

Fabrication of color tunable organic light-emitting diodes by an alignment free mask patterning method



Yibin Jiang^a, Jiarong Lian^c, Shuming Chen^{a,b,*}, Hoi-Sing Kwok^a

^a Center for Display Research and Department of Electronic and Computer Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, PR China

^b Department of Micro-Nano Materials and Devices, South University of Science and Technology of China, Shenzhen 518055, PR China

^c Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education, Shenzhen University, Shenzhen 518060, PR China

ARTICLE INFO

Article history:

Received 1 March 2013

Received in revised form 5 April 2013

Accepted 20 April 2013

Available online 9 May 2013

Keywords:

Organic light-emitting diodes

Lighting

Color tunability

Time sequential driving

Side-by-side

ABSTRACT

An alignment free mask patterning method has been proposed for fabricating the side-by-side color tunable organic light-emitting diodes (OLEDs). The demonstrated color tunable OLEDs consists of blue sub-OLEDs and inverted orange sub-OLEDs; both color sub-OLEDs share the same electrodes. With time sequential pulse driving, the blue sub-OLEDs and the inverted orange sub-OLEDs are alternately turned on. Tunable color, resulting from the mixing of the blue and the orange emission, has been realized by simply varying the amplitude ratio of the positive and negative pulses.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Since the demonstration of low-voltage organic light emitting diodes (OLEDs) in 1987 [1], OLEDs have attracted much attention for the application in flat panel display. Recently, people also begin to pay attention to OLEDs' application in solid-state lighting, especially the room lighting, due to their inherent advantages [2–4]. For example, the efficiency of the white light OLEDs can be as high as 100 lm/W at a illumination level of 1000 cd/m² [2], which is beyond that of the incandescent bulb and comparable with that of the fluorescent tube. OLEDs are a true surface/area lighting source thus inherently offering very uniform illumination; also heat dissipation is not as demanding as that of a point source like LEDs. OLEDs are mercury free thus environmentally friendly. More importantly, OLEDs can be flexible like paper, transparent like

window or reflective like mirror, which will open new architectural and design opportunities.

For decorative or color matching purposes, the color of the OLEDs are required to be tunable. The first demonstrated color tunable OLEDs make use of polymer blend [5,6]: each component of the blend emits at a different wavelength. The color is tuned by varying the bias voltage. Higher voltage leads to the emission increase from the blue component. However, this method cannot switch off the orange emission. As a result, the color can only be tuned from orange to white. Moreover, the luminance of individual color cannot be separately controlled. Yang and Pei reported using electrochemical doping to make the two color polymer LEDs, in which two colors can be obtained by changing the polarity of the bias voltage [7].

To truly achieve real time color tunability, tandem structure with two to three color sub-cells serial connected was employed [8–12]. By extracting the intermediate electrodes, each sub-cell can be separately addressed, thus offering a route for independently controlling the luminance of each sub-cell. Alternately, a side-by-side red,

* Corresponding author at: Department of Micro-Nano Materials and Devices, South University of Science and Technology of China, Shenzhen 518055, PR China.

E-mail address: chen.sm@sustc.edu.cn (S. Chen).

green and blue sub-cells arrangement scheme can be adopted for realizing the color tunability. In both cases, a wide range of color, defined by the color triangle of the sub-cells, can be obtained by separately tuning the luminance of each sub-cell. However, both methods require fine patterning/aligning either the intermediate electrodes for the tandem case or the organic layers for the side-by-side scenario. It is known that the fine mask alignment is an expensive, complicate and time consuming step [13], and thus it is desirable to eliminate the fine alignment in the fabrication of color tunable OLEDs.

In this work, an alignment free mask patterning method has been proposed for fabricating the side-by-side color tunable OLEDs. The demonstrated color tunable OLEDs consists of blue normal bottom-emitting sub-OLEDs (b-NBOLED) and orange inverted bottom-emitting sub-OLEDs (o-IBOLED); both sub-OLEDs share the same electrodes and hence only one sub-OLEDs can be turned on at a certain bias polarity. With alternate current (AC) driving, the b-NBOLED and the o-IBOLED are alternately turned on. The luminance of both sub-OLEDs can be separately controlled by varying the amplitude of the positive bias and the negative bias respectively. If the frequency of the AC driving is

high enough, a new color resulting from the mixing of the blue and the orange emission appears. By simply changing the amplitude ratio or duty ratio of the AC driving, the mixing color can be continuously tuned in a wide range.

