Enhanced efficiency of multilayer organic light-emitting diodes with a low-refractive index hole-transport layer: An effect of improved outcoupling?

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The authors report on an internal device modification for multilayer organic light-emitting diodes (OLEDs) with enhanced efficiency that promises high compatibility with conventional manufacturing processes. By copolymerization of a hole-conducting monomer with a compound possessing a lower refractive index, a hole-transport layer with reduced optical density but slightly reduced hole-transport properties is formed. Multilayer OLEDs based on this reduced-index layer show a 25% increased efficiency compared to reference devices. The results are compared to optical simulations of the dipole emission from thin organic films. It is found that the efficiency improvement is only to some extent due to enhanced outcoupling resulting directly from the reduced refractive index but primarily due to a change of the width of the emission zone. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2773930]

Since organic light-emitting diodes (OLEDs) are a promising technology for display or lighting applications,[1,2] very intense research is taking place to optimize performance[3] and lifetime.[4] Unfortunately, in standard OLED devices, only a small amount of the light generated within the organic layer is actually used. Due to waveguiding and reabsorption losses in the organic layers and in the substrate, the outcoupling efficiency is expected to be less than 20%.[5] Therefore, the total device efficiency can be significantly improved by enhancing the amount of extracted light.

Previous approaches to increase outcoupling in the viewing direction were mostly based on external outcoupling structures, such as microspheres[6] or microlens arrays,[7] which require additional and often expensive production steps while at the same time limiting the range of applications.

In the past, it was shown that the implementation of a layer with low refractive index [such as aerogel-interlayer ($n \sim 1$) between glass substrate and inium-tin-oxide (ITO) anode] can enhance the outcoupling efficiency by tuning the optical thickness of a multilayer OLED.[8] However, these layers are fragile and thus the deposition of further layers is complicated. Here, we present an internal modification of one active OLED layer that promises high compatibility with conventional manufacturing processes.

In our previous work, we demonstrated solution-processed multilayer OLEDs with improved device efficiency by using a photo-initiated oxetane-based cross-linking reaction to fabricate insoluble triphenylaminedimer (TPD)-based hole-transporting layers (HTLs).[3,9] We aim to use this cross-linking reaction to embed a reduced-index layer into a multilayer OLED. This can be achieved by copolymerizing a cross-linkable HTL or electroluminescent layer (EL) with an also cross-linkable material with lower refractive index. In this letter, we compare the enhanced efficiency experimentally observed when implementing a reduced-index HTL in a blue-emitting multilayer OLED to numerical simulation of dipole emission from thin organic films.

The refractive index of the HTL was decreased by copolymerizing the cross-linkable hole-conducting material QUPD (1) (*N,N'*-bis[4-(6-[(3-ethyloxetan-3-yl)methoxy]hexyloxy)-phenyl]-*N,N'*-bis(4-methoxyphenyl)biphenyl-4,4'-diamine)[9] with the alkyl compound (2) (1,6-bis([3-ethyloxetan-3-yl)methoxy]hexane). Both materials contain two oxetane moieties per molecule which can be cross-linked via cationic ring-opening polymerization to form an insoluble network. [4-octyloxydiphenyl-iodonium-hexafluoro-antimonate, (3)] was used as photoinitiator.

Insoluble HTLs were fabricated by spin coating a solution of (1) (73 wt %), (2) (25 wt %), and (3) (2 wt %) onto a substrate under inert gas atmosphere. The films were illuminated with UV light for 5 s, soft cured for 1 min at 100 °C, and subsequently rinsed with THF. We will refer to the pure films of (1) as "HTL-A" and (1) copolymerized with 25 wt % of (2) as "HTL-B."

Refractive index measurements were carried out by ellipsometry on thin cross-linked films (100 nm) at 532, 633, and 785 nm. A Cauchy function[10] was fitted to extrapolate the refractive index to the peak emission wavelength of the emitter (465 nm). Upon adding 25 wt % of (2) the refractive index at 465 nm is reduced from $n_{HTL-A} = 1.64$ to $n_{HTL-B} = 1.60$. $\Delta n = 0.04$ is constant over the visible part of the spectrum (see the inset of Fig. 1).

