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RESEARCH ARTICLE

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Laser-Induced Forward Transfer of Polymer Light-Emitting Diode Pixels with Increased Charge Injection

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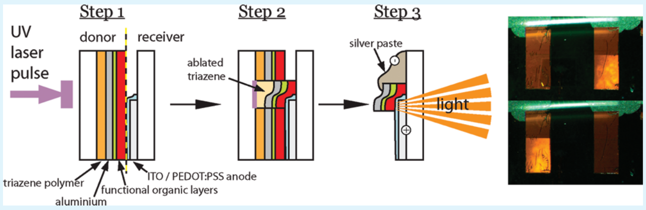

ABSTRACT: Laser-induced forward transfer (LIFT) has been used to print 0.6 mm × 0.5 mm polymer light-emitting diode (PLED) pixels with poly[2-methoxy, 5-(2-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) as the light-emitting polymer. The donor substrate used in the LIFT process is covered by a sacrificial triazene polymer (TP) release layer on top of which the aluminium cathode and functional MEH-PPV layers are deposited. To enhance electron injection into the MEH-PPV layer, a thin poly(ethylene oxide) (PEO) layer on the Al cathode or a blend of MEH-PPV and PEO was used. These donor substrates have been transferred onto both plain indium tin oxide (ITO) and bilayer ITO/PEDOT:PSS (poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) blend) receiver substrates to create the PLED pixels. For comparison, devices were fabricated in a conventional manner on ITO substrates coated with a PEDOT:PSS hole-transporting layer. Compared to multilayer devices without PEO, devices with ITO/PEDOT:PSS/MEH-PPV:PEO blend/Al architecture show a 100 fold increase of luminous efficiency (LE) reaching a maximum of 0.45 cd/A for the blend at a brightness of 400 cd/m^2. A similar increase is obtained for the polymer light-emitting diode (PLED) pixels deposited by the LIFT process, although the maximum luminous efficiency only reaches 0.05 cd/A for MEH-PPV:PEO blend, which we have attributed to the fact that LIFT transfer was carried out in an ambient atmosphere. For all devices, we confirm a strong increase in device performance and stability when using a PEDOT:PSS film on the ITO anode. For PLEDs produced by LIFT, we show that a 25 nm thick PEDOT:PSS layer on the ITO receiver substrate considerably reduces the laser fluence required for pixel transfer from 250 mJ/cm^2 without the layer to only 80 mJ/cm^2 with the layer.

KEYWORDS: laser deposition, LIFT, triazene polymer, PLED pixels

INTRODUCTION

Laser direct-write of thin solid films, i.e., laser-induced forward transfer (LIFT), first emerged in the 1980s as a patterned deposition technique for thin metallic films.[1] The technique was quickly developed to incorporate an intermediate dynamic release layer (DRL), which aids the conversion of incident laser energy into kinetic energy.[2] Also in the 1980s, research into the laser ablation of polymers was developing rapidly alongside the increasing availability of excimer UV lasers.[3] The main developments in terms of polymer ablation-assisted transfer focused around the use of a polymer matrix in a process termed MAPLE (matrix assisted pulse laser evaporation) direct write.[4] MAPLE has been used to deposit MEH-PPV films.[5] It was not until 2006 that a photodegradable organic material, triazene polymer, first used as a LIFT DRL to transfer mammalian neuroblast cells.[6] Since then, nanocrystal quantum dots,[7] thin ceramic films,[8] polymer biosensors,[9] and functioning polymer light-emitting diodes (PLEDs)[10] have all been successfully transferred using LIFT (i.e., LIFTed) using triazene polymer DRLs. Here, we attempt to build upon our initial MEH-PPV PLED breakthrough and investigate ways of improving the process and device efficiency. PLEDs have enormous potential as individual devices,[11] but OLEDs based on small evaporable molecules have been the main focus of research for commercial displays. Small-molecule OLEDs have a number of much better developed pixel deposition methods, most notably vacuum evaporation through a shadow mask[12] and laser-induced thermal imaging (LITI).[13] Highlighting the potential fleixibility of LIFT, tris 8-hydroxyquinoline aluminium (Alq$_3$), a sensitive small molecule organic light-emitting diode (OLED) material, has also been successfully transferred using a thick polymeric DRL.[14]

In the previous study, we used the single functional layer diode architecture with a transparent ITO-coated glass anode, the light-emitting MEH-PPV layer, and an aluminium top cathode (ITO/MEH-PPV/Al) to provide a proof of the principle that PLED pixels can indeed be fabricated by LIFT.[10] The performance of the simple LIFTed pixels was quite low, partly because

