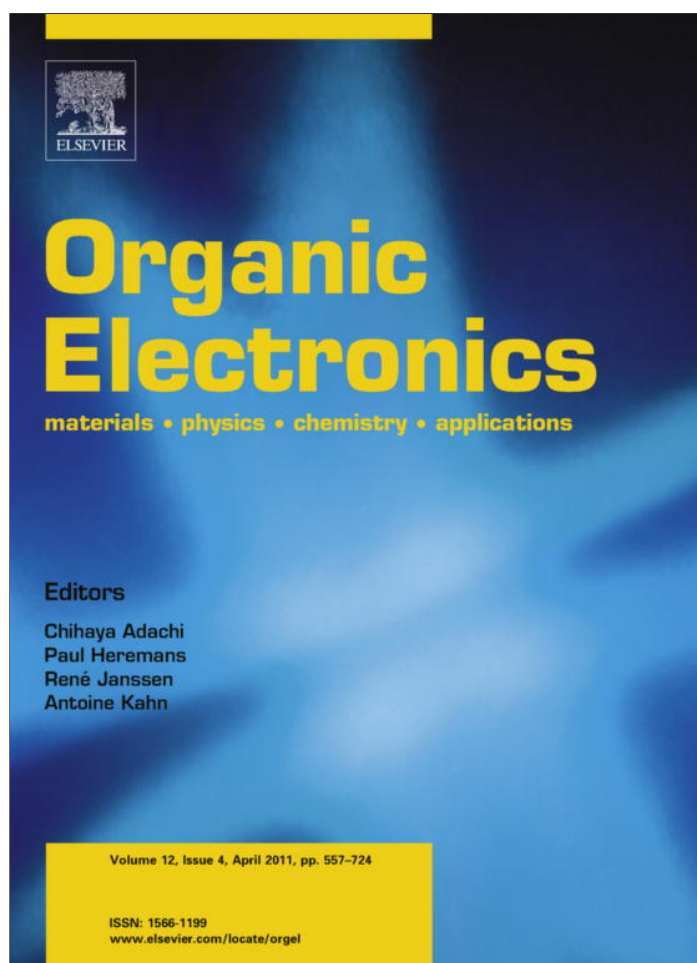


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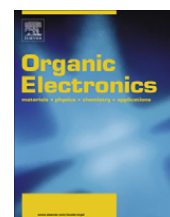
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Top-emitting white organic light-emitting diodes with a color conversion cap layer

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ARTICLE INFO

Article history:

Received 25 October 2010
Received in revised form 3 January 2011
Accepted 8 January 2011
Available online 22 January 2011

Keywords:

White organic light-emitting diodes
Top-emitting
Color conversion
Color stability

ABSTRACT

We report top-emitting white organic light-emitting diodes (WOLEDs) by thermally evaporating non-doped (4-(4-(1,2,2-triphenylvinyl)phenyl)-7-(5-(4-(1,2,2-triphenylvinyl)phenyl)thiophen-2yl)benzo[c][1,2,5]thiadiazole) (BTPETTD) as a color conversion cap layer on top-emitting blue OLEDs. With a 240 nm cap layer, 74.5% of the blue photon energy are absorbed and converted to red emission with a conversion efficiency of 40%. By mixing the unabsorbed blue emission and red emission, the resulting top-emitting WOLEDs exhibit a broad band spectra with CIE coordinates of (0.34, 0.35), high color stability over a wide range of driving voltages, and peak efficiency of 17.7 cd/A and 8.7 lm/W.

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1. Introduction

White organic light-emitting diodes (WOLEDs) are of considerable interests in recent years due to their potential applications in full color display and solid-state lighting [1–16,19]. Theoretically, the white color can be generated by additive mixing of three primary colors or two complementarily colors. Thus, WOLEDs is mainly constructed by combining multiple color light emissive layers [1,2], or employing a single emissive layer doped simultaneously with different color dopants [3,4], as well as stacking several OLED units with each unit emitting different colors [5,6]. Although efficient and bright WOLEDs have been realized of adopting these methods, the fabrication process is somewhat complicated. The exciton distribution profile and the doping concentration should be carefully tuned to achieve a balanced exciton distribution in each emissive layer or among the light emitting dopants [7,8]. Furthermore, such WOLEDs suffer low color stability, i.e., the white spectra change with driving voltages and/or

operation times, which is probably due to the shifting of the recombination zone and/or differential aging of different emitting materials [9,10].

