Printable candlelight-style organic light-emitting diode

J H Jou*, M Singh, W C Song and S H Liu

Department of Materials Science and Engineering, National Tsing Hua
University, Hsinchu 30013, Taiwan
E-mail: jjou@mx.nthu.edu.tw

Abstract

Candles or oil lamps are currently the most friendly lighting source to human eyes, physiology, ecosystems, artifacts, environment, and night skies due to their blue light-less emission. Candle light also exhibits high light-quality that provides visual comfort. However, they are relatively low in power efficacy (0.3 lm/W), making them energy-wasting, besides having problems like scorching hot, burning, catching fire, flickering, carbon blacking, oxygen consuming, and release of green house gas etc. In contrast, candlelight organic light-emitting diode (OLED) can be made blue-hazard free and energy-efficient. The remaining challenges are to maximize its light-quality and enable printing feasibility, the latter of which would pave a way to cost-effective manufacturing. We hence demonstrate herein the design and fabrication of a candlelight OLED via wet-process. From retina protection perspective, its emission is 13, 12 and 8 times better than those of the blue-enriched white CFL, LED and OLED. If used at night, it is 9, 6 and 4 times better from melatonin generation perspective.

Keywords: Candlelight, High Light-Quality, Melatonin Suppression, Retina Exposure Limit, Printable OLED.

1. Introduction

Intense visible light that consists of high energy blue radiation can penetrate cornea and lens of human eyes and damage the retinal cells. It can also cause an age-related macular degeneration (AMD), an irreversible blindness.[1-2] More exposure to modern lighting is increasing the percentage of vision loss due to AMD. Several medical studies also showed concern about intense white light, which can cause circadian disruption and sleep disorder by suppressing the melatonin secretion.[3-5] Kloog et al. reported that women exposed to bright light at night were found to have a higher risk of breast cancer occurrence than those to the least light exposure.[6] Brainard et al. reported that over exposure of light at night would disrupt the circadian clock by suppressing the melatonin-secretion, and cause breast cancer among women.[7-8] Moreover, some studies have been done on artifacts in Van Gogh museum and found that intense white light had deteriorated the actual colors of the oil paintings through bleaching.[9-10] The International Dark-Sky Association reported that high color temperature modern light disrupts the living-behavior of diverse nocturnal creatures and destructs the ecosystem.[11] The light pollution is a serious threat to nocturnal species, especially for fireflies, tree-frogs, monarch butterflies, sea turtles, and Atlantic salmon.

Steps toward modernization and development are also leading to the more exposure to the blue emission. People are frequently using portable display devices, TVs, computer screens, and artificial lighting. Blue emission hazards is increasing day by day. Therefore, the development of a good light that is at least safe

to retina, physiology and psychology, should become a priority of R&D in solid state lightings. In addition to energy-saving issues, US Department of Energy had also addressed the need for a human-friendly light source.[12]

It should be noted that candles have been used for more than 5000 years. Its continuous emission is free from ultraviolet and deep blue radiation. Candle exhibits low color temperature (1,850 K) chromaticity[13] and create a pleasant sensation, which may originate from the naturally occurring melatonin secretion and helps relax people. Therefore, a solid state lighting source that mimics the positive characteristics of candlelight, such as little deep-blue or violet emission, low color temperature, and continuous and diffused emission, and avoids the unpleasant smoke and burning hazards would be an ideal direction. Organic light emitting diode (OLED) is a preferred option due to its inherent design flexibility and easily tunable chromaticity.

OLEDs can be fabricated either through dry-process or wet-process. Dry-process involved thermal evaporation of organic materials under high vacuum. This approach is mostly preferred for small molecules to achieve high device performance, including high efficiency and long lifetime. However, there is some issues like confined area, high vacuum requirement, more material consumption, low throughput, and difficulties in multiple dopants co-evaporation etc. In contrast, wet-processed enables flexible, large area-size OLED devices. Wet-processed OLED is capable of realizing printable feasibility. By employing printing technique such as ink-jet, roll-to-roll, and letterpress application, OLED device fabrication can achieve cost-effective mass production.