Received: October 1, 2010
Accepted: January 2, 2011
Published: January 24, 2011

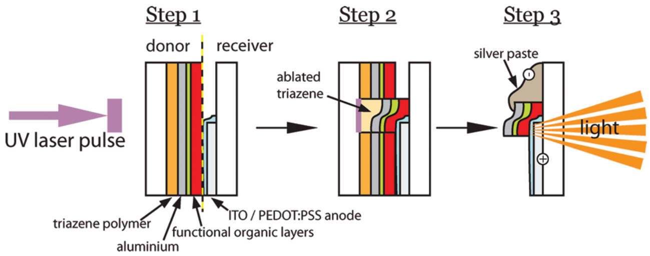

Figure 1. Schematic diagram of the LIFT process in three steps: Step 1 shows the prepared substrate architectures; the dashed line separates the donor substrate from the receiver substrate. Step 2 shows the transfer process as the pressure build up from the gaseous products of triazene ablation push the overlying layers onto the receiver substrate. Step 3 shows the receiver substrate after the donor substrate has been taken away and a bias is applied across the device for light emission.

of the low light emission efficiency of the MEH-PPV polymer, but also because of limitations of charge injection at the electrodes. Charge injection into conjugated polymers can be modelled as charge tunelling across a barrier given by the energy shift of the molecular orbitals of the organic semiconductor induced by the external applied bias.[11] To a first approximation, this behavior is outlined by the Fowler-Nordheim relationship,[15] but in a more elaborate model both thermal motion and image charge effects have to be included.[16] Given the limitations of a single-layer device, which is in essence a "hole-only" device with poor electron injection from the cathode,[15] we decided to improve charge injection in our devices. For our LIFT method, illustrated in Figure 1, we require to build up the device on the donor substrate in reverse order starting with the metal cathode which is then subsequently coated with the electroluminescent material. For this reason, low work function alkali or alkaline earth metals cannot be used because they would be corroded easily by the solvents or when exposed to the ambient atmosphere during laser transfer.

In this article, we report on modifying charge injection in MEH-PPV devices in a way that is compatible with our LIFT deposition process. To balance hole and electron currents during operation of the PLED and to achieve substantial performance increase, both the cathode as well as the anode interface were adjusted. On the cathode side, electron injection was increased by adding in a polyethylene oxide (PEO) electron-injection layer,[17,18] or by using a PEO:MEH-PPV blend[19] instead of a pristine MEH-PPV layer. This approach has the advantage that we can still use aluminium as the cathode metal, it being far more tolerant to oxygen and water exposure than earth or alkali earth metals. On the anode side, hole injection was controlled by inserting an appropriate low-conductive polyethylene dioxythiophene-polystyrene sulfonate blend (PEDOT:PSS) as a hole transport layer (HTL).[20,21] We also investigate the effect that covering the ITO glass receiver substrate with a PEDOT:PSS overlayer has on the laser-fluence required to transfer an intact OLED pixel. The updated LIFT process, showing the multilayer additions, is shown in Figure 1.

EXPERIMENTAL SECTION

Substrate Preparation. 25 mm × 25 mm square high-quality quartz-glass slides (suprasil 2 grade A, Quarzglas-Heinrich) were used as LIFT donor substrates. 25 mm x 25 mm silica glass slides, with patterned ITO coating (140 nm, 20 Ω/□), were used as both LIFT receiver substrates and the starting substrates for PLED devices fabricated by conventional spin-coating procedure (hereafter called conventionally fabricated devices). Both of these substrates types were cleaned by ultrasonication in an acetone and ethanol bath, scrubbed with special surfactant (Hellmanex, Hellma AG), before being rinsed in water purified by microfiltration.

The triazene polymer (TP) was synthesized in our group according to the synthesis procedure for TP-6-Me outlined previously.[22] To prepare the donor substrates used in our LIFT process, we spin-coated the triazene polymer onto quartz substrates from a 2.5 wt % TP in chlorobenzene:cyclohexanone (1:1) solution. The spin-coating conditions to obtain 150 nm thick films are 1500 rpm with a 1000 rpm/s ramp. Aluminium thin films were then evaporated (0.1 nm/s for the first 5 nm, then 0.2 nm/s) onto the triazene films in a vacuum ($<10^{-5}$ mbar) to a thickness of 80 nm, measured using a calibrated quartz microbalance. PEO (stated M_w = 400 000 g/mol; measured by gel permeation chromatography (GPC): M_n = 149 000, M_w = 274 000, D = 1.85) was bought from Sigma Aldrich, dissolved in acetonitrile and filtered through a 0.45 μm PTFE filter. The concentration was varied for fixed spin-coating conditions (6000 rpm) to give the best PEO film thickness for device performance regarding LIFT deposited diodes. This was found to be 0.2 wt % PEO in acetonitrile, giving a film thickness of 7 nm +/- 4 nm. MEH-PPV was bought from American Dye Source, and characterized using GPC as: M_n = 144 000 g/mol; M_w = 776 000 g/mol; D = 5.4. The MEH-PPV was dissolved in chlorobenzene to make 0.8 wt % solutions. These solutions were filtered through 1 μm PTFE filter and spin-coated at 1500 rpm. The blended solution was 9:1 MEH-PPV:PEO,[19] also dissolved in chlorobenzene to make a 0.8 wt % solution, and filtered and spin-coated in the same way as the pure MEH-PPV. In this way, three different PLED LIFT donor stacks were made: TP/Al/MEH-PPV (single-layer); TP/Al/PEO/MEH-PPV (bilayer); TP/Al/MEH-PPV:PEO (blend). All of the light-emitting polymer (LEP) layers had thicknesses of 70 nm ± 10 nm, as measured by an Ambios XP1 profilometer.