WOLEDs by combining blue OLEDs with a color down conversion layer (CCL) have been proposed to simplify the fabrication process and achieve high color stability [11–16]. However, most reports focused on bottom-emitting WOLEDs, in which the CCL, typically composed by a host layer doped with an organic/inorganic dye, is spin-coated/laminated on the back glass side [11–14], or deposited as an internal hole-injection and conversion layer for the bottom-emitting blue OLEDs [15]. It is desirable to develop top-emitting WOLEDs since they promise large aperture ratio and can be fabricated on opaque substrates such as silicon and metal. Moreover, the combination of top-emitting blue OLEDs with CCL can easily yield broad band spectra, which is difficult to achieve in conventional top-emitting structures mainly due to the well-known microcavity effect [19].

To construct the top-emitting WOLEDs, the CCL should be thermally evaporated on top of top-emitting blue OLEDs in order not to damage the underneath OLEDs. Thus conventional CCL [11–14], which require spin-coating technique and/or thicker layer (~10 μm) are impractical. Ji

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et al. employed thermal evaporated phosphors DPPO deposited on top-emitting blue OLEDs to construct top-emitting WOLEDs [16], but the efficiencies of the resulting WOLEDs are low. Tien et al. proposed color tunable double-emitting OLEDs by capping Alq₃: DCJTb/rubrene on the metal cathode to recycle a portion of the energy trapped by surface plasmon polariton [22]. In this work, we show that 4-(4-(1,2,2-triphenylvinyl)phenyl)-7-(5-(4-(1,2,2-triphenylvinyl)phenyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (BTPETTD) with aggregation-induced-emission (AIE) characteristics is an ideal CCL for top-emitting blue OLEDs. By thermally evaporating 240 nm BTPETTD on top of top-emitting blue OLEDs, 74.5% of the blue photon energy are absorbed and subsequently converted to red emission by photoluminescence (PL) with a conversion efficiency of 40%. Combining with the unabsorbed blue emission, the resulting top-emitting WOLEDs exhibit broad band spectra with 1931 Commission International de L'Eclairage (CIE) coordinates of (0.34, 0.35), demonstrate high color stability over a wide range of driving voltages, and perform peak efficiencies of 17.7 cd/A and 8.7 lm/W.

2. Experimental

The top-emitting blue OLEDs were fabricated in a multi-source vacuum chamber with a base pressure of around 5×10^{-7} Torr with structure glass/Al (100 nm)/MoO₃ (8 nm)/NPB 25 nm/TcTa 10 nm/CDBP:Firpic 12 wt.%, 20 nm/TAZ 10 nm/BPhen 20 nm/Yb 5 nm/Ag 20 nm, where Al, MoO₃ and NPB functions as reflective anode, hole-injection and hole-transporting layer, respectively, Firpic doped CDBP works as blue light-emitting layer, TcTa and TAZ serves as exciton-blocking layer, Bphen, Yb and Ag acts as electron-transporting, electron-injection layer and semi-transparent cathode, respectively. A 190 nm or 240 nm BTPETTD layer was further deposited on the top-emitting blue OLEDs without breaking vacuum as a non-doped CCL. The synthesized method and AIE characteristics of the BTPETTD were reported elsewhere [17]. The schematic illustration of the device structure is shown in the inset of Fig. 2(a). The current density–voltage–luminance

characteristics of the devices were measured by the HP4145B semiconductor parameter analyzer and a calibrated UDT PIN-25D silicon photodiode. The electroluminescent (EL) spectra were obtained with the PR650 spectrophotometer.

3. Results and discussion

Fig. 1(a) shows the refractive index n and extinction coefficient k of BTPETTD as measured by spectroscopic ellipsometer. The molecular structure of BTPETTD is also shown in Fig. 1(a). The calculated absorption spectra based on the measured k value agree well with the measured absorption spectra as shown in Fig. 1(b). The absorption peak at 470 nm matches well with the EL spectra of the top-emitting blue OLEDs, signifying that BTPETTD may absorb the blue photon energy and convert to red emission effectively via the PL process. To verify this assumption, two devices, one with 190 nm and the other with 240 nm BTPETTD layer were fabricated; the EL spectra of the devices are shown in Fig. 2(a). The top-emitting blue OLEDs exhibit a single peak at 472 nm; however, by introducing a 240 nm BTPETTD cap layer, a secondary peak at 610 nm appeared, confirming that some of the blue photons are absorbed and converted to red photons by the cap layer. Interestingly, the devices with a 190 nm cap layer exhibit a secondary peak at 550 nm, which is neither the intrinsic emission of Firpic nor the PL emission of BTPETTD. This peak is likely due to the microcavity effect, since in top-emitting OLEDs, the thickness of the cap layer can alter the optical properties of the OLED film stacks and hence shift the resonant wavelength of the cavity [18,19].

