High efficiency white organic light emitting diodes combining fluorescent and phosphorescent emitter systems

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ABSTRACT

We report on white organic light emitting diodes with three stacked emitter layers comprising the fluorescent blue emitter Spiro-DPVBi, the phosphorescent green emitter system TCTA:Ir(ppy)$_3$ and the phosphorescent red emitter system NPB:Ir(MDQ)$_2$(acac). A thin additional layer of mixed TCTA and TPBi separates the fluorescent and phosphorescent emitting regions, simultaneously confining excitons efficiently and letting electrons and holes easily pass. Furthermore, phosphorescence quenching by Dexter transfer to the non-radiative triplet state of Spiro-DPVBi is suppressed. Devices were optimized to get color coordinates very close to the warm white standard illuminant A. Best devices have a current efficiency of 13.8 cd/A, CIE color coordinates of (0.45, 0.42), and a color rendering index of 91 at a brightness of 1000 cd/m^2. Due to the use of electrically doped charge transport layers, the voltage needed for 1000 cd/m^2 was only 3.0 V, which leads to a power efficiency of 14.4 lm/W assuming Lambertian emission.

Keywords: white OLED, high power efficiency, PIN, phosphorescence, fluorescence, electrical doping

1. INTRODUCTION

White organic light emitting diodes (white OLEDs) show promise for a major role in ambient lighting in the future. Low material costs, a wide choice of materials with customized properties, and easy production methods are features of the OLED technology which have favoured its fast development and industrial application in recent time. The energetically broad emission spectra and almost Lambertian emission of OLEDs are especially favourable for lighting applications, since they lead to homogeneous illumination and high quality color rendering. The possibility to produce large area OLED panels will also open new ways for lighting design apart from common incandescent bulbs or fluorescent tubes.

In single color OLEDs, the major performance parameters like lifetime and efficiency have already reached a level,[1,2,3] where applications become industrially worthwhile. First products like monochromic signage and RGB displays based on OLED technology have recently entered the market. However, the performance requirements of the lighting industry cannot be met by OLEDs yet. Especially the simultaneous maximization of device lifetime and efficiency remains an unsolved problem. White OLEDs based on phosphorescent emitter systems[4,5] can show the highest efficiencies due to potentially up to 100% internal quantum efficiency of triplet emitters. However, the stability of efficient blue triplet emitters like iridium(III) bis(4,6-difluorophenylpyridinato)picolate (FIrpiq) is still very limited which consequently leads to short lifetimes of those devices. The exclusive use of stable fluorescent emitter systems can lead to longer lifetimes, however, the internal quantum efficiency is then limited to 25% due to fundamental quantum statistics. Therefore, a possible way to solve this conflict is the combination of a stable fluorescent blue and highly efficient phosphorescent green and red emitter systems.

In this work, we demonstrate such a combination as a stack of emitter layers in a single OLED with electrically doped charge transport layers (p-i-n OLED). Spiro-DPVBi was used as the fluorescent blue emitter, TCTA:Ir(ppy)$_3$ as the phosphorescent green and NPB:Ir(MDQ)$_2$(acac) as the phosphorescent red emitter system. Fluorescent emitters often have a low lying non-radiative triplet state which efficiently quenches phosphorescence when brought in direct contact. Therefore, we separate fluorescent and phosphorescent regions in our devices

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by introducing a thin additional layer of coevaporated TCTA and TPBi. Here, TCTA is the hole transporting material and TPBi is the electron transporting material which makes the mixture ambipolar, while excitons are confined within the separated regions. The most sensitive parameter for color tuning in our devices is the thickness of the TCTA:Ir(ppy)$_3$ layer which can be easily tuned to achieve warm white color coordinates very close to the standard illuminant A.