When copolymerizing (1) with (2), a compound possessing no hole-transporting properties, the charge transport properties are expected to change. Thus, hole-only devices (HODs) with the following structure were studied: ITO//PEDOT:PSS [poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate)] (35 nm)//HTL (100 nm)//Ag (150 nm). PEDOT:PSS (Baytron P® AI4083) was spin coated on precleaned, ozone-treated ITO-coated glass substrates and baked at 110 °C for 1 min to remove residual water. Subsequently the HTL was deposited as described above. Finally, the top electrode was evaporated in a vacuum chamber. We found that despite the relatively high amount of (2) being present in the material, the hole-conducting properties of HTL-B were only slightly reduced compared to

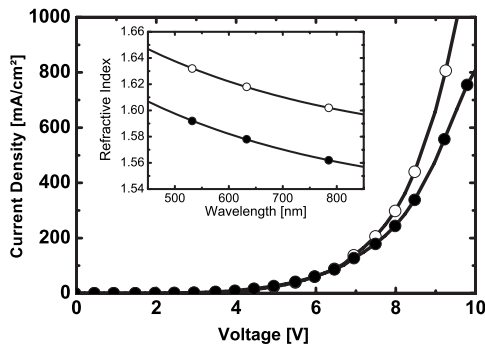a)Electronic mail: klaus.meerholz@uni-koeln.de

FIG. 1. Hole-only characteristics for devices with HTL-A (○) and HTL-B (●) as organic layer. Inset: Refractive index of HTL-A (○) and HTL-B (●) vs wavelength.

HTL-A, with the reduction being most pronounced at higher voltages (see Fig. 1).

In order to test the applicability of the modified HTL, blue-emitting OLEDs with the following general device structures were fabricated: ITO//PEDOT:PSS (35 nm)//HTL (20–60 nm)//EL (80–40 nm)//Ba (4 nm)//Ag (see Fig. 2, left). The devices were processed as described above. However, in addition, a fluorene-based electroluminescent polymer containing 10 mol% TPD-type hole conductor[11] was spin coated on top of the cross-linked HTL. The thickness of the HTL and the EL was varied so that a constant overall thickness of 100 nm was maintained. Both OLEDs, based on HTL-A and HTL-B, show similar EL spectra. With increasing HTL layer thickness, we observed a slight blueshift of the emission, in agreement with simulations using the software ETFOS (Version 1.3) (see Supplemental Material Fig. 1).[12] All spectra were color stable under varied voltage.

For both device series, the efficiency increases with HTL thickness (d_{HTL}), reaches a maximum for $d_{HTL}=40$ nm, and then drops slightly (see Fig. 3). Assuming an accumulation of holes at the internal HTL/EL interface, the improved efficiency at reduced EL thickness may result from an increase of the resulting electric field across this layer, improving charge injection. This view is supported by the observation of a gradually reduced onset voltage (Fig. 3, squares). If the density of charges is increased, the probability of recombination rises as well. For $d_{HTL}>40$ nm, quenching effects of the metal cathode may outbalance the above mentioned increase in electric field.

In all cases, devices with HTL-B show higher efficiencies although the current density is reduced (at a given voltage). For the device with optimized layer thickness, the efficiency enhancement was almost 25%. At the efficiency

FIG. 3. Peak efficiency (left axis) for OLEDs with HTL-A (○) and HTL-B (●) and onset voltage [right axis, brightness >3 cd/m², HTL-A (■)] vs layer thickness of HTL. (Similar onset voltages for devices with HTL-B.) The (★) symbol shows the efficiency of a reference device [80 nm EL, no HTL (right axis)], and the (☆) symbol the onset voltage (left axis). The (---) shows the calculated outcoupling efficiency for a 1/e width of the emission zone of 20 nm (left axis). It is rescaled so that the maximum coincides with the 40 nm HTL data.

maximum (at about 5 V), both devices show a light output of about 700 cd/m² (see Fig. 4). From the HOD experiments, we know that the hole current is decreased in HTL-B devices, so one expects the reduction of current density in OLEDs based on HTL-B compared to HTL-A to be due to reduced hole current as well. For the increased light output in HTL-B devices, there can be several reasons: (i) the reduction of the refractive index of the HTL alters the optical thickness of the multilayer OLED, (ii) the reduced amount of holes leads to a better charge balance for devices with HTL-B, and (iii) the decreased hole conduction for HTL-B leads to a change in the width of the recombination zone.

