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# Influence of the hole blocking layer on blue phosphorescent organic light-emitting devices using 3,6-di(9-carbazolyl)-9-(2-ethylhexyl)carbazole as host material

Nico Seidler,<sup>1,a)</sup> Sebastian Reineke,<sup>1</sup> Karsten Walzer,<sup>1</sup> Björn Lüssem,<sup>1</sup>  
Ausra Tomkeviciene,<sup>2</sup> Juozas V. Grazulevicius,<sup>2</sup> and Karl Leo<sup>1</sup>

<sup>1</sup>Institut für Angewandte Photophysik, Technische Universität Dresden, D-01062 Dresden, Germany

<sup>2</sup>Department of Organic Technology, Kaunas University of Technology, Kaunas LT-50254, Lithuania

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Organic blue light-emitting devices are essential for the development of future light sources and display technology. Here, we present a highly efficient host-guest system suitable for blue light emission, consisting of the wide gap host material 3,6-di(9-carbazolyl)-9-(2-ethylhexyl)carbazole (TCz1) and the phosphorescent blue emitter iridium(III)bis[(4,6-difluorophenyl)-pyridinato-N,C<sup>2'</sup>]picolinate (FIrpic). We investigate charge carrier balance as a function of hole blocking layer thickness. For optimized structures, devices with a quantum efficiency as high as 14.3% and a luminous efficacy of 21 lm/W at a luminance of 1000 cd/m<sup>2</sup> are realized. © 2010 American Institute of Physics. [doi:10.1063/1.3350890]

Organic light-emitting diodes (OLEDs) are surface-emitting light sources that can be produced in virtually any shape and color. White OLEDs hold great promise to be the light source of the future due to the high luminous efficacy of 90 lm/W already achieved and excellent color-rendering.<sup>1</sup> Essential elements of such highly efficient devices are phosphorescent red, green, and blue emitter materials, which are able to efficiently convert both types of electrical excitation that can be found in an OLED, singlet and triplet excitons, into light. Investigations on monochrome OLEDs help to gain a deeper understanding of the recombination processes under usage of phosphorescent emitters, to reveal potential loss channels, and to obtain a further simplification of white OLED stacks.

The development of blue light-emitting devices is particularly challenging since the rather high energies needed to produce blue light are demanding for the materials involved. An archetype blue emitter material is the phosphorescent iridium complex iridium(III)bis[(4,6-difluorophenyl)-pyridinato-N,C<sup>2'</sup>]picolinate (FIrpic). To create and confine such high energy excitations, electrons and holes have to be widely energetically separated, requiring the employment of materials with large band gap and high lying triplet states. Organosilicon compounds like UGH2 are often first choice for obtaining high external quantum efficiency (EQE) but their poor transport properties usually result in a high operating voltage.<sup>2</sup> This problem can be overcome by either using a mixed host structure<sup>3</sup> or a double emission layer (EML) structure,<sup>4</sup> employing both a hole-transport type and an electron-transport type host material. By carefully tuning the charge carrier balance both concepts lead to outstanding high efficiencies of more than 20% while the driving voltage is kept low.

Here, we use a single EML of FIrpic doped into the host material 3,6-di(9-carbazolyl)-9-(2-ethylhexyl)carbazole (TCz1). The chemical structures as well as the phosphorescence spectra of these two materials are shown in Fig. 1.

From the highest energy peaks of these spectra, it is possible to estimate the energy of the lowest excited triplet state ( $T_1$ -energy). A sufficiently higher  $T_1$ -level of the host allows efficient exciton confinement on the guest molecules, which is crucial for an ideal host-guest system.<sup>5</sup> As the diagram shows, the triplet energy of TCz1 is more than 0.2 eV larger than the  $T_1$ -energy of FIrpic, which also results in a high absolute photoluminescence quantum yield (PLQY) of 91% when measuring a single layer TCz1 doped with 2 wt % FIrpic in an integrating sphere.<sup>6</sup> These conditions make highly efficient blue light-emitting devices possible, as previously demonstrated by Tsai *et al.*<sup>7</sup> By usage of doped charge transport layers,<sup>8</sup> lower driving voltage and hence higher luminous efficacy is expected, similar to reports about red and green OLEDs.<sup>9,10</sup> Due to the large amount of free charge carriers in these layers, a conductivity of  $\sim 10^{-5}$  S/cm is reached,<sup>10</sup> so that the voltage drop over these layers is negligible and the injection at the electrodes is