2. EXPERIMENTAL

This will be shown in the following with a series of four devices with different TCTA:Ir(ppy)$_3$ layer thickness. ITO coated glass is used as substrate, the organics and the metal top electrode are deposited in a single chamber UHV tool (Kurt J. Lesker Company) by thermal evaporation. The series is made within a single run, using a wedge tool for the thickness variation, therefore ensuring maximum comparability of the devices. A proprietary material system (NHT5:NDP2) from Novaled AG, Dresden, is used as hole injection and transport layer and 2,2',7,7'-tetrakis-(N,N-diphenylamino)-9,9'-spirobifluoren (Spiro-TAD) is used as electron blocking layer. On the other side, 4,7-diphenyl-1,10-phenanthroline (BPhen) is used as the hole blocking layer and Cs-doped BPhen is the electron injection and transport layer. Al is used as cathode. Starting from the side facing the ITO anode, the emitter system consists of N,N'-di(naphthalen-1-yl)-N,N'-diphenyl-benzidine (NPB) doped with Iridium(III)bis(2-methyldibenzo-[f,h]quinoxaline)(acetylacetonate) (Ir(MDQ)$_2$(acac)), 4,4',4"-tris(N-carbazolyl)-triphenylamine (TCTA) doped with fac tris(2-phenylpyridine) iridium (Ir(ppy)$_3$) and 2,2',7,7'-tetrakis(2,2-diphenylvinyl)spiro-9,9'-bifluorene (Spiro-DPVBi). The separating layer of TCTA and 2'2"(1,3,5-benzenetriyl) tris-[1-phenyl-1H-benzimidazole] (TPBi) is placed between TCTA:Ir(ppy)$_3$ and Spiro-DPVBi. The thickness of NPB:Ir(MDQ)$_2$(acac) and Spiro-DPVBi are found to be irrelevant for the emission color within a range of 5 to 20 nm. Both charge blocking layers have a thickness of 10 nm. The thickness of the separating layer is kept constant at 3 nm to sufficiently suppress phosphorescence quenching and to keep ohmic losses in this layer low. The conductivity of both charge transport layers is about 10^{-5} S/cm, which is high enough to neglect ohmic losses in these layers as well. Furthermore, it is known that charge injection from the electrodes is strongly eased by the electrical doping.[6,7] The thickness of the TCTA:Ir(ppy)$_3$ layer is varied from 2 to 5 nm in 1 nm steps.

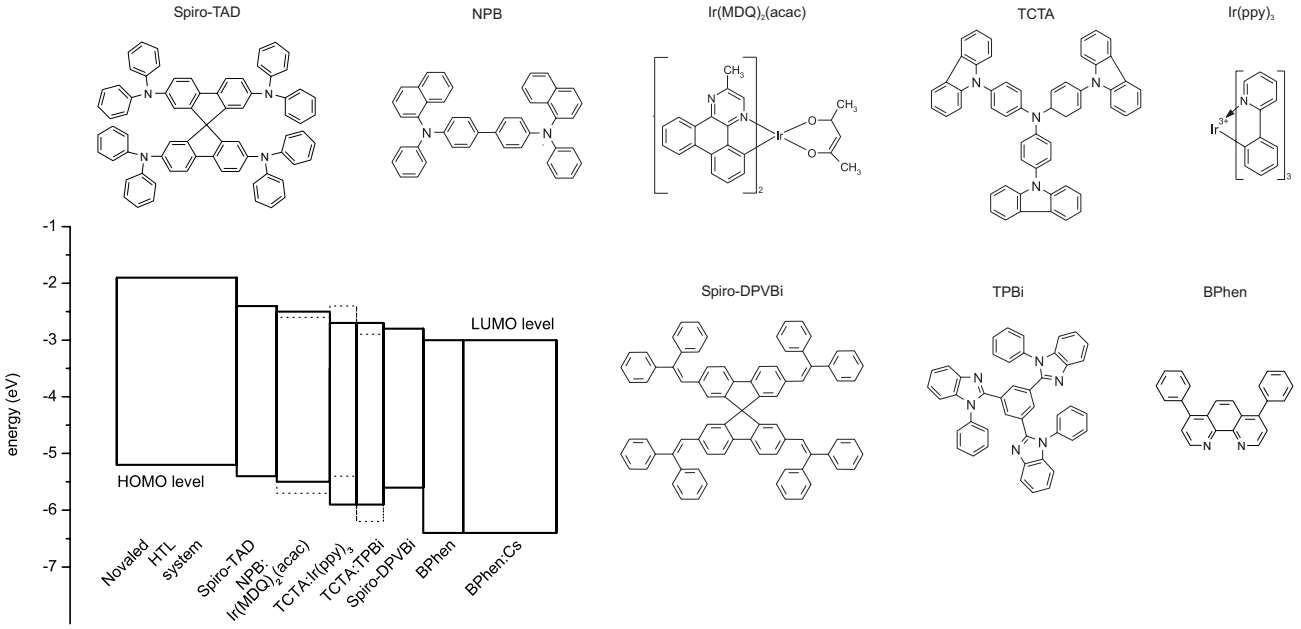

Figure 1. Organic layers of the presented white OLED structure and proposed energy level diagram. Also shown are the chemical structures of some of the used materials.

