Transparent organic light-emitting diodes with different bi-directional emission colors using color-conversion capping layers

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Abstract

We report a study on transparent organic light-emitting diodes (OLEDs) with different bi-directional emission colors, enabled by color-conversion organic capping layers. Starting from a transparent blue OLED with an uncapped Ag top electrode exhibiting an average transmittance of 33.9%, a 4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM)-doped tris-(8-hydroxy-quinolino)-aluminium (Alq3) capping layer is applied to achieve color-conversion from blue to orange-red on the top side while maintaining almost unchanged device transmittance. This color-conversion capping layer does not only change the color of the top side emission, but also enhances the overall device efficiency due to the optical interaction of the capping layer with the primary blue transparent OLED. Top white emission from the transparent bi-directional OLED exhibits a correlated color temperature around 6,000K-7,000K, with excellent color stability as evidenced by an extremely small

variation in color coordinate of $\Delta(x,y) = (0.002, 0.002)$ in the forward luminance range of 100-1000 cd m^{-2} . At the same time, the blue emission color of bottom side is not influenced by the color conversion capping layer, which finally results in different emission colors of the two opposite sides of our transparent OLEDs.

Keywords: Down-conversion white OLED, color conversion capping layer, transparent OLED, bi-directional OLED

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1. Introduction

Organic light-emitting diodes (OLEDs) are well known for offering an outstanding variety in device form factor: they can be built on plastic films or metal foils and thus can be ultra-thin and flexible [1-4]; they can be designed to emit light in a broad range of colors [5-7]; and most noticeably they can be made transparent by using transparent electrodes for both anode and cathode [8-10]. This transparency feature is considered to be among the key factors that distinguish OLEDs from other light-emitting devices. Since OLEDs contain self-emissive organic emitters and the generated light can pass through transparent electrodes on either side, transparent OLEDs (TOLEDs) exhibit bi-directional emission. This also means that the emission color occurs in both top and bottom direction is almost identical in TOLEDs, although slight difference in electroluminescence spectra may exist between the emission directions due to differences in transmittance/reflectance at each electrode.

In this work, we propose a novel type of TOLED that emits different colors in the two directions by combining a blue-emitting TOLED and an organic color-converting capping layer (CCL). We believe that this asymmetric emission color combined with the optical transparency is likely to draw noticeable attention for artistic and decorative lighting applications. Although the concept of using an organic CCL for down-conversion from blue photons to longer wavelength photons is not new, this approach has been applied only for opaque OLEDs with uni-directional emission [11-13]. Furthermore, most down-conversion type white OLEDs incorporating organic CCLs exhibit lower device efficiencies than pristine, unconverted OLEDs. In the present study, we focus on addressing the issues mentioned above by integrating the color-converting organic layer with a blue-emitting TOLED, and hence realize a TOLED with different bi-directional emission colors; while the bottom side emission remains blue, top side emission is changed to white by a partial down-conversion process. The organic CCL in our TOLED concurrently serves three purposes: (i) it works as a color-conversion layer, changing some of the primary blue photons to orange-red photons that are later mixed up to be white; (ii) it serves as optical capping layer adjusting the optical behavior of the TOLED to enhance its efficiency; (iii) it forms an outermost dielectric layer that preserves the overall visual transparency of the TOLEDs. These goals are simultaneously achieved by choosing an appropriate color-conversion organic capping layer with a suitable thickness that provides an effective conversion path length and is adequate for high transparency and enhanced efficiency.