For the conventionally fabricated devices and the LIFT receiver, the ITO-patterned glass substrates were cleaned in the same way as the quartz substrates, then treated with an UV-ozone cleaner. The PEDOT:PSS (Clevios P Al4083, H.C. Starck) was spin-coated from solution at (1) 1500 rpm with 1000 rpm/s ramp for 50 nm films, and (2) 5000 rpm with 3000 rpm/s ramp for 20 nm films. The substrates were then dried at 120 °C in air for 30 minutes. The conventionally fabricated light-emitting layers were spin-coated in the same way as for the LIFT donor substrates, outlined above, except that the PEO layer was spin-coated after the MEH-PPV, rather than before. Finally, aluminium was evaporated onto the light emitting layers through a mask which defined 8 separate devices, four with areas of 3.5 mm^2, and four with areas of 7 mm^2. Three different device architectures were made using this conventional process: the single-layer (ITO/PEDOT:PSS/MEH-PPV/Al), bilayer (ITO/PEDOT:PSS/MEH-PPV/PEO/Al), and blend (ITO/PEDOT:PSS/MEH-PPV:PEO/Al) devices.

LIFT Setup. The process is summarised in Figure 1. LIFT experiments were done using a 308 nm XeCl excimer laser source (pulse length of the main pulse is 30 ns). The laser beam was attenuated using a variable attenuator plate and passed through a 2 mm × 4.8 mm aperture. Using a normal achromatic UV laser lens, the image of the mask was demagnified four times to create a 0.5 mm × 1.2 mm rectangular image at the triazene polymer/quartz-glass interface. The transferred pixel overlapped with the ITO anode to give light-emitting pixels with dimensions 0.5 mm × 0.6 mm (0.3 mm^2), hereafter referred to as LIFTed devices. The laser energy was measured using a pyroelectric energy meter (Gentec QE12). The LIFT donor and receiver substrates were pressed together using spring-loaded ball-bearing screws with even pressures, applied to the four corners of the donor substrate (in a 23 mm square). Six different LIFTed devices were made in total: all three of the architectures mentioned above (single-layer, bilayer, and blend), both with and without the PEDOT:PSS HTL.

Device Characterization. Device characterization was undertaken using a homemade Labview program that integrates a Keithley 2400 sourcemeter and a Minolta LS-110 luminance-meter to measure the luminance, current whilst varying the voltage (a $L-J-V$ measurement). The LS-110 has on it a microscope objective, which reduces the area of detection to a 0.4 mm diameter circle, small enough to be completely covered by the LIFTed devices. For every luminance measurement, roughly 3 s are required to get an average value, and 0.5 V steps in the IV runs were used when the luminance was being measured. Samples were kept in an inert environment during measurements using a specially designed sample holder which has a glass-viewpoint at the top. The samples were loaded into the sample holder in the nitrogen atmosphere glove box, and the contacts aligned to the patterned ITO substrate. The LIFTed devices had the cathode contacts painted on using silver paste. To correct for small variations in the light-emitting layer thicknesses, we then divided the voltage by the thickness to have a value for the electric field strength (V/m)

Fluorescence measurements were made using a Jobin Yvon Horiba FL311 Fluorolog. Photoluminescence (PL) quantum efficiency measurements to characterize the polymer were done using an integrating sphere, according to the procedure outlined in the literature.[23] The MEH-PPV was found to have a PL quantum efficiency of about 15%, compared to a Rhodamine-6G standard of 65%. The standard fluorescence spectra of the films were made using normal frontside fluorescence. The electroluminescence (EL) measurements were done using an external setup where the light is coupled into the detector using a fiber-optic cable.

RESULTS AND DISCUSSION

The first part of this section concentrates on those devices made using conventional spin-coating onto a pre-patterned ITO glass substrate, before patterned aluminium cathode evaporation. The main observation is the different improvement in luminous efficiency provided by the bilayer blend devices. Secondly, we will look at the LIFT of the PLED stacks as a function of laser fluence, particularly at the successful LIFT onto an ITO/PEDOT:PSS bilayer receiver substrate which is achieved at much lower laser fluence than onto a single-layer ITO receiver substrate. Finally, we will look at the electroluminescent characteristics of the different devices fabricated by LIFT to see how they compare with one another and with the conventionally fabricated devices.

