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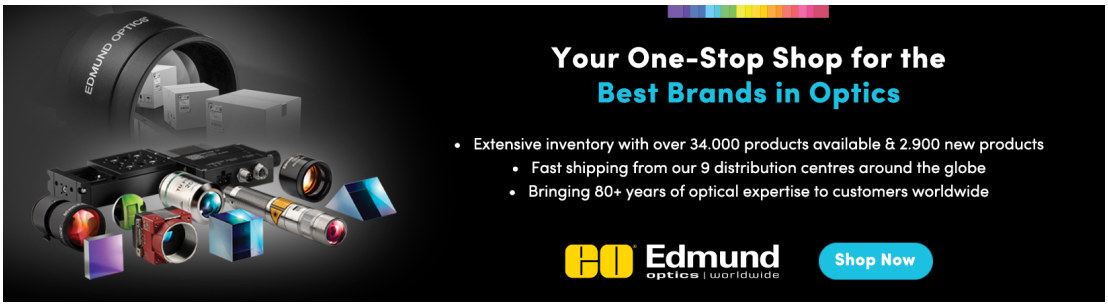

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Reduced efficiency roll-off in high-efficiency hybrid white organic light-emitting diodes

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White organic light emitting diodes harvesting triplet excitons from the fluorescent blue emitter N,N'-di-1-naphthalenyl-N,N'-diphenyl-[1,1′:4′,1″:4″,1‴-quaterphenyl]-4,4‴-diamine (4P-NPD) are presented. Direct doping of the phosphorescent orange iridium(III)bis(2-methyldibenzo-[f,h]quinoxaline)(acetylacetonate) into 4P-NPD results in a strongly reduced efficiency roll-off as compared to separate emission layers, and yields 49.3 lm W^{-1} total external power efficiency (24.1% quantum efficiency) at a luminance of 1000 cd m^{-2} [CIE 1931 chromaticity coordinates (0.49,0.41)], measured in an integrating sphere. Introduction of an exciton balancing interlayer improves the chromaticity (0.43,0.43) toward the CIE illuminant A warm white point and keeps a high efficiency of 40.7 lm W^{-1}, 20.3%. © *2008 American Institute of Physics*.
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White organic light emitting diodes (OLEDs) are promising new lighting sources which may help to solve the global energy crisis.[1] Phosphorescent emitters have long time been considered as crucial for high efficiency, since they allow full harvesting of all electrically generated singlet and triplet excitons in an OLED.[2–5] However, in particular, deep blue phosphorescent emitters still suffer from poor stability and incompatibility with most host materials.[6,7] For white OLED, it has been proposed to use fluorescent blue emitters for harvesting the electrically generated singlets and to transfer the triplets to phosphorescent green and red.[8] Recently, we have demonstrated a concept for high-efficiency white OLED employing a bulk fluorescent blue emitter with high triplet energy. This concept opens the possibility for a complete usage of all electrically generated excitons for light emission without requiring phosphorescent blue.[9] However, the devices still suffered from an unusual strong efficiency roll-off.

In this work, we demonstrate an improved device structure comprising a layer which simultaneously emits fluorescence and phosphorescence, thus, solving the roll-off issue and resulting in very high efficiency. Furthermore, an exciton balancing interlayer is introduced to improve the chromaticity while still keeping the high efficiency.

All devices shown in the following have been evaporated under high vacuum conditions (base pressure of 10^{-8} mbar) onto indium tin oxide (ITO)-coated glass substrates, and are based on the same charge injection and transport layer design, i.e., they all have a 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane doped N,N,N',N'-tetrakis(4-methoxyphenyl)-benzidine hole transport layer, a 1,1-bis[4-[N,N-di(p-tolyl)amino]phenyl]cyclohexane electron blocking layer, a Cs doped 4,7-diphenyl-1,10-phenanthroline (BPhen) electron transport layer, and a BPhen or 2,2′,2″(1,3,5-benzenetriyl) tris-[1-phenyl-1H-benzimidazole] (TPBi) hole blocking layer. Anode and cathode materials are ITO and Al, respectively. Details on layer thickness and doping concentration are summarized in Fig. 1. Samples were encapsulated under nitrogen atmosphere, measured with a Minolta CS100A luminance meter, and synchronized with a Keithley SM2400 source-measure unit. For each current density value, an electroluminescence (EL) spectrum has been taken as to correctly calculate the external quantum efficiency (EQE) from the measured luminance assuming Lambertian emission, to avoid errors due to changes of the EL spectrum with current density.[10]