2. Experimental

A series of phosphorescent TOLEDs based on *p-i-n* doped structures with thickness variation of the CCL was fabricated using the following device architecture: indium tin oxide (ITO) (90 nm)/*p*-type layer/1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC) (10 nm)/emissive layer (EML, 10 nm)/2-(diphenylphosphoryl)spirofluorene (SPPO1) (10 nm)/*n*-

type layer/Ag(15 nm)/CCL (variable thickness, denoted as X nm). All samples were deposited by thermal evaporation onto ITO-coated glass substrates in a UHV chamber (Kurt J. Lesker Co.) at a base pressure of around 10^{-7} mbar. For the *p*-type hole injection / transport layer, we used a 35 nm thick film of *N,N,N,N'*-tetrakis(4-methoxyphenyl)-benzidine (MeO-TPD) doped with 2 wt % of the Novaled dopant *p*-type 2 (NDP-2, Novaled AG, Dresden). For the *n*-type electron injection and transport layer, we used 30 nm of cesium (Cs)-doped BPhen, with conductivity comparable to the conductivity of the *p*-layer. 10 nm of TAPC and 10 nm of SPPO1 were used as electron and hole blocking layers, respectively, to confine charge carriers and excitons within the EML.[14]

The 10-nm thick blue EML consists of two host materials 4,4',4''-tris (*N*-carbazolyl)-triphenylamine (TCTA) (5 nm) and 2,6-bis(3-(carbazol-9-yl)phenyl)pyridine (26DCzPPy) (5 nm), both doped with 20% of the phosphorescent emitter iridium(III) bis(4,6-(difluorophenyl)pyridinato-N,C2') picolinate (FIrpic). Finally, as CCLs, we used tris-(8-hydroxyquinolinato)-aluminium (Alq3) doped with 2 wt% of 4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) with thicknesses varying from 0 nm to 265 nm and 435 nm.

For TOLEDs characterization, we utilized a Keithley Source Measure Unit 2400 to obtain current-voltage data, while an INSTRUMENT SYSTEMS GmbH CAS140 spectrometer and a calibrated silicon photodiode (Hamamatsu) were used to measure luminance and spectral radiant intensity in forward direction at the same time. Afterwards, spatial emission properties of the TOLEDs were evaluated with a spectrogoniometer setup to calculate external quantum efficiencies (error ranges of the current density (*J*) - voltage (*V*) - luminance (*L*) measurements, emission spectra (also radiant intensity and radiance), and device efficiencies are less than 1, 5, and 10%, respectively). The transmittance of the RSL was measured using a spectrophotometer (Hitachi U-3501).

3. Results and discussion

Figure 1(a) shows the device structure of the TOLEDs under study. It is based on the *p-i-n* structure for power efficient device operation, and the emission layer in the middle consists of double emission layers resulting in a broad emission zone and thus reduced *roll-off* [15]. The sky-blue organic emitter FIrpic with a peak emission wavelength at 475 nm was used as its emission is absorbed better by DCM molecules (absorption maximum at 480 nm) than the emission from fluorescent blue emitters [16]. In addition, it using phosphorescence from triplet excitons also improves device efficiency [17]. DCM-doped Alq3 (2 wt%) layers with various thicknesses were deposited on the top of the Ag cathode to perform color-conversion and create white emission in the top direction [16,18,19]. Since the color-conversion layer also forms an outermost dielectric capping layer, its thickness was optimized with a custom-made optical simulation tool considering dipole emission and Purcell effect [20] with results shown in Fig. 1(b). The external quantum efficiency (EQE) shown on the y-axis of the figure was calculated assuming 100% intrinsic radiative quantum yield (q) and an electrical efficiency (γ) close to unity [20]. As the capping layer thickness varies, reflectance intensity/phase at the top electrode also changes and so does the overall device efficiency. According to the simulation, the total sum of the bottom/top direction photon counts (i.e. total EQE) reaches local maxima at capping layer thickness values of 100 nm, 265 nm, 435 nm, 550 nm and so on. Although the absolute maximum in OLED efficiency occurs at a capping thickness of 100 nm, such a thin color-conversion layer will not provide sufficient conversion length to realize white light. We have therefore excluded the 100 nm case. As we also found that thicknesses beyond 500 nm significantly deteriorate device efficiency, we adopted two thickness values of 265 nm and 435 nm. Even though this optimization of capping layer thickness was performed assuming zero down-conversion (which is essentially a macroscopic randomizing process that is difficult to be taken into consideration in our calculation model),

we believe that it still provides a valid estimate of bi-directional total flux of our TOLEDs since (i) unconverted bottom emission is still dominant as can be seen in Fig. 1(c), and (ii) ratio between unconverted/converted photons in top emission is also high, as will be described later. Because the capping layer adjustment only affects the optical characteristics of the TOLEDs but not the electrical properties of the device, only the L - V curves show noticeable differences between devices while the J - V are identical within the margin of error as shown in Fig. 1(c).

