Balanced ambipolar charge carrier mobility in mixed layers for application in hybrid white organic light-emitting diodes

Gregor Schwartz,^{a)} Tung-Huei Ke,^{b)} Chung-Chih Wu,^{b)} Karsten Walzer, and Karl Leo^{c)}
Institut für Angewandte Photophysik, Technische Universität Dresden, 01069 Dresden, Germany

(Received 6 May 2008; accepted 30 July 2008; published online 20 August 2008)

We investigate the electron and hole mobility in mixed layers of *N,N'*-di(naphthalen-1-yl)-*N,N'*-diphenyl-benzidine and bis(2-methyl-8-quinolinato)-4-phenylphenolate aluminum with different mix ratios, using both space-charge limited currents of single-carrier devices with electrically doped charge transport layers and time-of-flight measurements. Both experimental methods yield consistent results. The 1:1 blend shows balanced ambipolar charge carrier transport, which is advantageous for the application as exciton blocking interlayer in hybrid white organic light-emitting diodes: The electroluminescence spectrum is rather stable against changes in interlayer thickness and driving current. Moreover, the external quantum efficiency is enhanced by a factor of 2.5 as compared to a device without interlayer. © 2008 American Institute of Physics. [DOI: 10.1063/1.2973151]

Hybrid white organic light-emitting diodes (OLEDs), which combine fluorescent blue and phosphorescent red and green emitters, promise to meet both the efficiency and lifetime requirements in future OLED lighting applications.¹⁻⁵ A straightforward concept is to sandwich a stack of two or three emission layers between charge transport and blocking layers. If the blue fluorescent emitter (fl-EML) has a low-lying nonradiative triplet state, an exciton blocking interlayer (IL) between fluorescent and phosphorescent regions is needed to suppress mutual exciton transfer, which leads to a balanced white electroluminescence (EL) spectrum and high efficiency.^{4,5} To ensure exciton generation on both sides of that IL, it must have ambipolar charge carrier transport ability. This can either be achieved by a single bipolar material such as 4,4'-*N,N'*-dicarbazole-biphenyl (see Ref. 5) or a blend of an electron transport and a hole transport material (see Ref. 4). However, both approaches usually show a strong dependence of the EL spectrum on the IL thickness and on the driving current. Both phenomena can be explained by an imbalance of electron and hole mobilities. If the absolute mobilities differ too much in the electric field range occurring within the IL during OLED operation, the balance between electrons and holes that reach the adjacent emission layers is strongly dependent on the IL thickness. Furthermore, if the field enhancement of the mobility differs too much for electrons and holes, the charge carrier balance depends on the driving voltage and current. Consequently, both mechanisms also change the EL spectrum, which is directly determined by the charge carrier balance between the emission layers.

In this work, we investigate the charge carrier mobility of mixed layers of *N,N'*-di(naphthalen-1-yl)-*N,N'*-diphenyl-benzidine (α -NPD) and bis(2-methyl-8-quinolinato)-4-phenylphenolate aluminum (BALq₂) with dif-

ferent mix ratios. The following two experimental methods to derive the charge carrier mobility are applied and compared: (i) from the space-charge-limited current (SCLC) region of single-carrier devices and (ii) from time-of-flight (TOF) experiments. Based on the results, hybrid OLEDs with 2,2',7,7'-tetrakis(2,2-diphenylvinyl)spiro-9,9'-bifluorene (spiro-DPVBi) as fluorescent blue emission layer and iridium(III)bis(2-methyldibenzo-[f,h]quinoxaline)(acetylacetonate) [Ir(MDQ)₂(acac)] doped α -NPD as red phosphorescent emission layer (ph-EML), separated by α -NPD:BAIq₂ blend ILs with different mix ratios are investigated and compared to devices without IL.