In 2013, Jou's group reported an innovative organic light-emitting diode (OLED) "candle light-style OLED", which can minimize the blue-emission hazards.[14] The device showed a color temperature of 1,970 K with an efficacy of 24.2 lm/W. They also reported a blue-hazard free general lighting based on candle light OLED with a color temperature of 2,279 K, a power efficiency of 85.4 lm/W.[15] In 2014, Zhang's group report low color temperature OLED 1,883 K with an efficacy of 8.3 lm/W[16] and Ma's group reported 54.6 lm/W a 1,910 K OLED.[17] All these efforts were to fabricate low color temperature OLEDs using hybrid process, multiple emissive layer, and interlayer.[17-19] A few efforts have been attempted to realize a low color temperature illumination via wet-process. In 2012, Jou's group reported a physiologically-friendly low color-temperature (1,773 K) OLED with an efficacy of 11.9 lm/W.[20] The device exhibited a much lower color temperature than incandescent bulb (2000-2500 K).

In this study, we have fabricated very-high light-quality candle light-style OLEDs via wet-processable emissive layer. An emissive layer was composed by four blackbody-radiation complementary emitters, namely sky blue, green, deep red, and yellow, doped in a host 4, 4, N N-dicarbazolebiphenyl (CBP). The fabricated devices showed a low melatonin suppression sensitivity (MSS) and high maximum retina admissible exposure limit "t" than those of blue enriched white CFL, LED and OLED. These high light-quality candle light-style OLEDs enabled a cost-effective method for healthy illumination.

2. Theoretical

2.1 Maximum retina admissible exposure limit "t"

The maximum retina admissible exposure limit "t" (sec) was formerly reported by International Electrotechnical Commission (IEC).[21] The value of "t" can be determined according to the IEC 62471 standard,[21] as shown below.

$$t = \frac{100}{E_B}$$ ....(1)

Where, E_B is defined as the blue-light weighted irradiance, and is calculated from the spectral irradiance and blue-light hazard function.

The permissible retinal exposure is calculated from the radiance of the given light source that is directed to the human eye. For eye protection, the blue-light effective radiation must be limited for a duration. The maximum exposure duration for blue light could be equal to or lower than 100 s if the human eye is directed to a light source of radiation $E_B = 1$ W/m^2.[22] If the radiance is less than 1 W/m^2, the exposure limit will exceed 100 s. The calculated exposure limit "t" can be classified into four risk groups namely, Risk Group 0, Risk Group 1, Risk Group 2, and Risk Group 3, if "t" is greater than 10,000 s, between 10,000 and 100 s, between 100 and 0.25 s, or less than 0.25 s, respectively. Risk group 0 is assigned for "no risk" to retina.

2.2 Melatonin Suppression Sensitivity determination

The action spectrum of MLT suppression per photon quanta, S_{PQ}, was first presented by Jou in the US patent.[23] The action spectrum of melatonin suppression power per photon quanta, S_{PQ} for a given monochromatic light, λ, relative to that of the reference light, λr, can be expressed as follows:

$$S_{PQ}(\lambda) = 10^{(\lambda r - \lambda)/C}$$ .... (2)

Where, C is a fitting constant.

The photopic luminosity function $V(\lambda)$ convert $S_{PQ}(\lambda)$ into the melatonin suppression power per lux, $S_{LC}(\lambda)$, in order to give it a practical meaning for general illumination purpose. The action spectrum of melatonin suppression per lux, $S_{LC}(\lambda)$

$$S_{LC}(\lambda) = \lambda S_{PQ}(\lambda)/V(\lambda)$$ ....(3)

The action spectrum of MLT suppression per lux for a given polychromatic light and can be expressed as following:

$$S_{LC}(\lambda) = \frac{\int \lambda S_{PQ}(\lambda) S_I(\lambda) d\lambda}{\int V(\lambda) S_I(\lambda) d\lambda}$$ .... (4)

Where, $S_I(\lambda)$ is the power spectrum of the studied light.