To verify this assertion, we used a rigorous classical electromagnetic method to model the interference effect of the top-emitting blue OLEDs with different cap layer thicknesses [20,21]. The simulated spectra are shown in Fig. 2(a). They agree well with the experimental results, confirming the accuracy of the model. Based on the model, the emission of Firpic at 550 nm is enhanced by introducing a 190 nm cap layer, and thus the combination of the modified blue emission with PL emission of BTPETTD

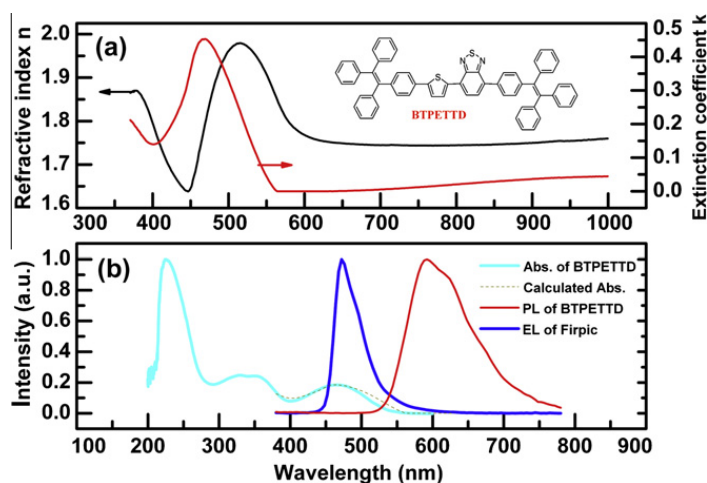


Fig. 1. (a) Refractive index n and extinction coefficient k of BTPETTD, inset: molecular structure of BTPETTD; (b) measured and calculated absorption spectra, PL spectra of BTPETTD, and EL spectra of top-emitting blue OLEDs based on Firpic emitter.

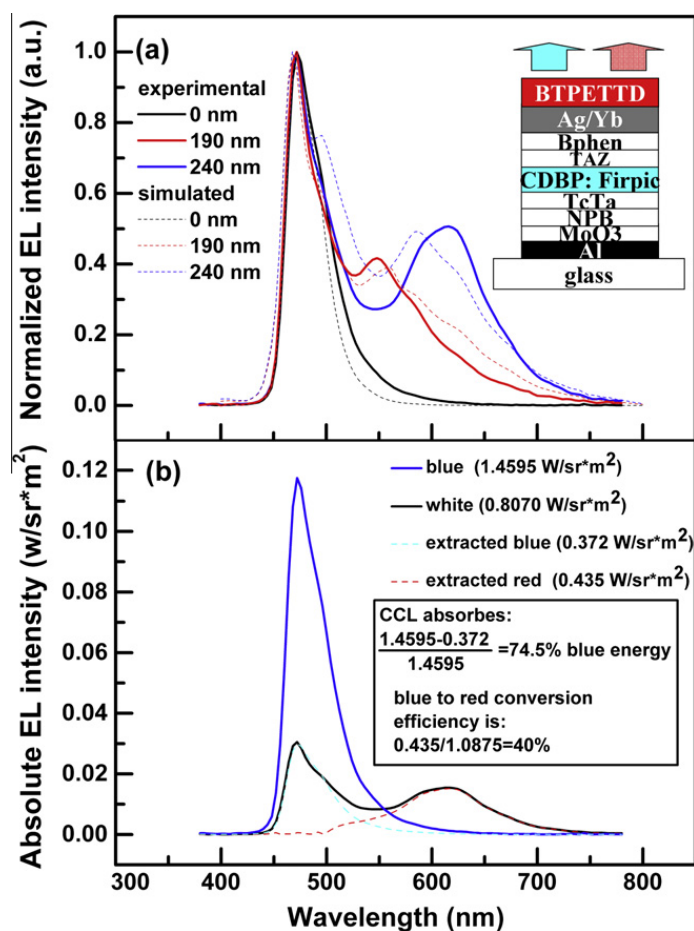


Fig. 2. (a) Normalized EL spectra of the devices with different thickness cap layer, inset: device structure; (b) absolute EL intensity of the devices without and with 240 nm cap layer.

exhibits a secondary peak at 550 nm. While with 240 nm cap layer, the resonant wavelength of the cavity is set equal to the peak intrinsic emission of Firpic, and hence the combination of the intrinsic emission of Firpic with PL emission of BTPETTD results in a secondary peak at 610 nm, similarly with the PL peak of BTPETTD. Therefore, to obtain pure white emission, the thickness of the cap layer should be carefully tuned to set the resonant wavelength equal to the peak intrinsic emission of Firpic, as well as to generate appropriate red emission intensity. As shown in Fig. 2(a), the mixture of the unabsorbed intrinsic blue emission of Firpic and the red PL emission of the 240 nm cap layer yields a white emission with CIE coordinates of (0.34, 0.35).