Conventionally Fabricated Devices. Devices were conventionally fabricated to characterize the MEH-PPV polymer's electroluminescence (EL) and to act as control devices for the devices fabricated using LIFT. PEDOT:PSS was added onto the ITO anode to act as an hole-transporting layer (HTL). Although this will not particularly improve hole-injection because injection from ITO is already good (the ITO work function (5.1 eV) is well-matched to the HOMO (5.2 eV) of the MEH-PPV) there are good reasons to use an intermediate PEDOT:PSS layer to improve device lifetime.[20,21]

The addition of a PEO layer shows mixed results for device performance. Figure 2a shows how the operating electric field strength increases, but Figure 2b shows the improved luminous efficiency of more than an order of magnitude greater than that obtained with single-layer MEH-PPV devices. The positive effect of a thin PEO film on electron injection has been observed before,[17,24] but the mechanism is debatable. The third type of device that we fabricate was a MEH-PPV:PEO blend, which showed even better device performance than the bilayer devices with a luminous efficiency (LE) over two orders of magnitude larger, and an operating electric field strength of about a half. Blend devices show a maximum luminous efficiency of 0.45 cd/A and a brightness of 400 cd/m^2 at 0.7 x 10^8 V/m. This is in comparison to single-layer devices which have a maximum LE of 0.004 cd/A and a brightness of 3.6 cd/m^2 at 1.1 × 10^8 V/m. The single-layer devices present similar efficiencies to the best MEH-PPV devices reported in the literature.[18]

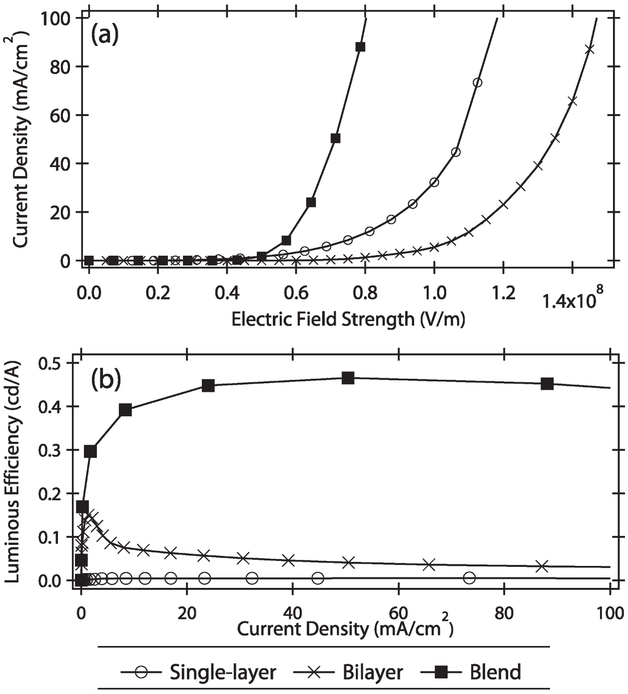

Figure 2. (a) Current density as a function of electric field strength, and (b) luminous efficiency as a function of current density for the three types of conventionally fabricated devices. The crosses represent bilayer devices; the solid squares represent blend devices; the hollow circles represent single-layer devices.

A mechanism whereby oxygen atoms from poly(ethylene glycol) (PEG) coordinate with aluminium atoms to form an ultrathin layer of interfacial n-type MEH-PPV (which would move the recombination zone further away from the quenching aluminium cathode) has been proposed to explain the electron-barrier lowering phenomenon that was observed in a MEH-PPV:PEG blend.[19] This mechanism can also be applied to a MEH-PPV:PEO blend as PEO incorporates the same monomeric chemical structure as PEG, but with a much greater molecular weight. A similar effect has been observed with other polar polymers and surfactants[25] after earlier research on metal cation-containing surfactants with the surfactant both blended and single-layered.[26] In the last study, an explanation was taken from the hypothesis that a self-assembled monolayer of orientated dipoles chemically attached to the electrode will have an electric field across the dipole layer which will increase the open circuit voltage.[27] Interfacial dipole layers are indeed well-known to induce considerable surface potential shifts and may well reduce the energy barrier for electron injection.[28] A stable interfacial layer may also act as a barrier to aluminium diffusion into the organic layers.[29,30] Another mechanism which should be kept in mind is phase separation of the blend[31] because this would probably have an effect on the depth distribution of PEO in the final films, as well as making lateral structures which would influence device characteristics.

The self-assembling dipole layer is a reasonable explanation for the effect of simply adding PEO, but there is another interesting

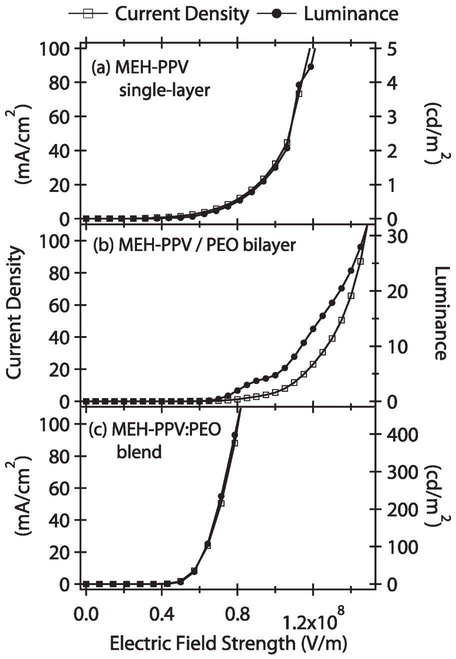

Figure 3. Current density and luminance as a function of electric field strength for the three types of conventionally fabricated devices: (a) single-layer, (b) bilayer, and (c) blend. The solid circles are the luminance, and the hollow squares are the current density.