To further understand the effect of the color-conversion capping layer on device performance, electroluminescence (EL) spectra in forward direction were recorded for all three devices under study (capped with 0 nm/265 nm/435 nm) and for both bottom/top directions. These are shown in Fig. 2(a) and (b) together with pictures of the operating devices. Bottom side EL spectra of the capped TOLEDs are similar to the uncapped TOLED with a slightly increased second shoulder peak of FIrpic at 500 nm indicating weak cavity effects in the devices. In contrast, top side EL spectra of the capped/uncapped TOLEDs exhibit a clear difference: The capping layer gives rise to another emission peak at a wavelength around 605 nm in the capped TOLED, creating white emission as shown in Fig. 2(b). Commission Internationale de l'Eclairage (CIE) 1931 color coordinates of the TOLEDs gradually shift from (0.164, 0.386) sky-blue color for the uncapped device to (0.328, 0.375) cold white color (6,000K) for the device with 435 nm thick capping layer.

The device performance including current efficacy (CE) and EQE of the devices are summarized in Fig. 3(a)-(d). At a driving current density of 1 mA cm^{-2} , the TOLEDs under study achieved a bottom side CE and EQE of $13.6 \text{ cd A}^{-1}/15.7 \text{ cd A}^{-1}/15.8 \text{ cd A}^{-1}$ and $5.6\%/6.5\%/6.3\%$ (for 0 nm/265 nm/435 nm capping layer thicknesses), respectively. Compared to the uncapped TOLED, the 265 nm-capped devices shows a $\sim 16\%$ EQE enhancement. Another noticeable consequence is that even device efficiencies in just the top

direction are further increased by applying the capping layer. CE and EQE values which are 2.8 cd A^{-1} and 1.2%, respectively, for the top side of the uncapped TOLED are increased to 3.4 cd A^{-1} and 1.6% for the device with 265 nm capping layer (at a current density of 1 mA cm^{-2}) – 21% and 33% improvement in terms of CE and EQE. The fact that the EQE increase is larger than the CE enhancement may be due to the rearrangement of light propagation directions caused by absorption of blue photons and re-emission of orange-red photons by DCM molecules, similar to mechanisms reported in the literatures [21-23]. This demonstrates that color-conversion is feasible without compromising the device efficiency. Increasing color-conversion layer thickness from 265 nm to 435 nm further increases this rearrangement effect. The thicker capping layer also leads to slight decreased device efficiency presumably due to increased absorption losses and the limited conversion efficiency of the capping layers. However, even with the thickest conversion layer of 435 nm, the capped TOLED exhibits EQE values higher than the uncapped device for a wide range of current density, demonstrating the usefulness of our approach.

CIE color coordinates of the top emission of the TOLEDs under study is shown in 10° steps of viewing angles in Fig. 4(a). The y-coordinate of the top blue emission from the uncapped TOLED varies from 0.381 (0° , at the substrate normal) to 0.335 (at 80° off-normal), owing to the cavity wavelength shift [24]. For top white emission from the TOLEDs, CIE coordinates range from (0.302, 0.389) at 0° to (0.256, 0.364) at 80° for the 265 nm-capped device and from (0.333, 0.366) at 0° to (0.300, 0.356) at 80° for the 435 nm-capped device. This corresponds to a relatively ‘cold white’ color with a correlated color temperature around 6,000-7,000K. We also measured the EL spectra and CIE coordinates in top direction at several representative forward luminance levels (100, 500 and $1,000 \text{ cd m}^{-2}$) for the 265 nm-capped TOLED as shown in Fig. 4(b). Differences were negligible [$\Delta(x,y)$ of (0.002, 0.002)] due to the intrinsic color stability advantage of the combination of a single-emitter OLED and

a color-conversion layer.. In addition, to verify whether the color-conversion organic capping layer has no negative impact on the transparency of the TOLEDs, overall transmittance values of the uncapped/265 nm/435 nm-capped TOLEDs were measured in the visible wavelength range and are shown in Fig. 5.