The device structure as well as the chemical structures of the relevant used materials are illustrated in Fig. 1. The devices are encapsulated with a cover glass and epoxy glue right after preparation in a nitrogen glove-

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box attached to the UHV system via a load lock and subsequently measured under ambient conditions. The current – voltage characteristics are measured with a Source Measurement Unit (Keithley). Simultaneously, the light output in forward direction, i.e. through the glass substrate, is measured with a silicon photodiode – filter combination (Hamamatsu) closely matching the sensitivity of the human eye. Thus, the photodiode signal is directly proportional to the luminance and the calculation of the current efficiency of the devices is straightforward, even if the emission spectrum is changing during measurement. The power efficiency is then calculated assuming Lambertian emission.

3. RESULTS AND DISCUSSION

We will now discuss in detail the influence of the TCTA:Ir(ppy)$_3$ layer thickness on our device characteristics. Important information concerning the charge carrier transport and exciton generation processes in each emitter layer can be derived from the change of the emission spectrum within the series. Fig. 2 shows the emission spectra of all four devices, measured at a luminance of 1000 cd/m^2.

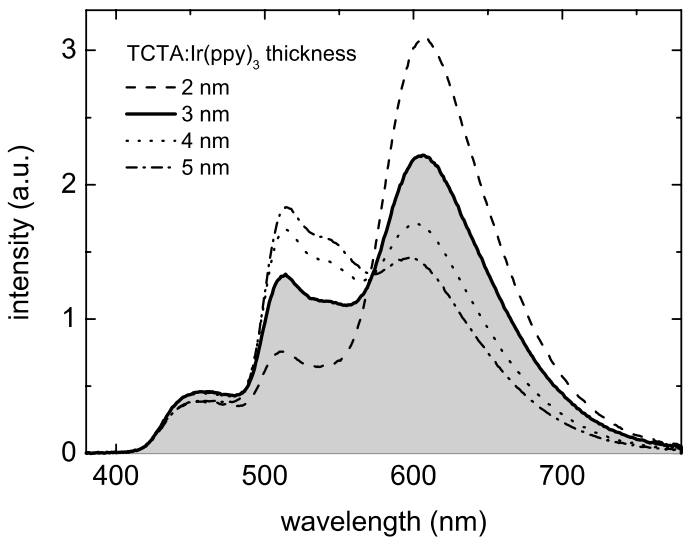

Figure 2. Electroluminescence spectra of the four devices of the described series, all measured at a luminance of 1000 cd/m^2. With 3 nm TCTA:Ir(ppy)$_3$ (solid line and grey area), the warm white standard illuminant A is nearly matched at CIE color coordinates of $(0.45, 0.42)$. The color rendering index of this spectrum is 91.

With increasing TCTA:Ir(ppy)$_3$ thickness, emission from this layer strongly increases as compared to the emission from Spiro-DPVBi, but also as compared to the emission from NPB:Ir(MDQ)$_2$(acac). The first observation can be explained simply by the fact that less holes arrive in the Spiro-DPVBi layer. They are trapped efficiently on the Ir(ppy)$_3$ molecules, because the HOMO level of Ir(ppy)$_3$ lies about 0.5 eV higher than the HOMO of TCTA. The second observation can have two possible reasons, depending on the mechanism of exciton creation in the NPB:Ir(MDQ)$_2$(acac) layer. The first mechanism is exciton generation via exciton transfer from TCTA:Ir(ppy)$_3$. The main generation zone of phosphorescent excitons would then be at the interface between TCTA:Ir(ppy)$_3$ and the separating TCTA:TPBi layer and excitons would first have to diffuse through the TCTA:Ir(ppy)$_3$ layer. This is very unlikely, because triplet excitons are efficiently formed on Ir(ppy)$_3$ and confined there due to the higher triplet exciton energy of TCTA. Diffusion is thus only possible in terms of thermally assisted hopping or tunnelling between the Ir(ppy)$_3$ sites. Furthermore, this generation path should depend on the Ir(ppy)$_3$ concentration, i.e. the relative increase of TCTA:Ir(ppy)$_3$ emission compared to emission from NPB:Ir(MDQ)$_2$(acac) should increase, if the Ir(ppy)$_3$ concentration is reduced far below the percolation threshold. As we see in our experiments, which will be published elsewhere,[8] this is not the case. Therefore, the second mechanism, i.e. electron transfer over the LUMO of TCTA and subsequent direct exciton generation in NPB:Ir(MDQ)$_2$(acac) is likely to be dominant. Since the electron transport properties of TCTA are not good and

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electrons are also efficiently captured by positively charged $Ir(ppy)_3$ molecules, the amount of electrons which arrive at the NPB:$Ir(MDQ)_2$(acac) layer is consequently strongly dependent on the TCTA:$Ir(ppy)_3$ thickness which is reflected in the strong change of the emission spectra.