observation from the bilayer device characteristics. At low current densities, there is a big peak in the luminous efficiency below 5 mA/cm^2, observable in Figure 2b. Figure 3 shows the current density and luminance plotted against electric field strength. In Figure 3b the shape of the luminance curve can be seen to differ with respect to the current density. This is in contrast to the both the single-layer and blend devices (Figure 3a, c) where the luminance and current density curves match each other almost identically. In conjunction with the increased operating electric field strength, one possible explanation for this heightened LE in the bilayer devices is that the PEO is forming an insulating layer. It has been observed that PEO is a good hole blocker and promotes electron injection when present as films 10 nm thick, with a calcium cathode.[24] The PEO layer in this work is less than 10 nm thick, but thick enough (7 nm ± 4 nm) to act like the insulating layer of a capacitor. The layer is thin enough that current may possibly pass through the PEO by electron field emission which would benefit the luminance in particular by moving the recombination zone away from the quenching aluminium cathode to the other side of the PEO film. However, there will also be migration of aluminium into the PEO; aggregate formation and diffusion from the initial evaporation,[29,30] which will then be annealed by applying a bias;[32] secondly by possible oxide barrier-layer formation, if there is any contamination;[33,34] and finally by electric field induced diffusion, if the bias applied is large enough.[35] As the electric field across the PEO film increases, electron tunnelling across the PEO will also increase, but eventually there will be a breakdown of the dielectric barrier by the formation of aluminium channels through the PEO from the mechanisms mentioned above. In this case then it would be expected that the original electron tunnelling, and corresponding luminous efficiency peak observed, will disappear if a second L−J−V run is made. For subsequent runs, there is indeed no initial LE peak, the operating voltage (or electric field strength) decreases, and the open-circuit voltage also increases. The latter observation suggests that a dipolar layer, similar to that proposed for the MEH-PPV:PEO blend, then acts as the main component of the MEH-PPV/Al electron-injecting interface, rather a dielectric PEO layer.

Fabricating Devices by LIFT. As outlined above, LIFT was carried out to fabricate three different types of OLEDs, both with and without a PEDOT:PSS HTL coated on top of an ITO receiver substrate. As a function of fluence, microscopy images of the transferred pixels of blend devices are shown in Figure 4 for a plain ITO receiver substrate, ITO coated with a 50 nm film of PEDOT:PSS and ITO coated with 20 nm of PEDOT:PSS. The pattern observed for this blend PLED transfer stack was the same for single-layer and the bilayer devices. The difference between plain ITO and ITO with a PEDOT:PSS coating is quite stark; the addition of PEDOT:PSS clearly reduces the fluence required for a successful transfer. Transfer onto a plain ITO receiver substrate was optimal at 200−300 mJ/cm^2, whereas transfer onto a bilayer ITO/PEDOT:PSS receiver substrate is achieved at only 70−100 mJ/cm^2. This is a distinct advantage for transfer quality because a lower fluence means less energy entering the system, and therefore a lower chance of damaging the sensitive transfer materials, in other words, a softer transfer. This was observed for all device architectures. From Figure 4 it can also be seen that at the fluence for the best transfer onto plain ITO (200−300 mJ/cm^2) there is also a slight improvement in transfer onto ITO/PEDOT:PSS. This looks like a second fluence regime for transfer.

Successful transfer onto PEDOT:PSS in the low fluence regime occurs at the lowest fluences at which complete delamination is achieved, giving a very soft transfer. For transfer onto ITO, the lack of success at low fluences is best explained by a lack of interfacial adhesion between the ITO and the MEH-PPV. Pixels were occasionally transferred onto plain ITO at low fluences, but they appeared to be very poorly stuck to the ITO surface. Successful LIFT onto plain ITO in the high fluence regime appears to have an upper limit at the fluence where the flyer begins to break up, either because of the thermal load from the laser or because of the impact with the receiver substrate.

At fluences between 100 and 200 mJ/cm^2 for all types of receiver substrate, there is poor or no transfer of the PLED stack, and the flyer is often returned to the donor substrate, delaminated, but back where it began (in Figure 4). Whether this feature is due to the shockwave accompanying the laser ablation is under investigation.[36,37] The fact that there is almost no difference in transfer quality as a function of fluence between the thick (50 nm) and thin (20 nm) PEDOT:PSS receiver substrates, suggests that the main benefit of PEDOT:PSS in comparison with plain ITO, is the stronger attractive surface force interactions with the transferred flyer that make the PEDOT:PSS "stickier" than plain ITO. The main barrier to transfer must be some sort of force opposing motion. At present we are investigating whether this is mainly due to the collision with the receiver substrate, or the reflected shockwave generated ahead of the flyer (which may pass through the air or, as they are in contact, through the receiver material).