To evaluate the conversion efficiency of the cap layer, the absolute EL spectra of the top-emitting blue OLEDs without and with a 240 nm cap layer, operating at a driving current of 5 mA/cm² and luminance of 1165 cd/m², 857 cd/m², respectively, were tested. As shown in Fig. 2(b), the output blue emission intensity without cap layer is 1.4595 W/sr m², obtained by integrating the blue spectra. By introducing a 240 nm cap layer, the intensity is reduced to 0.8070 W/sr m² white emission, which can further be decomposed to 0.3720 W/sr m² unabsorbed blue emission intensity and 0.4350 W/sr m² red emission intensity by integrating the extracted blue and red spectra,

respectively. Thus the cap layer absorbs $1.4595 - 0.3720 = 1.0875$ W/sr m² (74.5%) blue emission and subsequently converts it to 0.4350 W/sr m² red emission. Therefore the blue to red watt to watt conversion efficiency can be calculated as $0.4350/1.0875 = 40\%$. Taking account the output red photon energy at 600 nm is ~80% of the input blue photon energy at 472 nm, the quantum efficiency of the cap layer is about $40\%/80\% = 50\%$, which agree well with 55% as measured by integrated sphere [17]. Obviously, to enhance the conversion efficiency, CCL with higher quantum yield should be employed.

Fig. 3(a) shows the EL spectra of the devices with 240 nm cap layer under different driving voltages. Obviously, no significant EL spectra change can be observed as the driving voltages increased from 6 V to 10 V, indicating that the top-emitting WOLEDs demonstrated here have excellent color stability. Fig. 3(b) shows the EL spectra normalized to 472 nm under different viewing angles. By setting the resonant wavelength equal to the peak intrinsic emission of Firpic, the blue emission shows minimal blue shift with increased viewing angles. While the red emission exhibits a slightly blue shift, with its peak changing from 610 nm at normal viewing angle to 584 nm at 60° viewing angle. Interestingly, the red emission is enhanced significantly as increased of viewing angles, which may be likely due to the light at oblique angles experiencing

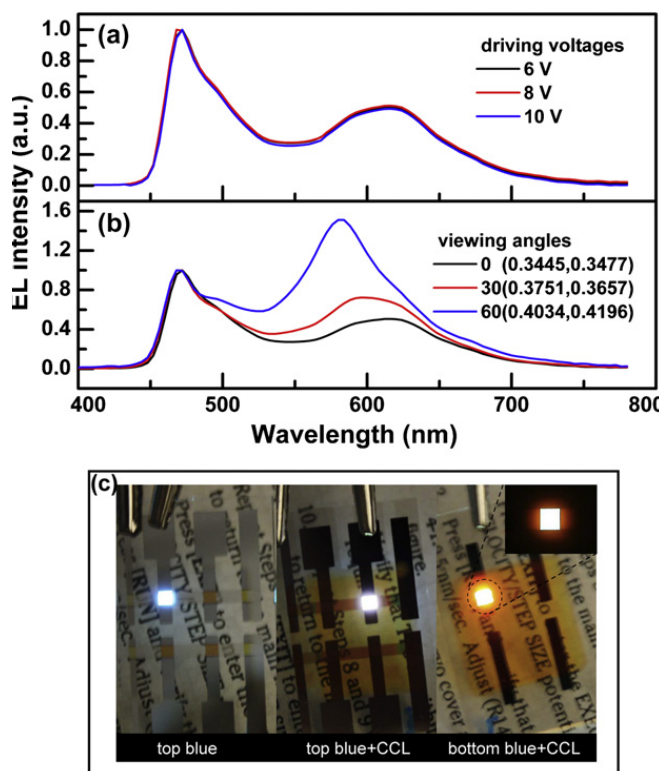


Fig. 3. (a) EL spectra under different driving voltages; (b) EL spectra under different view angles; (c) photos of the devices.