To gain further understanding of the efficiency increase in HTL-B devices, we performed the numerical calculations using the simulation software ETFOS that determines the outcoupling efficiency by calculating the far-field distribution of emissive dipoles in the emissive layer.[13] The following set of parameters was used as input: ITO (125 nm, $n_{ITO}=1.9$), PEDOT (35 nm, $n_{PEDOT}=1.5$), HTL-A or HTL-B (40 nm, $n_{HTL-A}=1.64$; $n_{HTL-B}=1.6$), EL (60 nm, $n_{EL}=1.8$), $n_{glass}=1.53$, and a PL spectrum of the emitter. We assume the
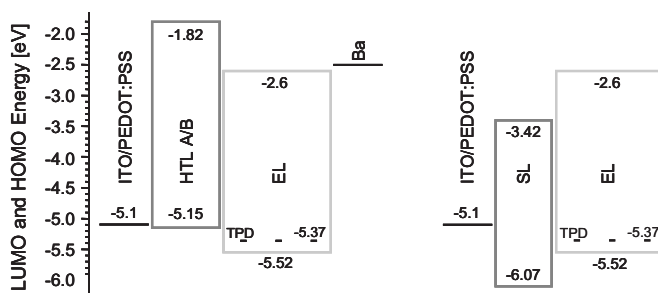

FIG. 2. HOMO/LUMO energies of devices with HTL-A or HTL-B (left) and with SL (right). HOMO energies were estimated from the electrochemically determined oxidation potential. LUMO energies were obtained from the HOMO value minus the optical band gap.
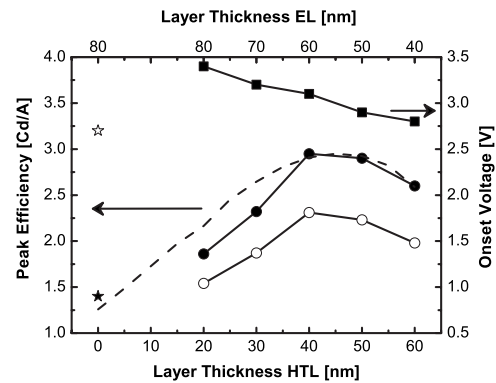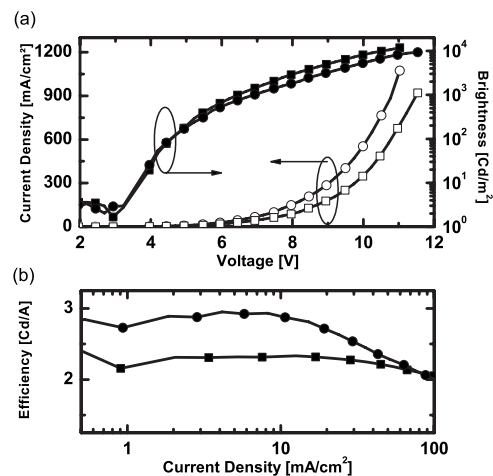