Characterization of LIFTed Devices. Figure 5 shows $J-V$ curves (a) and luminous efficiency vs current density (b) for 6 different device architectures, fabricated by LIFT (LIFTed devices). Figure 5a shows that the devices transferred onto plain ITO have a higher leakage current than those transferred onto PEDOT:PSS. The plain ITO anode devices also have very low efficiencies when compared to the devices made with PEDOT:PSS, seen in

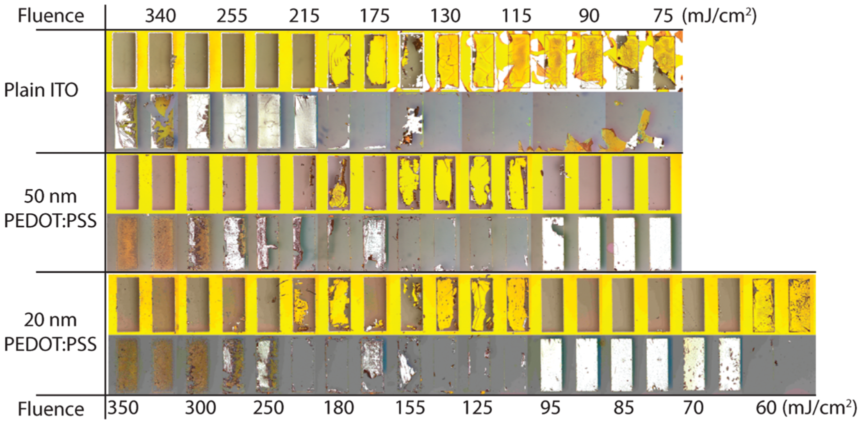

Figure 4. Matrix of transferred MEH-PPV:PEO/Al with 150 nm triazene polymer for decreasing fluence (from left to right). The top line for each different sample is the LIFT donor substrate, and the bottom line is the receiver substrate, viewed from above (so the aluminium is on top).

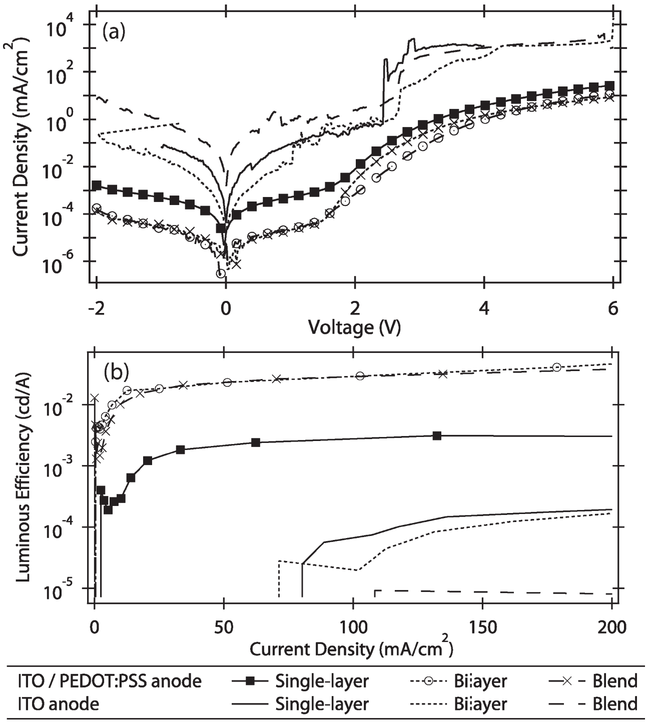

Figure 5. Transferred device characterisation, showing all six different types of devices. (a) shows how the current density varies as a function of voltage. (b) shows the luminous efficiency of these devices as a function of current density, on the first *I*—*V* run (see figure 6 for a graph of how these values changed with subsequent runs).

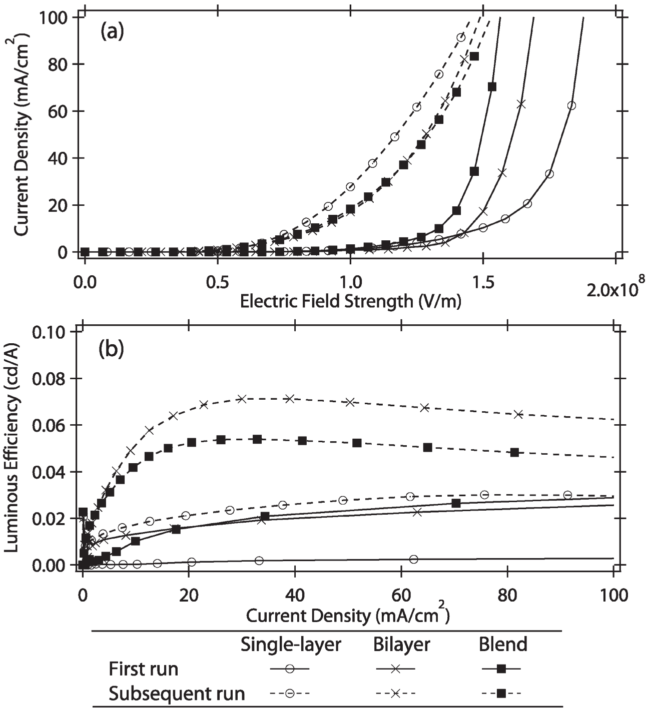

Figure 6. (a) Current density as a function of electric field strength, and (b) luminous efficiency as a function of current density for the three types of LIFTed devices on a first *I*—*V* run (solid lines), then showing the change upon a subsequent run (dotted lines). The crosses represent bilayer devices; the solid squares represent blend devices; the hollow circles represent single-layer devices.