2. Fabrication and driving method of the proposed color tunable OLEDs

Fig. 1 illustrates the fabrication steps of the proposed color tunable OLEDs and reveals the mask alignment free advantage of our method. Before the deposition, the ITO is pre-patterned to be an electrode for the OLEDs and an electrical contact for the Al electrode. Then, the o-IBOLED defined by a fine pattern shadow mask and a rough common shadow mask are deposited. At this step, the two masks mentioned above are used simultaneously to pattern the organic layers of o-IBOLED. Then the rough common shadow mask, which is used to protect the ITO contact from being covered by the organic layers, is removed and the remaining fine pattern shadow mask serves to define the Al anode of o-IBOLED alone. Here, ITO electrode which serves as the cathode for the o-IBOLED and

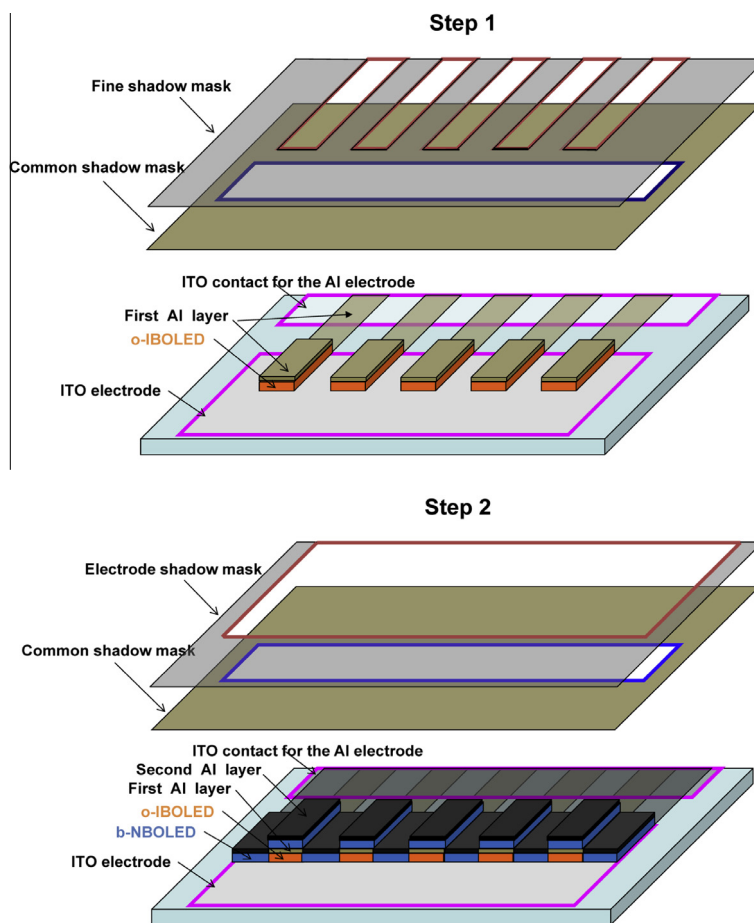


Fig. 1. Fabrication steps of the proposed color tunable OLED. The o-IBOLED is firstly deposited with a fine mask, followed by depositing the b-NBOLED without fine mask. Both o-IBOLED and b-NBOLED share the same electrodes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