Melatonin suppression sensitivity of a given light relative to the reference blue light of 480 nm i.e.

Relative melatonin suppression sensitivity $= \frac{S_{LC}(\lambda)}{S_{LC}(480\text{ nm})} \times 100\%$ .... (5)

2.3 Light-quality, SRI determination

The light quality of a given light can be quantified by the natural light spectrum resemblance index, SRI, according to Jou et al.[24] For human eye's perspective, the power spectrum of a given light source is converted to the luminance spectrum. The SRI, which is based on a direct comparison of the luminance spectrum of a given light source with the reference blackbody-radiation at the same color temperature, can be defined as following:

$$SRI = \frac{\int L(\lambda,T)\,d\lambda}{\int LBR(\lambda,T)\,d\lambda} \times 100\% \qquad\qquad \cdots\cdots (6\ )$$

Where, $L_{BR}(\lambda,T)$ is the luminance spectrum of the blackbody-radiation, and $L(\lambda,T)$ is the overlapping area between the luminance spectra of the studied light source and its corresponding blackbody-radiation.

3. Experimental

3.1 Device structure

Figure 1 showed the corresponding energy level diagram of all the studied candle light-style OLED devices. Wet-processed OLEDs consisted with a cross-linkable hole-transporting material as well as electron-confining layer of 3,6-bis(4-vinylphenyl)-9-ethylcarbazole (VPEC). The devices were composed by four candlelight complementary dyes, namely sky-blue, green, yellow, and deep-red. The emissive layer consisted of a host 4,4,NN-dicarbazolebiphenyl (CBP) doped with green dye tris(2phenyl-pyridine) iridium (Ir(ppy)3), sky-blue dye bis[3,5-difluoro-2-(2-pyridyl)phenyl]-(2carboxypyridyl) iridium(III) (Firpic), deep-red dye bis(1-phenylisoquinolinolato-C2,N) iridium (acetylacetonate) (Ir(piq)2(acac)), and yellow dye Iridium(III) bis(4-phenylthieno[3,2-c]pyridinatoN,C2) acetylacetonate (PO-01).
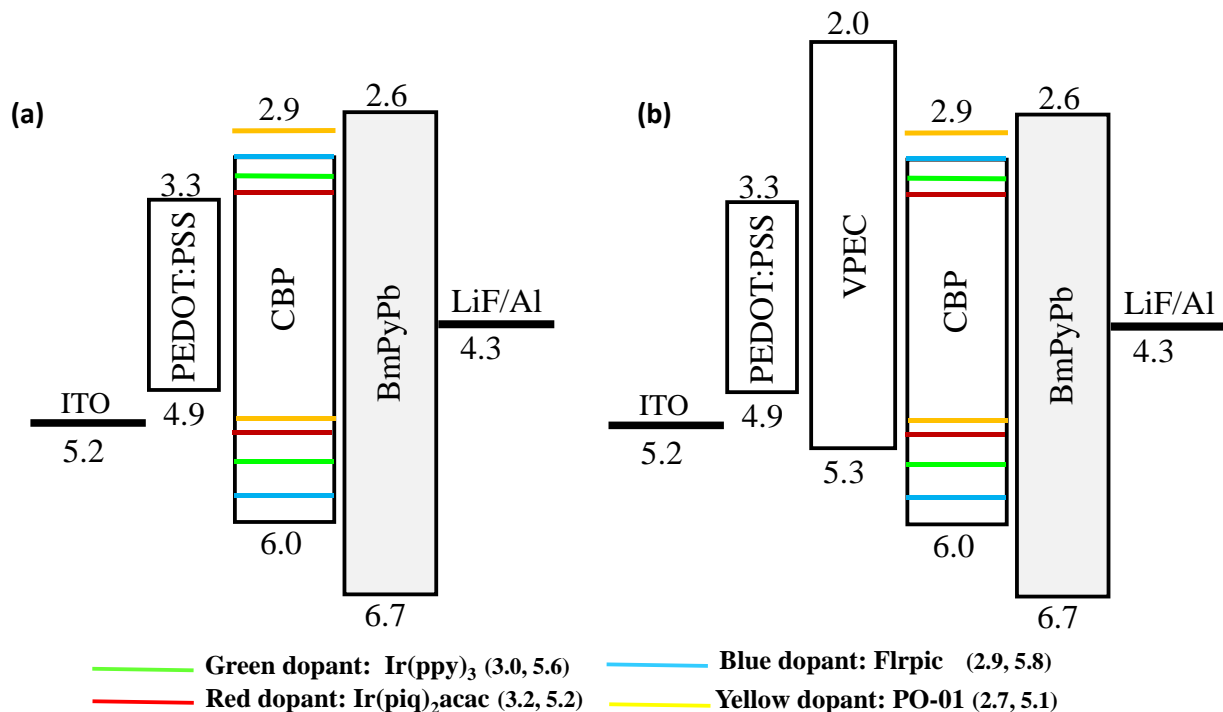