Next, we will discuss how the emission colors of the devices depend on the brightness. Higher brightness corresponds both to higher current density and higher driving voltage. Change of emission color corresponds most likely to a change of charge carrier balance, at least in the low current density range where exciton annihilation processes especially for the phosphorescent emitters can be neglected. Fig. 3 shows the CIE 1931 color coordinates of all four devices measured at different brightness levels.

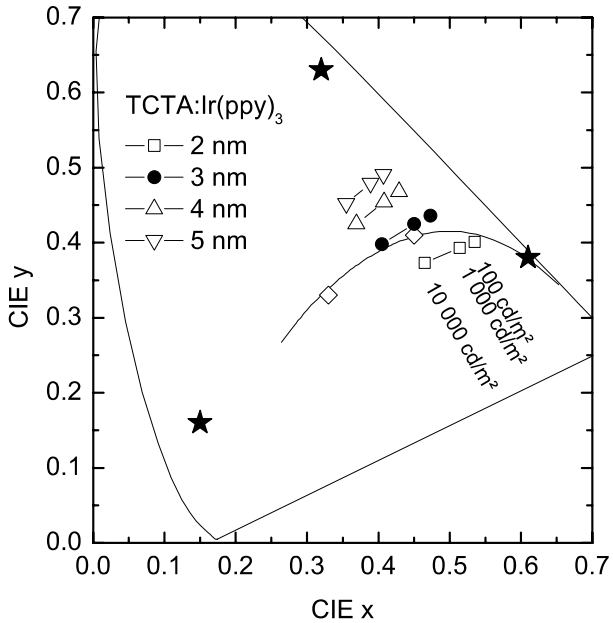

Figure 3. CIE 1931 color coordinates of the four devices measured at different brightness levels. Increased brightness leads to a blue shift of the emission. Also shown are the color coordinates of the used single emitter systems (stars) and the two most important white points E $(0.33, 0.33)$ and A $(0.45, 0.41)$ (diamonds).

In all four devices, the color coordinates shift towards the blue at higher brightness. The ratio between green and red emission shifts only slightly towards the green. The absolute difference does not depend on the TCTA:$Ir(ppy)_3$ layer thickness and is about $(\Delta x, \Delta y) = (-0.02, -0.01)$ from 100 cd/m^2 to 1000 cd/m^2 and $(-0.04, -0.03)$ from 1000 cd/m^2 to 10,000 cd/m^2.

Looking at the layer structure of the devices, this leads to the conclusion that the charge carrier balance is shifted towards the cathode side, i.e. holes are moving easier through the devices. Because of the quite complicated multi-layer structure of the devices, the particular reason for this observation is hard to find. However, the color shift from 100 cd/m^2 to 1000 cd/m^2, which is a brightness range suitable for most applications, is below 5%. Most white OLED structures reported show a color shift of this magnitude or larger. Thus, it is unlikely that the used mixed ambipolar TCTA:TPBi interlayer is the reason for the color shift. Furthermore, our experiments with unipolar interlayers as well as directly stacked emitter layers mostly show a much larger shift, which points at a color stabilizing function of the ambipolar interlayer.

Finally, we discuss the measured current – voltage and luminance – voltage characteristics of the four devices shown in Fig. 4. The variation of the current – voltage curves is only marginal, only in the range of the steep current increase around 2.5 V a small decrease of current for thicker TCTA:$Ir(ppy)_3$ layers due to ohmic losses can be seen.This confirms the high comparability of the single devices made within a single run. However, devices with thicker TCTA:$Ir(ppy)_3$ layers reach higher luminance at the same voltage. This is due to the fact that TCTA:$Ir(ppy)_3$ is the most efficient emitter system used in the device and emits in the wavelength range

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for which the human eye is most sensitive. All devices reach 100 cd/m^2 at around 2.7 V and 1000 cd/m^2 at 3.0 V. The spreading of the curves becomes significant only above 2000 cd/m^2. Depending on the TCTA:Ir(ppy)$_3$ layer thickness, the voltage needed for 10,000 cd/m^2 ranges from 4.35 V to 4.68 V.