Three device structures are compared in Fig. 1. The first is a reference device with all separate emission layers (EMLs), i.e., phosphorescent orange iridium(III)bis(2-methyldibenzo-[f,h]quinoxaline)(acetylacetonate) [$Ir(MDQ)_2(acac)$] doped N,N'-di(naphthalen-1-yl)-N,N'-diphenyl-benzidine (α-NPD), fluorescent blue N,N'-di-1-naphthalenyl-N,N'-diphenyl-[1,1′:4′,1″:4″,1‴-quaterphenyl]-4,4‴-diamine (4P-NPD), and phosphorescent green *fac*-tris(2-phenylpyridine)iridium [$Ir(ppy)_3$] doped TPBi. Although high EQE (see Fig. 2) at low current density is achieved (19.8% at 0.03 mA cm^{-2}) in forward direction, the efficiency decreases continuously, resulting in 14.3% at the illumination relevant brightness of 1000 cd m^{-2} (3.6 mA cm^{-2}). This unusual roll-off behavior can be attributed to strong triplet-triplet annihilation owing the fact that the triplet density in the 4P-NPD layer at the 4P-NPD/TPBi:$Ir(ppy)_3$ exciton generation interface is orders of magnitude higher than in conventional triplet emitting devices, since the direct radiative recombination of the 4P-NPD triplets is spin forbidden.[9] These long-living triplets first have to diffuse to the α-NPD:$Ir(MDQ)_2(acac)$ layer where they can be harvested for orange phosphorescence, since

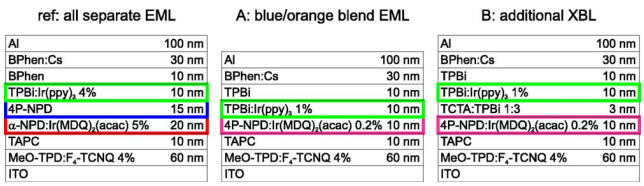

FIG. 1. (Color online) OLED structures discussed in this letter. Light emission is through ITO-on-glass substrate. EML: emission layer and XBL: exciton blocking layer. Doping concentrations in wt %.

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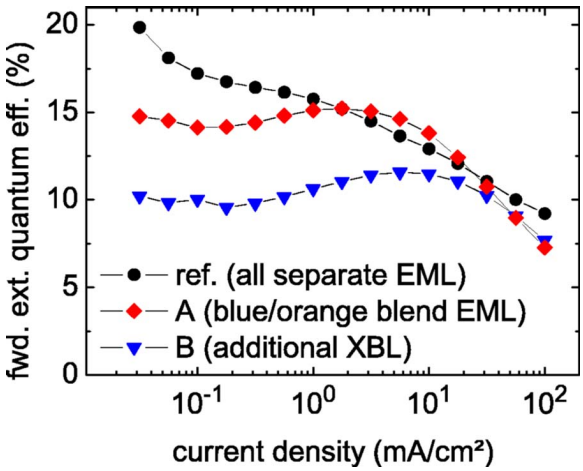

FIG. 2. (Color online) Forward viewing external quantum efficiency of the three OLEDs discussed. Efficiency roll-off is significantly reduced in devices A and B, as compared to the reference.

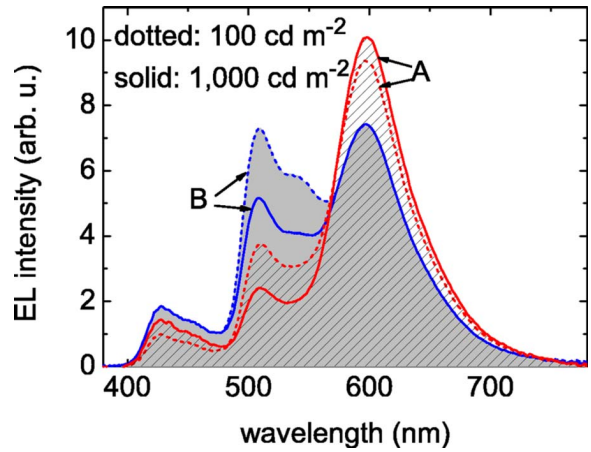

FIG. 3. (Color online) Electroluminescence spectra taken at different luminance levels of devices A and B. The observed change with luminance indicates the recombination zone shifting toward the 4P-NPD: $Ir(MDQ)_2(acac)$ layer for both devices, while the green emission is reduced, blue and red are enhanced at higher luminance.

their energy (2.3 eV) is higher than the energy of the $Ir(MDQ)_2(acac)$ triplets. However, to still get fluorescent blue emission from recombination of the 4P-NPD singlets on the blue emitter, instead of their transfer to the orange phosphor by Förster transfer,[11] the 4P-NPD layer must have a certain minimum thickness, which in this device is 15 nm.