FIG. 4. (a) Current-voltage-luminescence data of blue-emitting OLEDs with 40 nm HTL-A (●, ○) or HTL-B (■, □). Open symbols display the current density (left axis) and closed symbols the brightness (right axis) vs applied voltage. (b) Efficiency calculated from the IVL-curves in (a) vs current density.
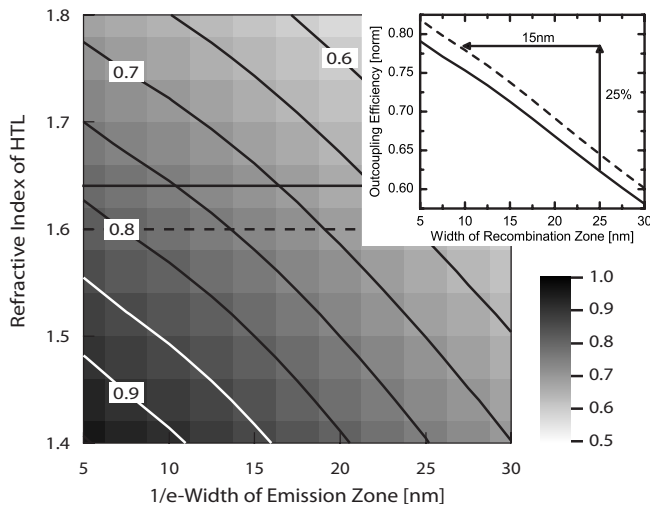
FIG. 5. Outcoupling efficiency as a function of the width of the emission zone (exponential decay from the HTL/EL interface toward the cathode) and of the refractive index of the HTL. The values were normalized to the maximum observed within the interval of parameters discussed here. The horizontal lines indicate the refractive indices of HTL-A (——) and HTL-B (---). Inset: Outcoupling efficiency vs width of emission zone for devices with 40 nm HTL-A (——) or HTL-B (---).

charge transport in the EL is dominated by electrons resulting in a recombination zone located at the HTL/EL-interface. Evidence for this is obtained by investigating OLEDs with a longer-wavelength-emitting sensing layer (SL) between PE-DOT and the blue-emitting EL[14] (see Fig. 2, right). Here, the dominant contribution in the EL spectra stems from the SL. A significant blue EL is only observed for $d_{SL} < 3$ nm (see Supplemental Material Fig. 2).[12]

This point of view is also supported by optical simulations, showing a thickness dependence of the outcoupling efficiency that is qualitatively similar to our experimental results (see Fig. 3, dashed line). Here, we assumed an exponential decay of the emission zone toward the cathode ($1/e$ width=20 nm). The simulation for an emission zone located at the EL/cathode interface with an exponential decay toward the HTL and the same $1/e$ width shows entirely different thickness dependences and in addition, the absolute values are about 80 times smaller as compared to the previous case (not shown).

Using the model, we calculated the change in outcoupling efficiency (in percent) upon reducing the refractive index of the HTL for different widths of the emission zone. An increase of only about 3% was obtained for all cases ($1/e$ width=5–30 nm, see the inset of Fig. 5). This indicates that in order to explain the 25% efficiency increase observed in the experiment, one has to consider the changed electrical properties of the device as well. Mixing the alkyl compound into the hole conductor leads to a decreased hole conduction in the HTL (see Fig. 1). This reduces the width of the recombination zone, since fewer holes are injected into the emissive layer and, as a result, they recombine with the electrons earlier on their way toward the cathode. A better charge balance is unlikely to be the reason for the enhanced efficiency, since we have shown that the charge transport in the EL is dominated by the electrons. Given that the device is already "short of holes" in the EL, a further reduction in hole density should not lead to a higher efficiency.

Figure 5 shows the calculated outcoupling efficiency for a range of refractive indices of the HTL and for different values of the $1/e$ width of the recombination zone. A higher efficiency is obtained not only when using HTLs with lower refractive indices but also when assuming a narrower emission zone. On the relevant scales, changes in the width of the emission zone have a more pronounced effect on the outcoupling than changes in the refractive index. Even for a constant refractive index, a relatively strong enhancement in outcoupling can be obtained. Taking both effects into account, the measured efficiency enhancement of about 25% can be explained by a reduction of the width of the emission zone from 25 nm for the device based on HTL-A (assuming $n = 1.64$) to 10 nm for the device with HTL-B (assuming $n = 1.60$).

In conclusion, we modified the HTL of multilayer OLEDs by copolymerizing the hole-transport material with a low-index alkyl compound and obtained an efficiency enhancement of about 25%. Optical simulations have shown that this improvement is mainly due to the changes of the electronic properties introduced by the nonconductive alkyl compound, leading to a narrowing of the emission zone.

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