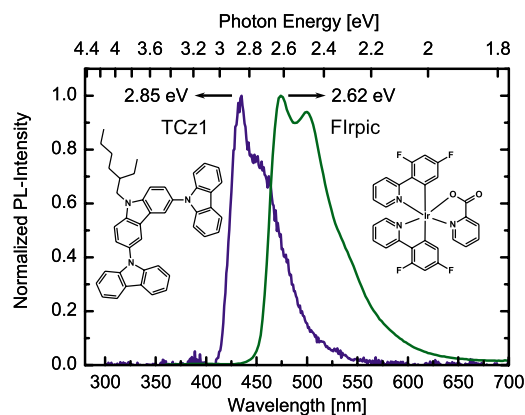


FIG. 1. (Color online) Phosphorescence spectra of TCz1 and FIrpic together with their chemical structures. The spectrum of TCz1 has been measured in solid polystyrene solution (2 wt %) at a temperature of 77 K about 1 s after pulsed laser excitation (337.1 nm). The PL of FIrpic has been measured on a 80 nm single layer of 2 wt % FIrpic doped into a matrix of 4,4',4''-tris(*N*-carbazolyl)-triphenylamine (TCTA) with a spectrofluorometer using a xenon arc lamp as excitation source.

<sup>a)</sup>Electronic mail: seidler.nico@gmail.com.

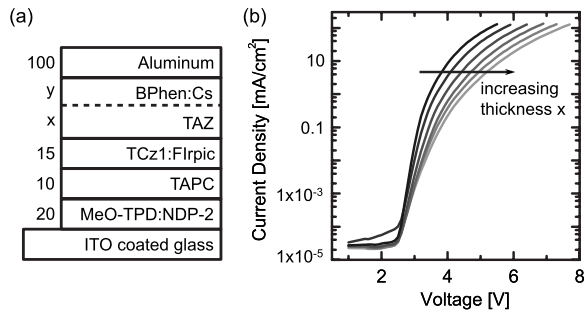


FIG. 2. (a) Layer sequence of the six samples prepared with different TAZ layer thicknesses  $x$  of 5, 10, 15, 20, 25, and 30 nm. The BPhen:Cs layer thickness  $y$  was varied accordingly to keep the total thickness constant at  $x+y=45$  nm. (b) The current density vs voltage of the devices. The thicker the TAZ thickness  $x$  the brighter the plotted lines.

improved. As hole conducting and electron blocking material, we use 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC), since its triplet energy of 2.87 eV is high enough to efficiently confine the excitons in the EML.<sup>11</sup> Finding a material that is suitable as hole blocking layer (HBL) is more challenging. With its high triplet energy and high ionization potential as well as high electron mobility, tris[3-(3-pyridyl)mesityl]borane (3TPYMB) should be a promising candidate to achieve both high efficiencies and low driving voltage.<sup>12</sup> Indeed, when using this material as HBL in an OLED stack with TCz1:Flrpic as EML, a luminance of 100 and 1000  $\text{cd}/\text{m}^2$  is reached at 3.19 V and 3.77 V, respectively. However, the EQE does not significantly exceed 5% even at low current density. One reason for this behavior is an extremely fast degradation of the material caused by excitons. Since the exciton generation zone is assumed to be located at the EML/HBL interface, the hole blocking material is exposed to high excitation densities. Second, a HBL with relatively high electron mobility seems to have a negative influence on the performance of a blue phosphorescent device. This fact has been reported recently by Xiao *et al.*<sup>13</sup> who used an organosilicon compound with low electron mobility as HBL to achieve high efficiencies close to the theoretical limit. In our studies, we use the material 3-(4-biphenyl)-4-phenyl-5-(4-tert-butylphenyl)-1,2,4-triazole (TAZ) as HBL in combination with Cesium doped 4,7-diphenyl-1,10-phenanthroline (BPhen) as electron transporting layer. With its high ionization potential (6.6 eV) and relatively high triplet energy of  $\sim 2.6$  eV it is well suited as a HBL.<sup>5,14</sup> Also, its LUMO matches the one of the host material (both  $\sim 2.6$  eV),<sup>15,5</sup> which allows electrons to be injected without major energy barriers. Nevertheless, since the electron mobility of this material is rather low ( $\sim 10^{-6}$   $\text{cm}^2/\text{Vs}$ ),<sup>16</sup> the current-voltage characteristics of the device can be significantly influenced by varying the TAZ layer thickness.