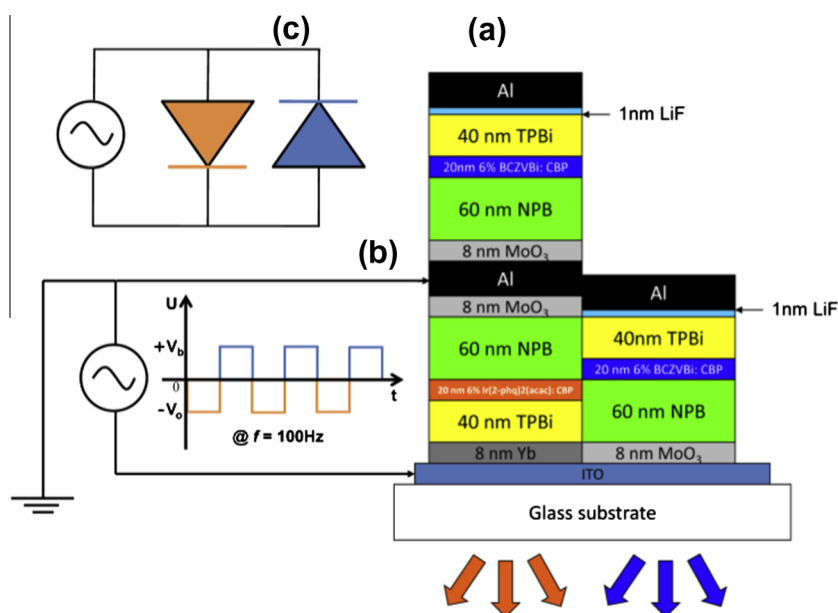


Fig. 2. (a) Cross section view of the proposed side-by-side color tunable OLED, (b) driving setting and (c) circuit diagram of the color tunable OLED. The o-IBOLED and b-NBOLED are alternately turned on by the AC source. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the anode for the b-NBOLED is not finely patterned, so no fine mask alignment is needed at this step. The second step is to deposit the b-NBOLED using two rough masks: common shadow mask and electrode shadow mask. Again, no fine alignment is needed at this step. At first, the organic layers of b-NBOLED are deposited through these two masks. Then the common shadow mask is removed and the Al cathode of b-NBOLED is defined to connect to the ITO contact by the electrode shadow mask. Although a part of the b-NBOLEDs are deposited over the previously defined o-IBOLEDs, they cannot work because no current is passing through them. Both o-IBOLED and b-NBOLED share the same ITO and Al electrodes. A schematic cross section and a circuit diagram of the proposed color tunable OLED are shown in Fig. 2.

The advantages of the proposed fabrication method are that: firstly, the ITO electrode need not to be fine patterned to a strip shape as it is the common electrode for both o-IBOLED and b-NBOLED; secondly, fine shadow mask alignment is not necessary during the deposition of the organic layers. Conventional side-by-side color tunable OLED usually requires fine pattern the ITO to be the electrode for the red, green and blue OLED and fine align the organic layers with their corresponding electrode [13]. The proposed method eliminates these requirements and hence may significantly reduce the process TAC time, improve the yield and cut down the manufacturing cost for industry.

To drive the devices, a square wave voltage source with frequency of 100 Hz and duty ratio 1:1 is applied to the ITO electrode while the Al electrode is connected to a common ground, as shown in Fig. 2b. The o-IBOLED and b-NBOLED are alternately turned on, i.e., when the negative pulse comes, only o-IBOLED works and emits orange light and when the positive pulse comes, only b-NBOLED works

and emits blue light. Therefore, the color tunable OLED actually emits flashing light. It is well known that when the flashing frequency is lower than 60 Hz, flickering can be detected by the human eye. By setting the frequency of the square wave to be 100 Hz, very stable emission has been observed. If the distance between the blue and the orange emission is shorter than human eye's spacing resolution, a new color resulting from the mixing of the blue and the orange emission appears. As will be shown below, the mixing color can be tuned to be any linear superposition of the orange and the blue emissions by varying the amplitude ratio of positive and negative pulses.

3. Results and discussion

To determine the driving voltage of the devices, the luminance–voltage characteristics of the devices were measured. As shown in Fig. 3a, the o-IBOLED exhibits a remarkably higher turn on voltage of 10.6 V than that of 3.7 V for the b-NBOLED, which is likely due to the poorer electron injection of the ITO/Yb cathode than that of the Al/LiF cathode. To further reduce the driving voltage of the o-IBOLED, electrical doping the electron transporting layer can be adopted [14,15]. The efficiency characteristics of the devices are also shown in Fig. 3b.