Therefore, to reduce the high triplet accumulation at the 4P-NPD/TPBi:$Ir(ppy)_3$ interface, the orange emitter $Ir(MDQ)_2(acac)$ is directly doped into the 4P-NPD layer in device A. Also here, Förster transfer of the 4P-NPD singlets to $Ir(MDQ)_2(acac)$ has to be avoided which is achieved by a very low doping concentration of only 0.2 wt %. A rough calculation assuming equal density and 1 nm molecule size for both, 4P-NPD and $Ir(MDQ)_2(acac)$ yield an average distance of 8 nm between the $Ir(MDQ)_2(acac)$ molecules. Thus, the triplets generated on 4P-NPD now have to diffuse only on average of 4 nm until they can be harvested on $Ir(MDQ)_2(acac)$. Consequently, the effective 4P-NPD triplet recombination rate is higher which yields a lower equilibrium triplet exciton density and, thus, a lower triplet-triplet annihilation rate.[12] Indeed, the EQE is found to be almost constant at low current density (maximum 15.3% at 0.02 mA cm^{-2}), and the roll-off starts at around 6 mA cm^{-2}. The critical current density, where the EQE is reduced to half of its initial value, is about 90 mA cm^{-2} which is within the range we also find for $Ir(ppy)_3$ based OLEDs.[13] Still, fluorescent blue emission is observed, indicating sufficient suppression of unwanted Förster transfer. Taking the EL spectrum (Fig. 3) at an illumination relevant luminance of 1000 cd m^{-2}, the CIE 1931 chromaticity coordinates are (0.49,0.41), and the color rendering index (CRI) is 62. The low driving voltage (3.5 V for 1000 cd m^{-2}) together with the high quantum efficiency (15.2%) yield in forward direction a high power efficiency of 31.6 lm W^{-1} (Fig. 4). By applying a light extraction enhancing microlens foil (Optmate HR592), the power efficiency in forward direction is improved to 36.0 lm W^{-1} (17.3% EQE), whereas the total external power efficiency measured inside an integrating sphere also collecting light from the substrate edges is 49.2 lm W^{-1} (24.3% EQE). It is worth mentioning that the difference in chromaticity coordinates is very low ($\Delta x < 0.005$, $\Delta y < 0.005$) when light is collected only in forward direction or also from the edges, meaning that the whole spectral region contributes to the additional power efficiency. Moreover, the forward viewing efficiency is verified by measurements within the integrating sphere with covered substrate edges, indicating true Lambertian emission characteristics in forward direction.

It is apparent from the EL spectrum that most emission comes from the phosphorescent orange emitter $Ir(MDQ)_2(acac)$ and the chromaticity coordinates of the