Figure 1. Schematic diagrams of the energy levels of the candle light-style OLEDs with a wet-processed emissive layer (a) without and (b) with a cross-linkable electron confining layer, VPEC.

3.2 Device fabrication

Each device consisted of a pre-cleaned 125 nm indium tin oxide (ITO) anode layer. A hole-injection layer (HIL) of an aqueous solution of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS)

was spin-coated at 4000 rpm for 20s. The resulting hole-injection layer was baked at 160 °C for 40 mins. VPEC polymer dissolved in the solvent chlorobenzene and resulting solution was spin-coated at 3,000 rpm for 20s onto the per dried PEDOT:PSS layer to form a 10 nm hole transporting layer (HTL). The HTL was baked at 120 °C for 20 mins to remove residual solvent, then heated at 230 °C for 40 mins for crosslinking reaction.[25] Thereafter, an emissive layer solution was spin-coated at 2500 rpm for 20 s. A 32 nm 1,3-bis(3,5-dipyrid-3-yl-phenyl) benzene (BmPyPb) electron transporting layer, a 1 nm lithium fluoride (LiF) electron injection layer and a 100 nm aluminum (Al) cathode layer were deposited via a thermal evaporation process at the pressure of 10^{-4} Torr.

3.3 Characterization

All devices were measured under atmospheric condition. The current density-voltage and luminance (J-V-L) characteristics of the resultant devices were measured through a Keithley 2400 electrometer with Minolta CS-100A luminance-meter, while the spectrum and CIE color chromatic coordinates were measured by using PR-655 spectrascan spectroradiometer. Further, quality of emission spectrum were defined in terms of color rendering index, CRI and natural light-style spectrum resemblance index, SRI. Emission spectrum of the devices was also characterized for melatonin suppression sensitivity (MSS) and maximum permissible retina exposure (MPE) limit "t".

4. Results and discussion

Table 1. Effect of doping concentrations on color temperature (CT), light quality, maximum permissible exposure limit (MPE), and melatonin suppression sensitivity (MSS %) of the studied wet-processed candlelight-style OLEDs. Devices 2 and 3 represent VPEC based OLEDs.