To drive the devices, a square wave with positive and negative pulse amplitude V_b and V_o , which control the luminance of b-NBOLED and o-IBOLED respectively, is applied to the ITO electrode. Three typical driving settings and the resultant emission spectra are summarized in Fig. 4. In case 1, by setting $V_b = 8\text{ V}$ and $V_o = 0\text{ V}$, the b-NBOLED is turned on while the o-IBOLED is switched off, resulting in a pure blue emission. In case 2, by pulling

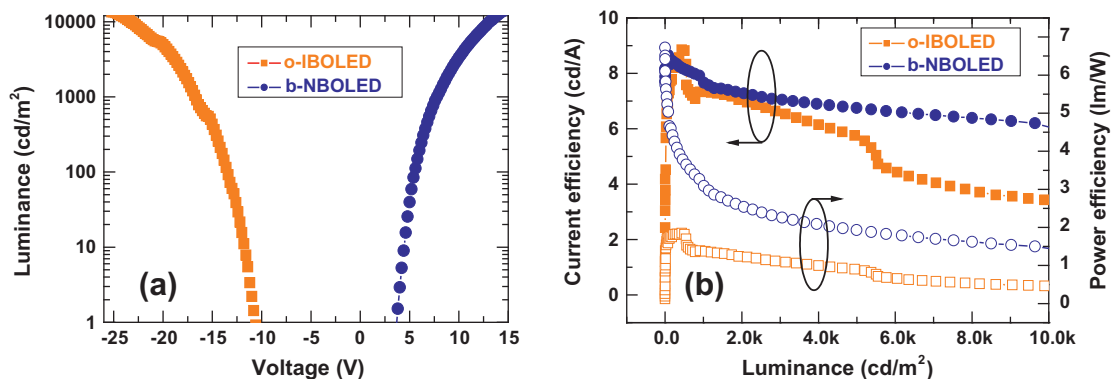


Fig. 3. (a) Luminance–voltage and (b) efficiency characteristics of the o-IBOLED and b-NBOLED.

down the V_o to -16.6 V, both b-IBOLED and o-NBOLED are alternately turned on with a frequency of 100 Hz. It seems that the blue and the orange emission come from the same position as they are close enough. As a result, color mixing effect occurs. By carefully tuning the intensity of the blue and the orange emission, the resultant mixing color exhibit a CIE coordinate of (0.38, 0.29) and a color rendering index (CRI) of 54.2. To further achieve pure white color and higher CRI, sub-OLEDs with complementary emission such as

blue and yellow should be adopted [4]. In case 3, the blue emission is switched off by setting $V_b = 0$; thus only orange emission can be observed.

Theoretically, the color can be freely and continuously tuned in a wide range: from pure blue to pure orange by simply adjusting the V_b and the V_o . For example, by fixing the $V_b = 8$ V and gradually decreasing the V_o from -14.2 to -16.6 V, the orange emission is enhanced accordingly, which in turn shifts the CIE coordinates from near blue