The derivation of the mobility from SCLC requires a unipolar current through the layer under investigation that must not be injection limited. However, for hole injection to the highest occupied molecular orbital of α -NPD (-5.4 eV) and electron injection to the lowest unoccupied molecular orbital of BALq₂ (-3.1 eV) commonly used electrodes do not provide Ohmic contacts. Therefore, we use a novel approach by applying *p*-type or *n*-type doped charge transport layers between the undoped (-i-) layer under investigation and both the injection and the extraction electrode which results in symmetric hole-only (*p-i-p*) and electron-only (*n-i-n*) devices. This ensures efficient quasi-Ohmic tunnel injection and extraction of charge carriers through a very thin space-charge layer.⁶ Since the conductivity in the doped charge transport layer is by orders of magnitude higher than in the undoped layer under investigation,⁷ the electric field drops virtually only in the intrinsic layer. Moreover, the symmetric device architecture eliminates the built-in-potential and interface effects usually observed in single-carrier devices without doped charge transport layers,^{8,9} since the Fermi level in the organic layers is not determined by the organic-electrode interfaces, but only by the doping. In the *p-i-p* devices, the *p*-layers consist of 30 nm α -NPD doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (30 mol %) or NDP2 (6 wt %) from Novaled AG, Dresden. No difference in the electrical device characteristics is observed for the different dopants. Both electrodes consist of Au. In the *n-i-n* devices, the *n*-layers consist of 30 nm Cs-

^{a)}Electronic mail: schwartz@iapp.de.

^{b)}Present address: Department of Electrical Engineering, Graduate Institute of Electro-Optical Engineering, and Graduate Institute of Electronics Engineering, National Taiwan University, Taipei, Taiwan 106, Republic of China.

^{c)}Electronic mail: leo@iapp.de.

FIG. 1. (Color online) Current density-voltage characteristics of *p-i-p* (hole-only) devices with 200 nm α -NPD:BAI q_2 *i*-layer (α -NPD content given in percentage) and corresponding SCLC fits assuming field enhanced or trap-limited mobility, respectively.

doped 4,7-diphenyl-1,10-phenanthroline (BPhen) or NET5:NDN1 from Novald AG, Dresden. Again, no significant differences in electrical device characteristics are observed. Both electrodes consist of Al. The *i*-layers consist of 200 or 300 nm α -NPD:BAI q_2 blend layers with different mix ratios. The current-voltage characteristics are analyzed assuming a Poole-Frenkel-type field-dependent mobility with shallow traps,¹⁰

$$J(V) = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_0 \exp(0.89 \gamma \sqrt{V/L}) \frac{V^2}{L^3}, \quad (1)$$

where the dielectric constant of the material is always assumed as $\varepsilon_r=3$, μ_0 is the effective mobility at zero field, γ is the field enhancement factor of the mobility, and L is the thickness of the *i*-layer where the electric field is present. Figure 1 exemplarily shows the current-voltage curves of the *p-i-p* devices with 200 nm *i*-layer together with the fits according to Eq. (1). At low voltage $V < 0.1$ V, where it is likely that space charges do not build up yet, the currents are Ohmic. For the devices containing 100% [$\mu_0=3.2 \times 10^{-4}$ cm² V s⁻¹, $\gamma=0.8 \times 10^{-3}$ (cm/V)^{0.5}] and 90% [3.2×10^{-4} , 1.6×10^{-3}] α -NPD, SCLC-fit and measurement nicely agree for $V > 0.1$ V. For the device containing 50% α -NPD, the fit [1.4×10^{-7} , 5.8×10^{-3}] is good only for $V > 0.7$ V. However, if one assumes trap-limited SCLC with reasonable parameters (mobility as for pure α -NPD, trap density $N_t=1.7 \times 10^{19}$ cm⁻³, and trap distribution parameter $T_t=633$ K), the fit agrees well, also at lower voltage. The device with 10% α -NPD is Ohmic at $V < 5$ V and does not show a SCLC region within the measured voltage range, which is a hint to an even higher trap concentration. The characteristics of the *n-i-n* devices (not shown) can all be fitted well for $V > 0.2$ V according to Eq. (1). The derived zero-field mobilities and field enhancement factors have been determined for BAI q_2 contents of 100% [9.5×10^{-7} cm² V s⁻¹, 3.8×10^{-3} (cm/V)^{0.5}], 90% [7.0×10^{-7} , 3.8×10^{-3}], 50% [4.9×10^{-7} , 3.6×10^{-3}], and 10% [2.7×10^{-9} , 4.0×10^{-3}]. We point out here that for all single-carrier devices, a built-in potential does not have to be assumed and the current-voltage characteristics are symmetric upon a change in the polarity of the driving voltage, which confirms the previous assumptions. Furthermore, the derived mobility does not depend on the thickness of the *i*-layers, which validates the assumed field-dependent mobility and makes a direct comparison to the TOF results possible.