For this investigation, six samples with the same layer sequence, illustrated in Fig. 2(a), but different HBL thickness were prepared. A 20 nm thick layer of  $N,N,N',N'$ -tetrakis(4-methoxyphenyl)-benzidine (MeO-TPD) doped with NDP-2 (Novaled AG) was evaporated on an indium tin oxide (ITO) coated glass substrate as hole injection and transport layer.<sup>17</sup> As mentioned above, 10 nm of TAPC was used as electron blocking layer. 15 nm of TCz1 doped with 8 wt % Flrpic form the EML. The HBL was prepared in steps of 5 nm, ranging from 5 to 30 nm. The

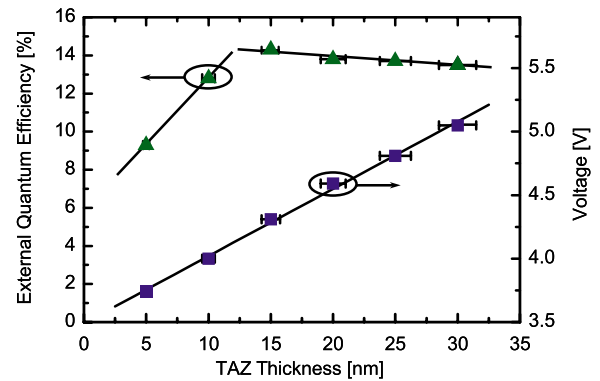


FIG. 3. (Color online) External quantum efficiency and applied voltage at a luminance of 1,000  $\text{cd}/\text{m}^2$  in dependence of the thickness of the TAZ layer. The drawn lines between the EQE data points are guides for the eye while the line for the voltage data is the best-fit line with a slope of  $5.3 \times 10^5$  V/cm. The error bars represent a relative error of 5% due to layer thickness variations across the sample.

thickness of the following Bphen:Cs layer was varied accordingly, so that the total thickness of TAZ and Bphen was kept constant at 45 nm. All single layers including the 100 nm aluminum contact were evaporated successively without breaking the vacuum ( $p \sim 10^{-8}$  mbar) in a single chamber evaporation system. By using a shadow mask for thickness variation, all six devices were prepared on one glass substrate, ensuring high comparability.

Figure 2(b) shows the current density versus the applied voltage for all devices. Due to the low electron mobility of TAZ, the resistance increases strongly with increasing TAZ thickness. Electrons moving through the highly conductive ETL can only slowly drift through the TAZ toward the EML and therefore accumulate at the HBL/ETL interface. At the opposite EML/HBL interface, holes are efficiently blocked due to the high ionization potential of TAZ (6.6 eV),<sup>5</sup> which leads to a significant voltage drop  $V$ , increasing linearly with layer thickness  $a$  as  $V=E \times a$ , where  $E$  is the electrical field inside the layer.

The driving voltage of the devices required to reach a current density of 3.5  $\text{mA}/\text{cm}^2$ , roughly corresponding to a luminance of 1000  $\text{cd}/\text{m}^2$ , is shown in Fig. 3. The slope of the fit line  $dV/da=5.3 \times 10^5$  V/cm gives an approximate value for the electrical field inside the HBL caused by the ohmic behavior of the TAZ layer.

Figure 3 also shows the EQE of the devices measured with a calibrated photodiode at a luminance of 1000  $\text{cd}/\text{m}^2$  in forward direction, assuming Lambertian emission characteristics. This assumption has been proven by additional measurement in an integrating sphere, where, by covering the edges of the sample, the total luminous flux emitted into the forward half sphere is collected. Starting from 5 nm, the efficiency can be raised by 54% when increasing the thickness to 15 nm. A further increase results in a slow decrease in efficiency but even at a thickness of 30 nm the EQE still reaches 94% of its maximum value.