Device	Dopant wt%				CIE(x,y)	CT(K)	SRI	CRI	MLT suppression Sensitivity (%)	Max. Exposure limit "t" @ 100 lx
	Blue (Flrpic)	Green (Ir(ppy)$_3$)	Red (Ir(piq)$_2$acac)	Yellow (PO-01)	@ 1,000 cd/m^2					
1	14	0.3	0.9	0.5	(0.51, 0.43)	2300	90	90	9.8	2535
2	14	0.3	0.9	0.5	(0.56, 0.41)	1807	88	91	3.0	4248
3	12	0.3	1.1	0.5	(0.55, 0.41)	1862	89	92	3.2	4328

The OLED devices were fabricated by using various doping concentrations of deep-red dye, Ir(piq)2acac, and sky-blue dye, Flrpic, with a fixed composition of two other complementary dyes: green and yellow as shown in Table 1. With 14 wt.% of sky-blue, 0.3 wt.% of green, 0.9 wt.% of deep-red, and 0.5 wt.% of yellow dye, Device 1 exhibited a color temperature of 2,300 K with an SRI and CRI of 90. The employment of multiple emitters in a single emissive layer extended the emission from 380 to 780 nm (Figure 2a) and realized a very-high CRI and SRI. Emission in the short wavelength region from 380 to 450 nm contributed to a higher color temperature 2,300 K than that of the candlelight (1,850 K) counterpart.

The incorporation of a cross-linkable hole-transport layer of VPEC reduced the color temperature by suppressing the emission in deep blue region (up to 450 nm) while maintained the desirable high light-quality. As can be seen in Figure 2 (a), the wide electroluminescent spectra exhibited four emission bands with a plateau in the long wavelength side. The resulting Device 2 showed a color temperature of 1,807 K with an 88 SRI and a 91 CRI. The lower color temperature OLED showed a decrement in melatonin suppression sensitivity from 9.8 to 3% and an increment of 67% (from 2535 to 4248s) in maximum retina exposure limit. Further, with 12 wt% sky-blue dye and 1.1 wt.% of deep-red dye, Device 3 showed a color temperature of 1,862 K, a very-high CRI of 92, an 89 SRI, and chromaticity (CIEx,y: 0.55, 0.41) analogous

to the black-body radiation, as shown in figure 2(b). The device showed a 3.2% melatonin suppression sensitivity and 4328 s (72 minutes) exposure time to the retina.
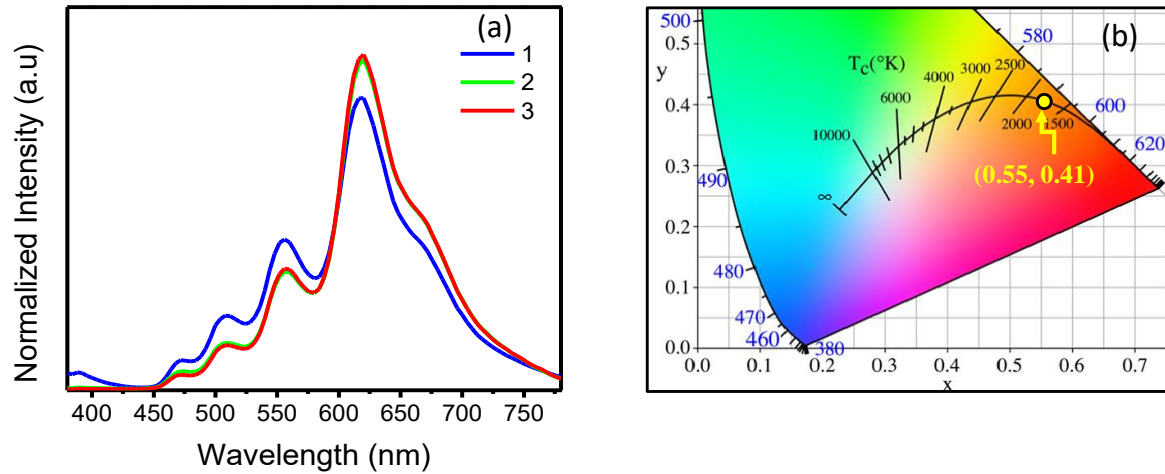

Figure 2.(a) Electroluminescent spectra of wet-processed candlelight-style OLEDs and (b) CIE chromaticity coordinates (0.55, 0.41) of Device 3.