TOF measurements are carried out on 2 μ m thick layers of the different α -NPD:BAI q_2 blends sandwiched between

FIG. 2. (Color online) Charge carrier mobilities vs electric field of α -NPD:BAI q_2 blend layers (α -NPD content given in percentage), determined by SCLC (lines) and TOF (symbols).

semitransparent indium tin oxide (ITO) (coated on glass) and Al. The samples are excited by a pulsed N₂ laser (337 nm) through the ITO. The TOF transients mostly show a constant-current plateau followed by a rapid falloff, which is a hint to nondispersive transport.¹¹ Using the carrier transit time evaluated from the intersection point of the asymptotes to the plateau and to the tail sections in a double logarithmic plot, the mobilities are determined (see Fig. 2).

Generally, both methods give very similar results both for the absolute mobility values and the field dependence (see Fig. 2). Deviations are significant only for samples which show less pronounced TOF transients (the electron current in the sample with pure BAI q_2 and 10% α -NPD) due to more dispersive transport. In this case, the transient mobility is likely to be different from the steady-state mobility. Most remarkably, the 1:1 blend shows well balanced ambipolar mobilities in the electric field range from 100 to 5000 kV cm⁻¹ typically present in OLEDs.

The hole mobility decreases exponentially over more than three orders of magnitude when the content of the hole transport material α -NPD is decreased from 100% to 50%. The electron mobility decreases exponentially by less than one order of magnitude when the content of the electron transport material BAI q_2 is decreased from 100% to 50% (see Fig. 3), followed by a more rapid decrease when the BAI q_2 content is only 10%. The mobility decrease is typical for homogenous mixtures of amorphous materials, as similar observations have been reported in blends of C₆₀ and copper phthalocyanine^{12,13} and blends of α -NPD and tris(8-hydroxyquinoline) aluminum.¹⁴ The stronger decrease in the hole mobility can be explained by a significant introduction of traps (see SCLC results) due to increased disorder, addi-

FIG. 3. (Color online) Hole (closed symbols) and electron (open symbols) mobilities determined by SCLC vs α -NPD and BAI q_2 content at zero field and at 250 kV/cm. The lines are guides to the eye.

FIG. 4. (Color online) Characteristics of hybrid OLEDs with 5 nm α -NPD and BAIq₂ blend ILs of different mix ratios between the fl-EML and ph-EML compared to a device without IL. (a) Current-voltage. The inset schematically shows the general OLED stack. (b) External quantum efficiency vs current density. (c) EL spectra measured at 1000 cd m⁻².

tional to the reduced hopping transport due to increased intersite distance.¹⁵

Based on these results, hybrid OLEDs have been prepared and characterized. On ITO-coated glass, the following stack is evaporated under high vacuum conditions (base pressure of 10⁻⁷ mbar): 60 nm NDP2 doped α -NPD (6 wt %) (hole transport layer), 10 nm α -NPD (electron blocking layer), 20 nm Ir(MDQ)₂(acac) doped α -NPD (5 wt %) (red ph-EML), 0, 2, 5, or 10 nm α -NPD:BAIq₂ (9:1, 1:1, or 1:9) (IL), 10 nm spiro-DPVBi (blue fl-EML), 10 nm BPhen (hole blocking layer), 30 nm BPhen:Cs (electron transport layer), and 100 nm Al (cathode). The device without IL shows the highest current at a given voltage, followed by the device with the 1:1 blend IL (see Fig. 4). The device with the 1:9 α -NPD:BAIq₂ shows by far the lowest currents as it is limited by the large hole trap concentration in the IL. The EQEs can only be compared by considering the corresponding EL spectra since the ph-EML intrinsically has an EQE higher by about a factor of 4 than the fl-EML due to spin statistics. Interestingly, the device without IL indeed shows an intensity ratio between fl-EML and ph-EML of about 1:4 measured at a luminance of 1000 cd m⁻², as it is expected in case both emitters have a comparable photoluminescence quantum yield. However, this result is rather by chance, since mutual exciton transfer between the two EML could as well yield a completely different ratio. A clear hint to the actual presence of exciton transfer is the low EQE (<2%) of this device, caused by the low-lying triplet state of spiro-DPVBi acting as phosphorescence quencher.⁴ Furthermore, the EL spectrum changes with the driving current, which is reflected in the CIE 1932 chromaticity coordinates changing from (0.53, 0.36) at 100 cd m² to (0.47, 0.34) at 1000 cd m⁻². Remarkably, the devices with a 1:1 blend IL show almost the same intensity ratio of 1:4 and CIE coordinates of (0.48, 0.35), completely independent of the IL thickness and the driving current. Moreover, the EQE is enhanced by more than a factor of 2.5 as compared to the device without IL, also almost independent of the IL thickness. This means that the IL suppresses the exciton transfer between the two EMLs, whereas it ensures exciton generation on both sides due to its bipolar character. In fact, the charge carrier balance and thus the exciton generation rate can even be assumed equal in both EMLs, since the intensity ratio reflects the fraction of generated excitons usable for light gen-