Figure 5b. These two observations are easy to explain, because the samples were transferred at much higher fluences which increases the thermal and mechanical load on the pixel, increasing the chance of the aluminium short-circuiting the LEP. It is harder to compare the *J*—*V* curves of the different LEP compositions, but the one thing that is maybe distinguishable is a slightly higher current for single-layer MEH-PPV on PEDOT:PSS at lower voltages which is perhaps because the single-layer MEH-PPV film was 60 nm thick whereas the bilayer and blend films were 70 nm thick. The efficiencies of the devices transferred onto PEDOT:PSS shown in Figure 5b demonstrate that the single-layer MEH-PPV device has a considerably lower luminous efficiency compared to both PEO-containing devices. However, this difference is only so large for the first device operation run; Figure 6 demonstrates that this first run acts as a sort of electrical annealing step, and improved device performance is subsequently observed.

Being exposed to ambient conditions, the LIFTed devices are possibly limited by oxygen and water damage of the organic layers and the electrodes.[33,38] Water uptake by the hygroscopic PEDOT:PSS and ITO on the receiver substrates is most likely to be the main source of contamination.[20,21] This aside, the devices still show good device characteristics. On the first run, it appears that the devices show the differences expected from those observed

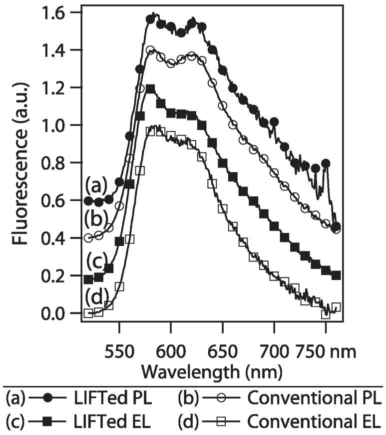

Figure 7. Fluorescence spectra of MEH-PPV:PEO films showing photoluminescence of (a) LIFTed pixels (on PEDOT:PSS/ITO), and (b) pristine LIFT donor; and electroluminescence of (c) a LIFTed pixel, and (d) conventionally fabricated device (both on PEDOT:PSS/ITO).

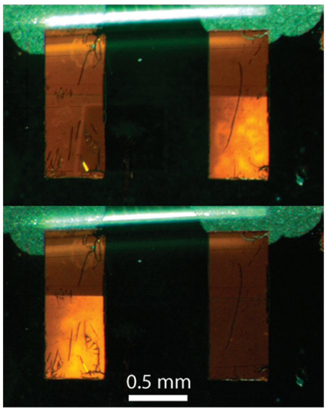

Figure 8. Electroluminescence from two LIFTed devices with the architecture ITO/PEDOT:PSS/MEH-PPV:PEO/Al. They are shown side-by-side to illustrate the contrast between their on and off states. The light-emitting section of the diodes (the lower half) is where overlap between the aluminium cathode and the ITO anode occurs (see Figure 1).

with conventionally made devices, but subsequent runs show a distinct change, shown in Figure 6. The single-layer device initially shows an efficiency of around 0.003 cd/A at a fairly high electric field strength of 1.8×10^8 V/m. However, after this initial $I-V$ run the efficiency jumps up to above 0.01 cd/A and reaches nearly 0.03 cd/A at a much lower electric field strength of 1.3×10^8 V/m. In Figure 6b, both the PEO bilayer and blend devices have efficiencies that start off above 0.01 cd/A and increase considerably on subsequent runs, although not above 0.1 cd/A. The tunnelling peak observed for the conventionally fabricated MEH-PPV/PEO bilayer devices (in Figure 2b) is not observed for the LIFTed devices. In fact, the bilayer exhibits marginally better device performance than the MEH-PPV:PEO blend. The reason for the lack of a dielectric layer could be that the PEO film is redissolved by the MEH-PPV solution subsequently spin-coated on top of the PEO layer on the LIFT donor substrates; PEO powder is soluble in chlorobenzene, as seen in the MEH-PPV:PEO blend solutions. If the PEO layer is redissolved, we would expect the blend and bilayer devices to have the same performance. Indeed, the operating electric field strengths, both on the first runs and on subsequent runs, appear to be the same, and the luminous efficiencies are also very similar. The single-layer device seems to have a slightly higher initial operating electric field strength, but on the subsequent run the operating electric field strength comes down to that of the PEO-containing devices, Figure 6a. The luminous efficiency, however, only reaches that of the PEO-containing devices on their first run, Figure 6b.