While the uncapped TOLED exhibits an average transmittance of 33.9%, 265 nm color-conversion organic layer slightly enhanced the average transmittance of the capped TOLED to be 34.9%. Hence, the thin layer of DCM-doped Alq₃ functions as an excellent non-scattering, non-diffusive color-conversion layer, while preserving the visual clarity of the TOLEDs by complementing the absorption loss with the optical capping effect. However, the TOLED with the 435 nm thick capping layer shows a reduced average transmittance of 30.0%, consistent with the absorbing/directional redistributing nature of the DCM-doped Alq₃ layer. This shows that careful control of the capping layer thickness can lead to both high efficacy and excellent transparency if a trade-off is obtained between the following three factors: 1) sufficient conversion length for down-conversion to white color, 2) optimal optical capping for maximized overall device efficiency, 3) restrained absorption from the capping layer to maintain the device transmittance.

4. Conclusions

To sum up, we have proposed a new type of transparent OLED that emits distinct colors into top and bottom direction. While the bottom-side emission exhibits blue light by the emission from FIrpic molecules, the DCM-doped Alq₃ organic capping layer placed on top of the Ag top-electrode absorbs a portion of the blue photons and converts them into orange-red photons to create mixed white emission on the top side. The organic color-conversion capping layer plays three roles simultaneously in our color-asymmetric TOLEDs: as a color-conversion layer for the primary blue emission; as an outermost dielectric layer that alters the transmittance and reflectance at the top electrode to boost efficiencies in both top/bottom

directions; and finally as an optical capping layer to maintain device transparency even with the absorption occurring within it. Our best bi-directional, color-asymmetric TOLED exhibited current efficacy (CE) and external quantum efficiency (EQE) of 15.7 cd A⁻¹ and 6.5%, respectively, in the blue bottom side emission and 3.4 cd A⁻¹ and 1.6%, respectively, in the cold white top side emission at a current density of 1 mA cm⁻², while keeping the average device transmittance in the visible range of 400 nm – 750 nm at 34.9%. Considering the unique visual behavior, this new type of TOLED is expected to turn into a whole new category of devices for OLED lighting.

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Figure Captions

Figure 1

(a) Device structure of the proposed TOLEDs (b) Result of optical simulation of the external quantum efficiency of the TOLED versus capping layer thickness (c) J - V - L graphs of the devices under study

Figure 2

Electroluminescence (EL) spectra of the devices with various capping layer thicknesses measured in the forward direction and pictures of operating devices, (a) at bottom side and (b) top side. EL spectra were obtained at a driving current of 3 mA and photos were taken at a driving current of 1 mA.

Figure 3

Current efficiency (CE) measured normal to the substrate (a) at bottom side (b) at top side, and external quantum efficiency (EQE) measured at (c) bottom side and (d) top side versus current density. Enhancement in EQE is larger than in CE, indicating that the color conversion capping layer redistributes light propagation direction within TOLEDs.

Figure 4

(a) Shifts in CIE 1931 xy -coordinates for the top side emission of three TOLEDs according to the viewing angle changes, measured from 0° (direction normal to the substrate) to 80° . (b) EL spectra and CIE coordinates of the 265-nm capped TOLED at various luminance values in the top side emission, demonstrating an exceptional color stability.

Figure 5

Transmittance of the TOLEDs under study measured in the visible wavelength range. The average transmittance is 33.9%/34.9%/30.0% for the 0 nm/265 nm/435 nm-capped device, respectively, which is appropriate for see-through applications.

Figure1
Fig.1

Figure 2
Fig.2

(a)

(b)

Figure3
Fig.3

Figure 4
Fig.4

Figure 5
Fig.5