eration. On the other hand, the devices with the 9:1 and the 1:9 α -NPD:BAIq₂ have EL spectra dominated by emission from either the fl-EML or the ph-EML which is consistent with the measured large mobility differences for electrons and holes in each blend.

In conclusion, we have determined the charge carrier mobility in α -NPD:BAIq₂ blend layers with different mix ratios from SCLC in single-carrier devices with electrically doped charge transport layers, consistent with TOF measurements. The 1:1 blend shows well balanced ambipolar charge carrier transport. When applied as exciton blocking IL in hybrid OLEDs, it stabilizes the EL spectrum against changes in IL thickness and driving current. Moreover, the EQE is enhanced by a factor of 2.5 as compared to a device without IL.

This work is financially supported by the European Commission within the sixth framework IST program under Contract No. IST-2002-004607 ("OLLA"-project) and by Deutscher Akademischer Austausch Dienst (DAAD).

¹Y. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson, and S. R. Forrest, *Nature (London)* **440**, 908 (2006).

²A. Hunze, R. Krause, S. Seidel, O. Weiss, F. Kozlowski, G. Schmid, J. Meyer, M. Kroeger, H. H. Johannes, W. Kowalsky, and T. Dobbertin, *Proc. SPIE* **6555**, 66550X/1 (2007).

³G. Schwartz, S. Reineke, K. Walzer, and K. Leo, *Appl. Phys. Lett.* **92**, 053311 (2008).

⁴G. Schwartz, K. Fehse, M. Pfeiffer, K. Walzer, and K. Leo, *Appl. Phys. Lett.* **89**, 083509 (2006).

⁵P. C. Chen, W. Xie, J. Li, T. Guan, Y. Duan, Y. Zhao, S. Liu, C. Ma, L. Zhang, and B. Li, *Appl. Phys. Lett.* **91**, 023505 (2007).

⁶J. Blochwitz, M. Pfeiffer, T. Fritz, and K. Leo, *Appl. Phys. Lett.* **73**, 729 (1998).

⁷M. Pfeiffer, A. Beyer, T. Fritz, and K. Leo, *Appl. Phys. Lett.* **73**, 3202 (1998).

⁸P. W. M. Blom, C. Tanase, D. M. de Leeuw, and R. Coehorn, *Appl. Phys. Lett.* **86**, 092105 (2005).

⁹T.-Y. Chu and O.-K. Song, *Appl. Phys. Lett.* **90**, 203512 (2007).

¹⁰P. N. Murgatroyd, *J. Phys. D* **3**, 151 (1970).

¹¹W.-Y. Hung, T.-H. Ke, Y.-T. Lin, C.-C. Wu, T.-H. Hung, T.-C. Chao, K.-T. Wong, and C.-I. Wu, *Appl. Phys. Lett.* **88**, 064102 (2006).

¹²A. Opitz, M. Bronner, and W. Brütting, *J. Appl. Phys.* **101**, 063709 (2007).

¹³B. P. Rand, J. Xue, S. Uchida, and S. R. Forrest, *J. Appl. Phys.* **98**, 124902 (2005).

¹⁴S.-W. Liu, J.-H. Lee, C.-C. Lee, C.-T. Chen, and J.-K. Wang, *Appl. Phys. Lett.* **91**, 142106 (2007).

¹⁵H. Bässler, *Phys. Status Solidi B* **175**, 15 (1993).