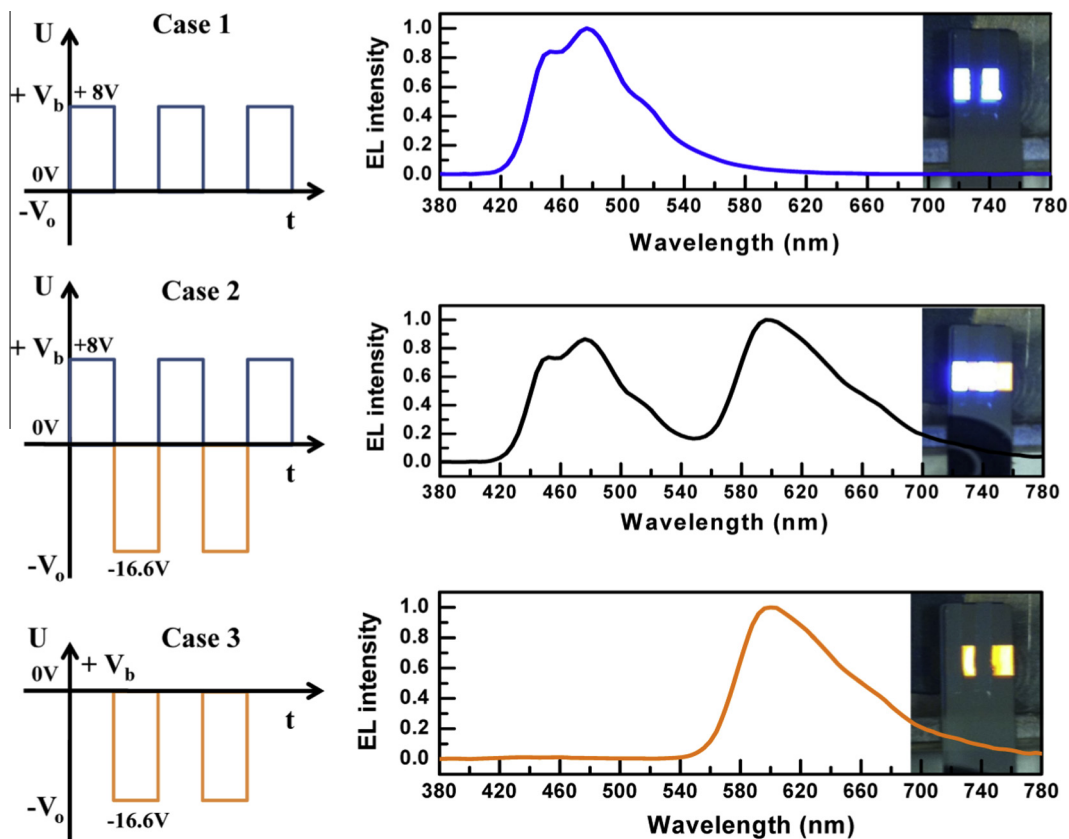


Fig. 4. Driving settings, EL spectra and corresponding device photos when the device is tuned to emit blue light (case 1), white light (case 2) and orange light (case 3) respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