Table 2: Comparison of a printable candlelight-style OLED (1,862 K) with current lighting measures in terms of maximum permissible exposure limit (s) and melatonin suppression sensitivity (%). The presented OLED is a promising candidate to safeguard human eye and physiology due to its blue-hazard free or low color temperature emission.

Light Source	Emission Spectrum	Maximum permissible exposure limit (s)		Melatonin Suppression Sensitivity (%)
		@100 lx	@500 lx	
Candlelight OLED (1,862 K)		4328	847	3.2
Candle (1,850 K)		2616	523	4
Cold-white OLED (5,000 K)		546	109	12
Cold-white LED (5,501 K)		343	67	20
Cold-white CFL (5,921 K)		316	63	29

The fabricated candlelight OLED (1,862 K) is compared with current lighting measures such as cold-white CFL, LED and OLED in terms of melatonin suppression sensitivity (%) and maximum permissible exposure limit (s) at 100 lx and 500 lx. As seen in Table 2, melatonin suppression sensitivity of the candlelight OLED is 3.2% to that of the 480 nm blue light. Whilst, it is 4% for candles. The candlelight OLED is 9, 6 and 4 times safer than those of the cold-white CFL, LED and OLED, respectively. At 100 lx, the OLED showed 13, 12 and 8 times more retina exposure time than those of the blue-enriched white CFL, LED and OLED. By increasing the applied illuminance from 100 to 500 lx, exposure limit would be decreased by 5 times. It should be noted that both color temperature of the emission spectrum and applied illuminance affect the maximum permissible exposure limit to retina.
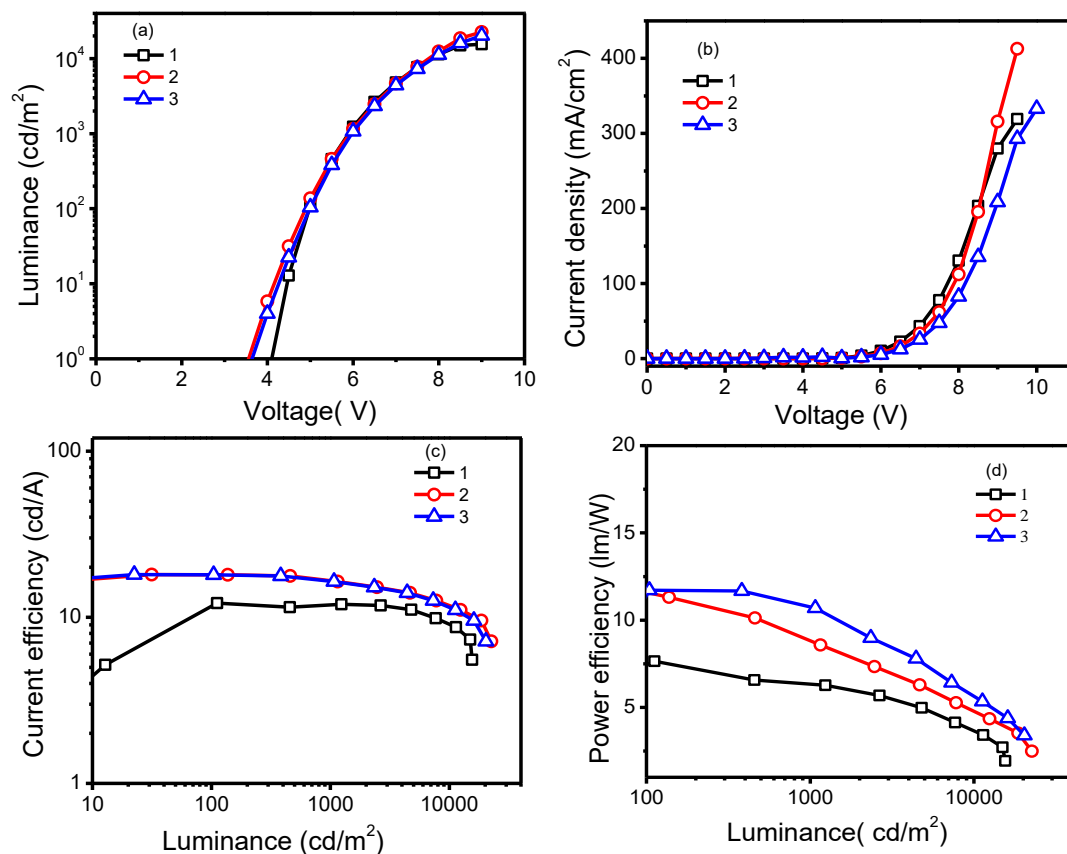