This demonstrates that a certain thickness of the hole blocking material TAZ is necessary to obtain a maximum EQE. Due to the low electron mobility of TAZ, electrons are slowed down in this layer and hence accumulate at the HBL/ETL interface. Separating the region where electrons accumulate far enough from the recombination zone therefore seems to have a positive effect on the efficiency of the de-

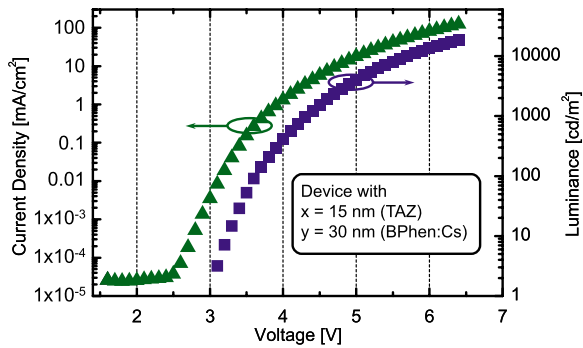


FIG. 4. (Color online) Current density-voltage and luminance-voltage characteristics of the device with 15 nm TAZ as HBL.

vice. Most probable reason for this is an effective suppression of exciton-polaron quenching at the EML/HBL interface. Figure 3 shows that the optimal thickness is reached at a value of about 15 nm. A further increase in the TAZ thickness will not help to further suppress the exciton-polaron quenching while the chance of nonradiative deactivation is increased.

In Fig. 4 the current density-luminance-voltage characteristics of the device with 15 nm HBL is shown. Owing to the low electron mobility of TAZ, a brightness of 1,000  $\text{cd/m}^2$  is only reached at a voltage of 4.3 V. With the value of the electrical field obtained above, a voltage drop over the TAZ layer of  $V = E \times 15 \text{ nm} = 0.8 \text{ V}$ , caused by the low electron mobility of this material can be estimated. This increase in the driving voltage has to be accepted to reach high quantum efficiency, although much lower voltages of theoretically  $4.3 \text{ V} - 0.8 \text{ V} = 3.5 \text{ V}$  at  $1000 \text{ cd/m}^2$  are possible with the employed emitter system.

For the 15 nm TAZ case, the external quantum efficiency as well as the luminous efficacy in dependence of the brightness are shown in Fig. 5. At a luminance below  $10 \text{ cd/m}^2$ , high efficiency of almost 20% is reached, proving a well adjusted charge carrier balance. With increasing brightness,

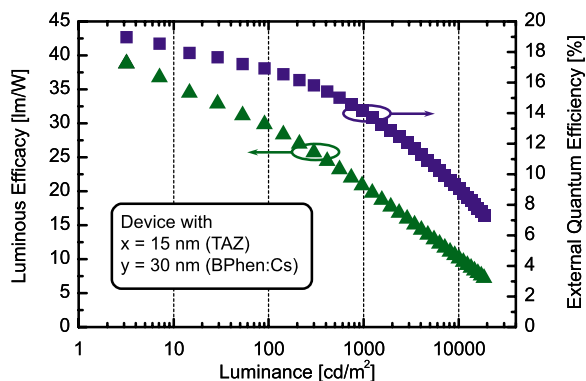


FIG. 5. (Color online) Luminous efficacy and external quantum efficiency of the 15 nm TAZ device in dependence of luminance.

the efficiency drops due to bimolecular quenching processes typical for phosphorescent emitters.<sup>18</sup> Furthermore, an increasing energy transfer to the TAZ molecules with a subsequent nonradiative decay becomes more important at high excitation density. Finally, these quenching processes are superposed by a significant degradation of the device during measurement. Nevertheless, a high external quantum efficiency of 14.3% and a luminous efficacy of 21  $\text{lm/W}$  can still be obtained at a brightness of  $1000 \text{ cd/m}^2$ .

In conclusion, our results show that doped charge transport layers cause an overflow of electrons when using Flrpic doped into a carbazole host material. Keeping electrons away from the EML/HBL interface by a 15 nm thick layer of the weakly electron conducting material TAZ allows high external quantum efficiency of more than 14% at  $1000 \text{ cd/m}^2$ .

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