thicker CCL than its counterpart at normal angle; hence more blue photon energy are absorbed, resulting in an enhanced red emission and a shifting of CIE coordinates. As shown in Fig. 3(c), by depositing a 240 nm cap layer on top of top-emitting blue OLEDs, the blue emission has been modified as a uniform white emission. The photo of the bottom-emitting blue OLED with its back glass side covered by BTPETTD is also shown for comparison. Unlike the top-emitting WOLEDs with uniform white emission,

the bottom-emitting WOLEDs are surrounded by a red ring, indicating that all the blue emission in the edges is absorbed and converted to red emission completely. Such phenomena may be mainly due to the light diffusing effect induced by thick glass substrate, resulting in a weak edges blue emission. The weak edges blue emission is subsequently converted to red emission by the CCL completely. To eliminate this effect, the CCL should be directly deposited on the blue OLEDs. Thus the combination of top-emitting blue OLEDs with CCL cap is superior to the bottom-emitting blue OLEDs with external CCL in terms of white lighting qualities.

Fig. 4 shows the luminance-voltage-current density and external quantum efficiency–luminance–power efficiency characteristics of the devices with different cap layer thickness. All devices show identical current density–voltage characteristics since the cap layer does not alter the electrical characteristics of the devices. Due to conversion loss, the luminance decreases as increased of cap layer thickness; for example, at a driving current of 5 mA/cm², the luminance decreases from 1165 cd/m² to 914 cd/m², 857 cd/m², corresponding to a external quantum efficiency of 10% (23 cd/A, 10 lm/W), 6.8% (18.3 cd/A, 7.2 lm/W) and 6% (17.1 cd/A, 6.6 lm/W), for the devices with 0 nm, 190 nm and 240 nm cap layer, respectively. The efficiency of the top-emitting WOLEDs can be further enhanced by developing efficient top-emitting blue OLEDs, employing high quantum yield CCL, as well as adopting light out-coupling techniques.

4. Summary

In summary, we have demonstrated an easily fabricated top-emitting WOLEDs by thermally evaporating a non-doped BTPETTD cap layer on top of top-emitting blue OLEDs. By carefully tuning the cap layer thickness, the top-emitting WOLEDs emit pure white light emission with CIE coordinates of (0.34, 0.35), exhibit extremely high color

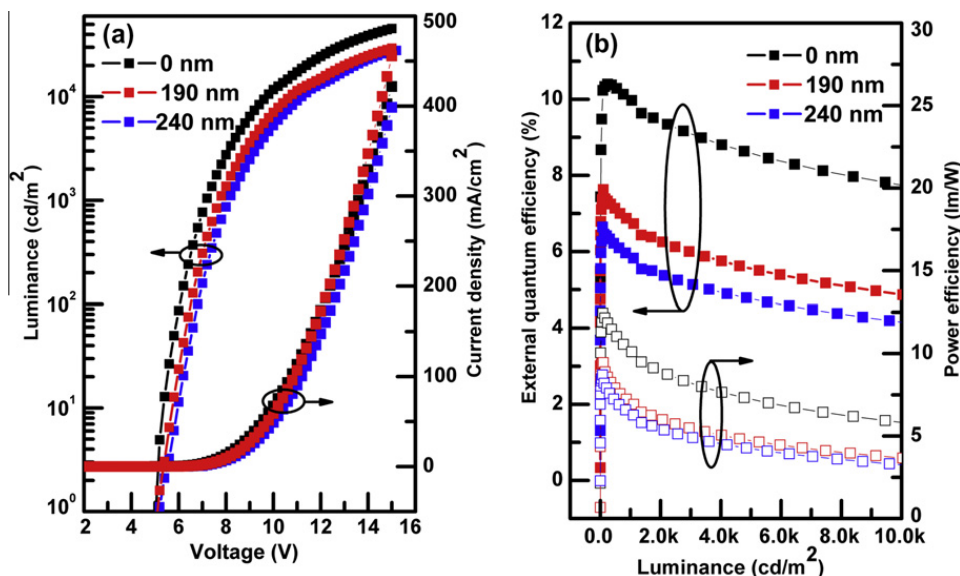


Fig. 4. (a) Luminance–voltage–current density; (b) external quantum efficiency–luminance–power efficiency characteristics of the devices.

stability over a wide range of driving voltages, and perform a peak efficiency of 6.6%, 17.7 cd/A and 8.7 lm/W.

Acknowledgments

The authors thank Dr. Zujin Zhao and Prof. Ben Zhong Tang for providing the BTPETTD. This work was supported by the Hong Kong Government Research Grants Council Grant Number AOE/P0308PG2.

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