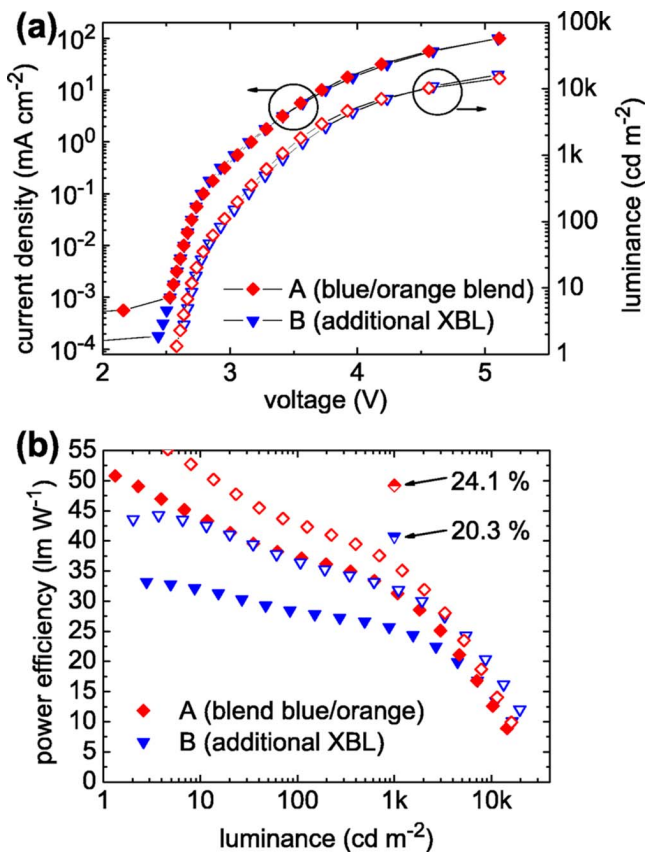

FIG. 4. (Color online) (a) Current–luminance–voltage characteristics and (b) power efficiency of the discussed OLED. In (b), closed symbols indicate measurement in forward direction without outcoupling enhancement, open symbols are with applied microlens foil, and half filled symbols measured within an integrating sphere (total external quantum efficiency also stated).

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standard illuminant A relevant for lighting (0.45,0.41) are not reached by device A. This is explained by the very narrow exciton generation zone at the interface between the two emission layers due to the predominant hole transporting 4P-NPD at one side and the predominant electron transporting TPBi at the other side.[9] Also, most excitons generated in the TPBi:$Ir(ppy)_3$ layer are transferred to the $Ir(MDQ)_2$(acac) emitter nearby Dexter or Förster transfer.[14,15] Indeed, upon further reduction of the $Ir(MDQ)_2$(acac) concentration, more green emission from $Ir(ppy)_3$ is observed. However, the quantum efficiency drops significantly to below 9%. In this case, triplet excitons are lost since they cannot be harvested efficiently anymore due to a too low concentration of phosphorescent molecules.

Therefore, one needs to suppress the intrinsically occurring exciton transfer from $Ir(ppy)_3$ to $Ir(MDQ)_2$(acac), without reducing the phosphor concentrations. It has been shown that a thin ambipolar exciton blocking interlayer between two EMLs can be used to allow exciton generation on both sides, simultaneously suppressing mutual exciton transfer.[10] Optimal exciton harvesting within the 4P-NPD: $Ir(MDQ)_2$(acac) layer fixes the blue-to-orange EL intensity ratio equal to the intrinsic electrically generated singlet to triplet exciton ratio, i.e., 1:3.[16] Aiming at an EL spectrum with chromaticity close to illuminant A, the charge carriers should ideally be balanced by the interlayer such that about two-thirds of the excitons are generated in 4P-NPD:$Ir(MDQ)_2$(acac) and one-third is generated in TPBi:$Ir(ppy)_3$, which totally yields a blue to green to orange EL intensity ratio of 16.7:33.3:50. Adopting the results from Ref. 10 device B comprises a 3 nm 4,4′,4″-tris(*N*-carbazolyl)-triphenylamine (TCTA):TPBi blend interlayer with a mixing ratio of 1:3, as to assure bipolarity with slightly predominant electron transport. The EL spectrum taken at 1000 cd m^{-2} indeed indicates about the desired intensity ratio. The chromaticity coordinates (0.43,0.43) are close to color point A and the CRI is improved to 82, indicating that the device is well suited for lighting applications. The EQE at 1000 cd m^{-2} is 11.2%, the driving voltage is increased by 0.05 to 3.45 V, and 25.4 lm W^{-1} power efficiency is achieved in forward direction. Applying the same microlens foil as for device A, the power efficiency is enhanced to 32.3 lm W^{-1} (14.1%), and the total external power efficiency measured in the integrative sphere is 40.7 lm W^{-1} (20.3%). There may be several reasons for the reduced EQE, as compared to device A. First, the 4P-NPD fluorescence and/or TPBi:$Ir(ppy)_3$ phosphorescence quantum yields may be less than the 4P-NPD: $Ir(MDQ)_2$(acac) phosphorescence quantum yield. Since the EL spectrum of device B contains less orange than that of device A, the total EQE would then be lower. Second, there may be losses induced by the interlayer, e.g., by exciplex formation at the interfaces or by the enforcement of a different charge carrier balance. Also, the cause of the special shape of the EQE-current density plot with its local maximum at around 12 mA cm^{-2} is not yet understood completely.

To summarize, we have demonstrated an improved concept for harvesting triplet excitons from a fluorescent blue emitter in white OLEDs, which results in a reduced efficiency roll-off. The key is to directly dope the orange phosphor into the fluorescent blue emission layer with low concentration (0.2 wt %) such that triplets are quickly transferred and the equilibrium triplet density is reduced. Furthermore, we demonstrate an approach to tune the EL spectrum toward illuminant A without wasting excitons by adding a charge carrier balancing interlayer.

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