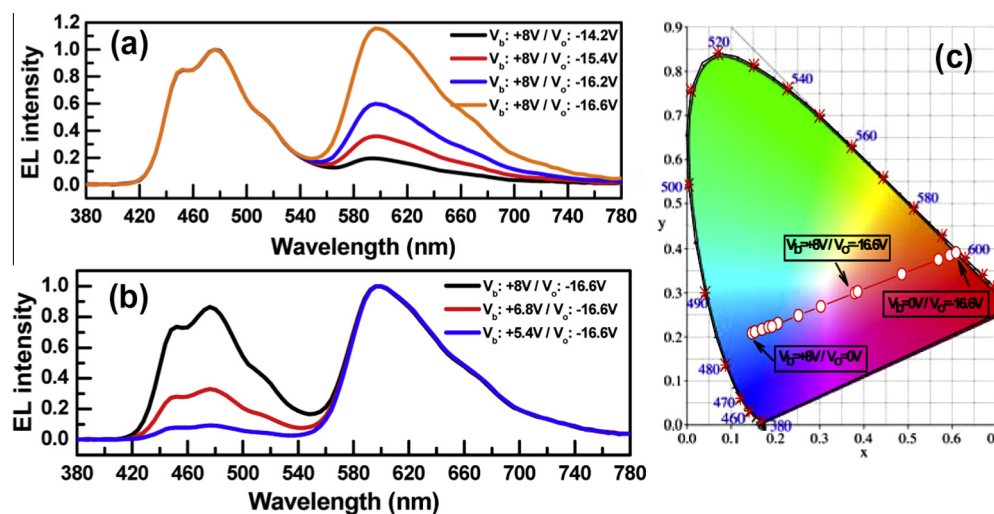


Fig. 5. (a) EL spectra of the device when the negative pulse amplitude (a) or the positive pulse amplitude (b) is continuously changed. (c) The color range that can be achieved by using the proposed driving settings. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(0.21, 0.23) to near white (0.38, 0.29), as shown in Fig. 5a. While by fixing the $V_o = -16.6$ V and gradually decreasing the V_p from 8 V to 5.4 V, the blue emission is reduced and therefore changes the CIE coordinates from near white (0.38, 0.29) to near orange (0.57, 0.37). As shown in Fig. 5a and b, the light emitted from red and blue elements of the device can be varied independently of the other, allowing for continuous color tuning between the extremes of the color offered by the individual element. In Fig. 5c, the CIE coordinate of the spectra in Fig. 5a and b is calculated and plotted, to illustrate the color tuning range that has been achieved.

It is also worth to be noted that the proposed driving scheme not only can tune the color easily, but also improve the lifetime of the devices effectively. Because when one color sub-OLED works the other color sub-OLED is reversely biased. It has been pointed out that the buildup of trapped space charges or the mobile ions during the forward bias is harmful to the stability of organic material [16]. With the help of the reverse bias, the accumulated space charges or the mobile ions can be driven out from the organic layers and therefore improve the lifetime of the devices [16–18].

4. Summary

In summary, by combining b-NBOLED and o-IBOLED together, we have achieved the fabrication of side-by-side color tunable OLEDs without mask alignment. The intensity of b-NBOLED and o-IBOLED can be independently controlled by the positive and the negative pulses of the square wave voltage source. Continuous color tuning has been demonstrated by simply adjusting the amplitude ratio of the positive and negative pulses. Due to elimination of mask alignment, the process TAC time may be reduced, yield may be improved and therefore manufacturing cost may be cut down. The performance of the demonstrated

color tunable OLEDs can be further improved with finer metal mask and efficient electron injection layer for the o-IBOLED.

5. Experiment

The device was fabricated on 80 nm thick ITO coated glass with a sheet resistance of $25 \Omega/\square$. The o-IBOLED was grown first by sequential evaporation with structure glass/ITO (80 nm)/Yb (8 nm)/TPBi (40 nm)/6% Ir(2-phq)₂(-acac):CBP (20 nm)/NPB (60 nm)/MoO₃ (8 nm)/Al (150 nm), (ITO: indium-tin-oxide; TPBi: 2,2',2''-(1,3,5-benzinetriyl)tris(1-phenyl-1-H-benzimidazole); Ir(2-phq)₂(-acac):bis(2-phenylquinoline)(acetylacetonate)iridium(III); CBP: 4,4'-bis(carbazol-9-yl)biphenyl; NPB:N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine), where ITO, Yb and TPBi function as cathode, electron injection layer and electron transporting layer, respectively, Ir(2-phq)₂(acac) was chosen as orange emission dopant and CBP works as the host, NPB, MoO₃ and Al serve as hole transporting layer, hole injection layer and anode respectively. After the fabrication of o-IBOLED, mask was removed and b-NBOLED was deposited with structure glass/ITO(80 nm)/MoO₃ (8 nm)/NPB (60 nm)/6% BCZVBi:CBP (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (150 nm), (BCZVBi: 4,4-bis(9-ethyl-3-carbazovinylenyl)-1,1-biphenyl), where ITO, MoO₃ and NPB act as anode, hole injection layer and hole transporting layer, respectively, BCZVBi was selected as blue emission dopant, TPBi, LiF and Al function as electron transporting layer, electron injection layer and cathode respectively. All organic layers were thermally evaporated in a multi-source vacuum organic chamber at a base pressure of around 5×10^{-7} Torr, while all inorganic layers were thermally evaporated in metal chamber with the same vacuum condition. The luminance–voltage characteristic of the device was measured by the HP4145B semiconductor parameter analyzer and a cali-

brated UDT PIN-25D silicon photodiode. The electroluminescent (EL) spectra were obtained with the PR650 spectrophotometer.

Acknowledgements

Y. Jiang and J. Lian contributed equally to this work. This work was financially supported by the Hong Kong Government Research Grants Council Theme Based Research Scheme number T23-713/11-1, AoE P03/08 and HKUST2/CRF/10. Natural Science Foundation of China (Grand No. 61106094 and 20972097), Educational Commission of Guangdong Province (Grant No. LYM11111).