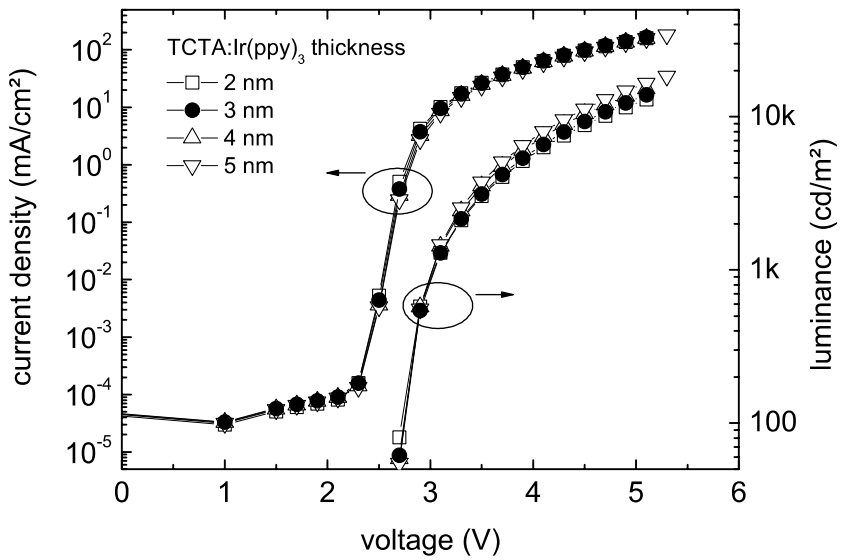

Figure 4. Current – voltage and luminance – voltage characteristics of the four devices. Devices with thicker TCTA:Ir(ppy)$_3$ layers show higher luminance at the same voltage, because TCTA:Ir(ppy)$_3$ is the most efficient emitter system in the devices.

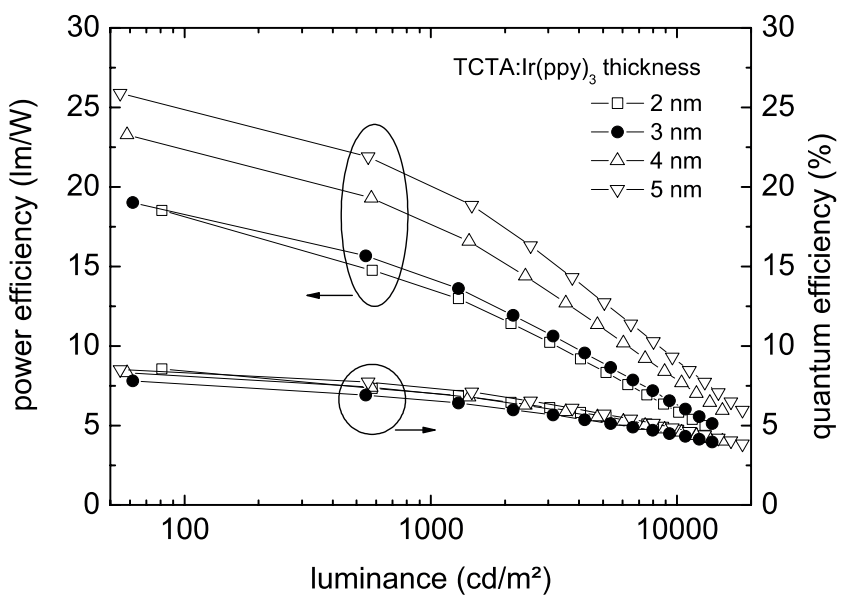

Figure 5. Calculated power efficiencies in forward direction and corresponding quantum efficiencies.

Especially for white devices, these are very low driving voltages which is due to the consequent use of electrically doped charge transport layers which reduce the overall thickness of the intrinsic layers responsible for ohmic losses below 70 nm. Consequently, high current efficiencies together with low driving voltage lead to high

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power efficiencies of the devices, which is shown in Fig. 5. For the device with warm white emission, i.e. with 3 nm TCTA:Ir(ppy)$_3$, the power efficiency is 18.7 lm/W at 100 cd/m^2, 14.4 lm/W at 1000 cd/m^2 and 6.0 lm/W at 10,000 cd/m^2. The quantum efficiency slightly reduces with increasing luminance, which is mainly due to the already discussed color shift towards blue. Because of the use of a fluorescent emitter, the internal quantum efficiency of the blue emission is limited to 25%. At highest luminances, also exciton – exciton annihilation processes become relevant and contribute to the quantum efficiency drop.

4. CONCLUSIONS

In conclusion, we have shown that the combination of phosphorescent red and green emitter systems with a fluorescent blue leads to high efficiency color stable warm white OLEDs, if an ambipolar interlayer is used to separate fluorescent and phosphorescent regions. Furthermore, the driving voltage of our OLEDs is very low due to electrically doped charge transport layers. In summary, we could present a white OLED with CIE chromaticity coordinates of $(0.45, 0.42)$ and color rendering index of 91 at 1000 cd/m^2 with a driving voltage of 3.0 V and a power efficiency of 14.4 lm/W.

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