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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′-dioctylfluorene) (PFO) HBL. The highest efficiency for both single-layer and bilayer devices is achieved when the total polymer layer thickness is ~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.

1. Introduction

In conventional polymer light-emitting diodes (PLEDs), the emissive layer is sandwiched between a PEDOT:PSS (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 exciton 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.

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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(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, MoO_3/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 ($E_{HOMO} = -5.8$ 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.

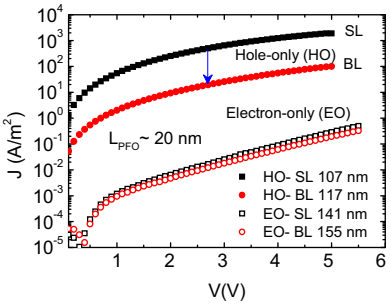

Fig. 2. Hole and electron transport in both single-layer (SL) and bilayer (BL) devices.

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

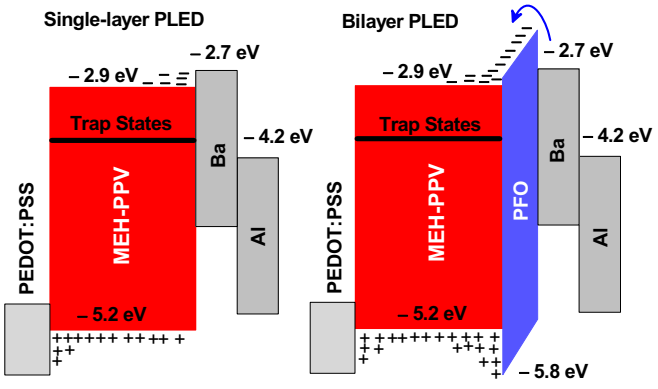

Fig. 1. Schematic device structure of single-layer and bilayer PLEDs showing energy levels of MEH-PPV and PFO polymers.

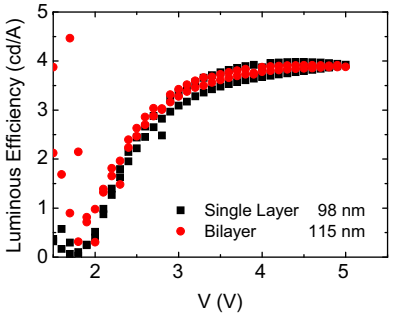

Fig. 3. Luminous efficiency vs. voltage of a SL MEH-PPV PLED with 98 nm thickness and a BL MEH-PPV (95 nm)/PFO (20 nm) PLED with total thickness of 115 nm.