Figure 3. Comparison of (a) luminance, (b) current density, (c) current efficiency, and (d) power efficiency of the fabricated wet-processed candlelight-style OLED 1, 2 and 3.

The measured current density–voltage–luminance characteristics for Devices 1, 2 and 3 are shown in figure 3. Initially, Device 1 exhibited a maximum luminance of 15,520 cd/m^2, a power efficiency of 7.2 lm/W and a current efficiency of 11.3 cd/A at 100 cd/m^2. The comparatively lower device efficiency may be due to concentration quenching effect.[26] However, there existed triplet exciton energy transfer routes, including energy transfer from the sky-blue emitter to the host, CBP, due to its high triplet energy (2.65 eV), as comparing 2.55 eV for CBP, and then from the host to the other three emitters. Additionally, the electron-transport layer, BmPyPb, functioned in two ways; i) it provided a balanced charge injection because of its high electron mobility (1×10^{-4} cm^{2}V^{-1}s^{-1})[27] and ii) its deep HOMO level (-6.7 eV) and high

triplet energy (2.65 eV) blocked the holes and confined the excitons in the emissive layer, respectively. Exciton confinement by the electron-transport layer could lead to a high luminous OLED device.

By incorporating a hole-transport layer, VPEC, the device showed a maximum luminance of 22,610 cd/m^2, and a power efficiency of 11.8 lm/W and a current efficiency of 18 cd/A. As seen in the current density-voltage result, Figure 3b, a 60% improvement in current density was observed as a VPEC layer was incorporated in OLED device. That is because the hole-transporting VPEC layer provided a relatively lower energy barrier (0.4 eV) as comparing with the large energy barrier (1.1 eV) between the interface of PEDOT:PSS and CBP host (Device 1), and hence greatly improved the injection of hole, leading to the observed higher current density. The effect of having a high current density can be seen in the luminance-voltage plot shown in Figure 3 a, wherein the VPEC based devices (2 and 3) showed slightly lower driving voltages and improved maximum luminescence. The incorporation of the cross-linkable hole-transport layer of VPEC enhanced the device performance by facilitating a balanced carrier injection in the emissive layer. A relatively lower (0.7 eV) HOMO level of VPEC than that of CBP host allows a smoother hole injection from the anode to emissive layer and a high (-2.0 eV) LUMO level can effectively prevent overflow of the electrons from the emissive layer. The OLEDs with VPEC also showed better performance either from the viewpoint of current efficiency or power efficiency (Figures 3c and d). Device 3 showed a slightly higher efficacy as comparing with Device 2 at high brightness. It is because of the high triplet energy (2.88 eV)[25] of VPEC effectively can prevent the out-diffusion of exciton formed in the sky-blue emitter and enhance efficacy. In summary, the performance enhancements may be attributed to the hole transport material, VPEC, that enables a favorable hole-injection as well as effective electron- and exciton-confinement.