The differences between the conventional and LIFTed devices are not just constrained to the PEO-containing devices. The single-layer MEH-PPV LIFTed device, on the subsequent run, exhibits a luminous efficiency of an order of magnitude greater than the single-layer conventionally fabricated device (Figure 2). One reason for this difference may be the different fabrication methods, particularly at the Al cathode interface. The aluminium evaporation directly onto the MEH-PPV in the conventional orientation is likely to have a detrimental effect on device performance. Evaporated aluminium will diffuse into the light emitting polymer (LEP), creating aggregates and a porous structure, and react with the top layer of the LEP.[30] This aluminium diffusion in the conventional device architecture effectively increases the surface area of the LEP/Al interface and therefore also increases the chances of exciton quenching relative to the chances of quenching at the smoother LEP/Al interface of LIFTed devices. If there is PEO at the top of the LEP this will, in effect, make the polymer surface more reactive (similar to activating the surface with plasma treatment) and reduce metal diffusion into the polymer,[39] which helps to explain why the PEO-containing conventionally fabricated devices exhibit such high efficiencies. For the LIFT donor substrates, the LEP is spin-coated on top of the stable Al film. Aluminium diffusion from evaporation, and the consequent porous interface,[30] will not occur, and reactions with the LEP layer are much less likely with the spin-coating deposition process at room temperature. Two other methods of diffusion which may still occur for LIFTed devices upon operation are the electric field induced ionic drift[35] and electric field driven metal diffusion and subsequent oxidation.[33,34] However, by spin-coating on top of a uniform Al film to fabricate the LIFT donor substrates, a much more homogeneous and stable Al_2O_3 barrier layer is likely to be formed as the Al/LEP interface, according to Mott's Theory of the Formation of Protective Oxide Films on Metals.[34] This oxide film may degrade the LIFTed devices in terms of making them less conductive, but will also keep the cathode/LEP interface more uniform, reducing nonradiative quenching of the electron-hole pairs. It has been observed that local spikes during operation, which may be enhanced by a nonuniform cathode/LEP interface, will cause rapid device degradation.[40]

The observation from Figure 6 that the devices improve on subsequent $I-V$ runs after the initial run is very interesting. It appears to be linked to electrical thermal annealing, possibly simply removing oxygen and water contamination,[41] but further work is needed to fully understand this phenomenon.

In Figure 7, the photoluminescence spectra of LIFTed MEH-PPV:PEO pixels are in good agreement with the PL spectra of the pristine MEH-PPV:PEO film indicating that minimal thermal load was placed upon the MEH-PPV:PEO film during transfer. The spectra show the expected degree of aggregation of MEH-PPV films spin-coated from 1 % chlorobenzene solutions.[42] Also shown in Figure 7, the electroluminescence spectra are in good agreement and may even hint at the recombination layer containing fewer aggregates than the average of the whole film, seen by the PL spectra. However, the difference is not really significant enough to make a conclusion.

Two working devices showing the distinctive orange-red electroluminescence are shown in Figure 8. The area where the transferred pixel overlaps with the ITO on the receiver substrate, i.e. where electroluminescence is observed, is the LIFTed device. Some cracks in the aluminium can be seen clearly through the MEH-PPV, and the inhomogeneity of light intensity across the device is visible too, but the EL functionality is clearly maintained. The defects observed can probably be removed by optimizing the transfer, so there is room for improvement.

■ CONCLUSIONS

The transfer of functioning PLED stacks has been demonstrated, and some degree of versatility shown. Modifications to basic single-layer MEH-PPV devices have been added. In particular, PEO has been used both as a cathode buffer layer and in a blend with the MEH-PPV, improving device performance in both cases for conventionally fabricated devices. When the MEH-PPV is spin-coated on top of the PEO for bilayer LIFT donor substrate fabrication, it is likely that the PEO is redissolved by the chlorobenzene and blends into the MEH-PPV film. The improved efficiency of PEO-containing devices can be explained nicely by a self-assembling dipolar monolayer theory,[27] although there is also some evidence for electron field emission for the conventional PEO bilayer device. The LIFTed devices, compared with the conventionally fabricated devices, show a different pattern in device performance, presumably because of the inverted deposition of the LIFT donor substrate changing the nature of both of the electrode interfaces. The overall performance of the LIFTed PEO-containing devices was slightly lower than for conventional devices, possibly because of oxygen and water damage by putting the substrates together in air or because of differing film formation, but the plain MEH-PPV device showed elevated performance, presumably mainly due to the different LEP/Al interface. Successful LIFT was shown to be aided greatly by the presence of PEDOT:PSS on the receiver substrate by reducing the required fluence by more than 50%, from 250 to 80 mJ/cm^2.

Future transfer experiments will be undertaken using a new setup whereby the receiver and donor substrates are inserted into the sample holder together in an inert environment, and kept together during the LIFT process, so as to minimize the air and water diffusion into the donor subtrate and especially the receiver substrate, where the PEDOT:PSS is particularly good at absorbing water, reducing the device performance significantly.

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■ ACKNOWLEDGMENT

GPC measurements were done by Dr. Thomas Geiger at Empa. The work was funded by the Swiss National Science Foundation and the EU, through the e-LIFT project.

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