References

- [1] C.W. Tang, S.A. VanSlyke, Organic electroluminescent diodes, *Appl. Phys. Lett.* 51 (1987) 913–915.
- [2] S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lüssem, K. Leo, White organic light-emitting diodes with fluorescent tube efficiency, *Nature* 459 (2009) 234–239.
- [3] S. Chen, G. Tang, W.-Y. Wong, H.-S. Kwok, White organic light-emitting diodes with evenly separated red, green and blue colors for efficiency/color-rendition trade-off optimization, *Adv. Funct. Mater.* 21 (2001) 3785–3793.
- [4] S. Chen, Z. Zhao, Z. Wang, P. Lu, Z. Gao, Y. Ma, B.Z. Tang, H.-S. Kwok, Bi-layer non-doped small-molecular white organic light-emitting diodes with high colour stability, *J. Phys. D: Appl. Phys.* 44 (2011) 145101.
- [5] M. Berggren, O. Inganäs, G. Gustafsson, J. Rasmussen, M.R. Anderson, T. Hjertberg, O. Wennerstrom, Light-emitting diodes with variable colours from polymer blends, *Nature* 372 (1994) 444–446.
- [6] M. Granstrom, O. Inganäs, White light emission from a polymer blend light emitting diode, *Appl. Phys. Lett.* 68 (1996) 147–149.
- [7] Y. Yang, Q. Pei, Voltage controlled two color light-emitting electrochemical cells, *Appl. Phys. Lett.* 68 (1996) 2708–2710.
- [8] P.E. Burrows, S.R. Forrest, S.P. Sibley, M.E. Thompson, Color-tunable organic light-emitting devices, *Appl. Phys. Lett.* 69 (1996) 2959–2961.
- [9] Z. Shen, P.E. Burrows, V. Bulovic, S.R. Forrest, M.E. Thompson, Three-color, tunable, organic light-emitting devices, *Science* 276 (1997) 2009–2011.
- [10] G. Gu, V. Khalfin, S.R. Forrest, High-efficiency, low-drive-voltage, semitransparent stacked organic light-emitting device, *Appl. Phys. Lett.* 73 (1998) 2399–2401.
- [11] G. Parthasarathy, G. Gu, S.R. Forrest, A full-color transparent metal-free stacked organic light emitting device with simplified pixel biasing, *Adv. Mater.* 11 (1999) 907–910.
- [12] G. Gu, G. Parthasarathy, S.R. Forrest, A metal-free, full-color stacked organic light-emitting device, *Appl. Phys. Lett.* 74 (1999) 305–307.
- [13] S. Chen, H.-S. Kwok, Full color organic electroluminescent display with shared blue light-emitting layer for reducing one fine metal shadow mask, *Org. Electron.* 13 (2012) 31–35.
- [14] S.-Y. Chen, T.-Y. Chu, J.-F. Chen, C.-Y. Su, C.H. Chen, Stable inverted bottom-emitting organic electroluminescent devices with molecular doping and morphology improvement, *Appl. Phys. Lett.* 89 (2006) 053518.
- [15] D.-S. Leem, S.-Y. Kim, J.-H. Lee, J.-J. Kim, High efficiency p-i-n top emitting organic light-emitting diodes with a nearly Lambertian emission pattern, *J. Appl. Phys.* 106 (2009) 063114.
- [16] S.A. VanSlyke, C.H. Chen, C.W. Tang, Organic electroluminescent devices with improved stability, *Appl. Phys. Lett.* 69 (1996) 2160–2162.
- [17] T. Tsujioka, Y. Hamada, H. Takahashi, Operating current mode dependence of luminescence properties of rubrene-doped yellow organic light emitting diodes, *Jpn. J. Appl. Phys.* 39 (2000) 3463–3465.
- [18] M. Yahiro, D. Zou, T. Tsutsui, Recoverable degradation phenomena of quantum efficiency in organic EL devices, *Synth. Met.* 111–112 (2000) 245–247.