the comparison of devices with similar thicknesses, it is observed that the efficiency of bilayer devices is higher than single-layer devices for the complete range of thicknesses. This enhancement in efficiency is considerably greater for thinner devices and smaller for thicker PLEDs. Besides this, we also see a more gradual increase in efficiency with increasing device current for single-layer devices, while bilayer devices a steep increase in the low current regime. The slow increase in single-layer PLEDs is due to trapping light such that with increasing bias more light is generated effectively away from the cathode. The steep efficiency increase observed in bilayer PLEDs is an indication for the absence of exciton quenching near the cathode.

In order to evaluate the effect of an HBL on the efficiency of a PLED we investigate single-layer and bilayer PLEDs in a wide range of thicknesses. The luminous efficiencies at a current density of 100 A/m² for both single-layer and bilayer PLEDs, for the full range of device thicknesses, are summarized in Fig. 6(a). Both single-layer and bilayer devices show a peak in efficiency with the maximum value at a total active layer thickness of 90 nm. Addition of an HBL increases the PLED efficiency at this current density from 3.5 cd/A to 5.5 cd/A, which is more than the expected 20% increase. It is well known that the efficiency of a PLED strongly depends on the active layer thickness due to microcavity effects, showing an oscillatory behavior [5]. This behavior originates from the interference between the emitter and the retarded radiation from the virtual image oscillator [6,7]. As a result, the optimum layer thickness for a PLED also depends on the wavelength of the emitted light. For orange-emitting MEH-PPV, the optimum active layer thickness was found to be around 90 nm, similar to our current findings [5]. Addition of a thin HBL between the emissive layer and the cathode will not only affect the exciton quenching, but also the interference in the microcavity and therefore also the efficiency of the PLED. For organic LEDs (OLEDs) based on small molecules, similar cavity effects have been reported [8–10]. An extensive study on the role of microcavity effects in multilayer
small molecule OLEDs was recently performed by Furno et al. [11]. In this study, the thickness of the HBL was systematically varied between 50 and 300 nm and a strong oscillatory behavior of the OLED efficiency on HBL thickness was observed.

The condition for constructive interference inside a PLED is given by

$$n(\lambda)d = (2m + 1)\lambda/4$$  \hspace{1cm} (1)$$

where $\lambda$ is the wavelength of the emitted light, $n(\lambda)$ is the refractive index of the polymer at specific wavelength, $d$ is the device thickness and $m$ is natural number, 0, 1, 2, . . . . . The highest efficiency was observed at 90 nm of MEH-PPV or MEH-PPV/PFO, as expected for $m = 0$, $\lambda = 600$ nm and $n = 1.6$. In Fig. 6(a), for a single-layer device, we observe that the efficiency goes to zero when the active layer thickness approaches 25 nm. In other words, all excitons are quenched at the electrodes in PLED devices with a thickness less than 25 nm. This value is double the reported exciton quenching length for a metallic cathode in PLEDs. In previous work on blue-emitting electron dominated PLEDs, we have shown that the PEDOT:PSS anode is equally effective in quenching excitons as the metallic cathode [12]. Therefore, the cut-off in PLED efficiency at 25 nm originates from the combined effect of anode and cathode quenching.

Fig. 6(b) shows the relative enhancement of efficiency in BL PLEDs as derived from interpolated points in Fig. 6(a) and plotted as a function of device layer thickness. It is observed that for thin PLEDs with an active layer thickness of ~50 nm, elimination of cathode quenching seems to lead to much larger enhancement of the device efficiency than the expected 20%. In an earlier study we analyzed the relative magnitude of the loss processes in PLEDs as a function of layer thickness [13]. It was shown that for a PLED with a typical thickness of 100 nm only 50% of the excitons recombine via Langevin recombination, about 20% is quenched at the cathode and 30% is lost via non-radiative trap-assisted recombination. However, for thin PLEDs with an active layer thickness of 30 nm only 30% of the recombination is of the Langevin type, whereas the cathode quenching increases to 40% and trap-assisted recombination remains at 30%. However, for these thin PLEDs the insertion of a hole-blocking layer not only prevents the 40% exciton quenching at the cathode, but also confines the recombination zone near the MEH-PPV/PFO interface, resulting in enhanced hole and electron densities in the emission zone. It should be noted that radiative bimolecular Langevin recombination is proportional to the product of hole and electron densities, $R_e \sim np$, whereas trap-assisted recombination is proportional to the free hole density ($p$) multiplied by electron trap density ($N_t$),$R_{SBH} \sim N_t p$ [1]. As a result, radiative Langevin recombination is quadratic in charge density, whereas trap-assisted recombination scales only linearly. Therefore, incorporation of a blocking layer not only eliminates the 40% losses due to cathode quenching, but also strongly reduces the contribution of trap-assisted recombination due to the increased carrier densities. As a result, due to the near cancellation of both loss processes upon insertion of the hole blocking layer the Langevin contribution for a 30 nm film goes up from 30% to nearly 100%, leading to a PLED efficiency increase of ~300%, as also experimentally observed. So in a thin bilayer device, the addition of an HBL not only reduces exciton quenching, but due to carrier accumulation also strongly enhances radiative recombination in favor of trap-assisted recombination, resulting in a sharp increase of efficiency with current.

4. Conclusion

In summary, the effect of hole blocking layers on exciton quenching was investigated in bilayer MEH-PPV/PFO PLEDs. In a single layer PLED all excitons are quenched by the electrodes when the active layer thickness is 25 nm or less. Insertion of a 20 nm PFO hole blocking layer considerably enhances the efficiency of the PLED under the condition that the total active layer thickness remains unchanged. Both single-layer bilayer PLEDs reach their optimum efficiency at a layer thickness of 90 nm due to microcavity effects. As a result, care should be taken that upon insertion of a HBL to reduce exciton quenching in a PLED, the optical modes in the microcavity are not altered.

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