5. Conclusion

In this study, we have fabricated wet-processed candlelight-style OLED devices. Multiple complementary emitters in a single emissive layer provided a wide-wavelength spectrum ranging from 450 to 780 nm. The fabricated candlelight-style OLED exhibited a blue-hazard free, human eye- and physiological-friendly low color temperature emission. Its emission spectrum should presumably permit 13 times more exposure duration to retina before causing any damage to retina cells and shows 6 times less suppression sensitivity to melatonin-secretion as comparing with the high color temperature cold-white CFL. The presented candlelight-style OLEDs showed a very-high light-quality emission that provides visual-comfort without hydrocarbon burning issues. It can be used as a human- and environment-friendly lighting source.

References

[1]   Singerman L J and Miller D G, *Rev Ophthalmol.* **10,** 88 (2003).
[2]   Melton R, *Rev opt.* **2**, 151 (2014).
[3]   Pauley S M, *Med. Hypotheses.* **63**, 588 (2004).
[4]   Mills P R, Tomkins S C and Schlangen L J M, *J. Circadian Rhythm.* **5**, 1 (2007).

[5] Sato M, Sakaguchi T and Morita T, *Biol. Rhythm. Res.* **36**, 287 (2005).

[6] Kloog I, Haim A, Stevens R G, Barchanade M and Portnov B A, *Chronobiology Intl.* **25**, 65 (2008).

[7] Stevens R G, Brainard G C, Blask D E, Lockley S W and Motta M E, *CA Cancer J. Clin.* **64**, 207 (2014).

[8] Davis S, Mirick D K and Stevens R G, *J. Natl. Cancer Inst.* **93**, 1557 (2001).

[9] http://www.vangogh.ua.ac.be

[10] Monico L et al. *S. Anal. Chem*. **85**, 851 (2013).

[11] http://www.darksky.org

[12] Solid-State Lighting Research and Development: Multi-Year Program Plan, Office of Energy Efficiency and Renewable Energy, U.S. Department of Energy, Washington, DC p. 52 (April 2013).

[13] Jou J H, Su Y T, Liu S H, He Z K, Sahoo S, Yu H H, Chen S Z, Wang C W and Lee J R, , *J. Mater. Chem.* C **4**, 6070 (2016).

[14] Jou J H, Hsieh C Y, Tseng J R, Peng S H, Jou, Y C, Hong J H, Shen S M, Tang M C, Chen P C, and Lin C H, *Adv. Funct. Mater.* **23**, 2750 (2013).

[15] Jou J H, Kumar S. An C C, Singh M, Yu H H, Hsieh C Y, Lin Y X, Sung C F and Wang C W, *Optics Express*. **23**, 576 (2015).

[16] Y Gong Y, Liu J, Zhang Y, He G, Lu Y, Fan W B, Yuan W Z, Sun J Z and Zhang Y, *J. Mater. Chem.* C **2**, 7552 (2014).

[17] Hu Y, Zhang T, Chen J, Ma D and Cheng C H, *Isr. J. Chem.* **54**, 979 (2014).

[18] Jou J H, Wang H C, Shen S M, Peng S H, Wu M H, Chen S H and Wu P H, *J. Mater. Chem.* **22**, 8117 (2012).

[19] Jou J H, et al. *J. Mater. Chem*. **21**, 17850 (2011).

[20] Jou J H, *Org. Electron*. **13**, 1349 (2012).

[21] International Electrotechnical Commission. "IEC 62471: 2006." Photobiological safety of lamps and lamp systems. Geneva: IEC (2006).

[22] ICNIRP, "ICNIRP guidelines on limits of exposure to incoherent visible and infrared radiation", Health Physics 105 (1), (2013).

[23] Jou J H, Melatonin suppression extent measuring device. Patent S20120303282 A1 (2012).

[24] Jou J H, et al. A universal, easy-to-apply light-quality index based on natural light spectrum resemblance, Appl. Phys. Lett. 104, 203304-203309, DOI: 10.1063/1.4879635 (2014).

[25] Jou J H, Hwang P Y, Wang W B, Lin C W, Jou Y C, Chen Y L, Shyue J J, Shen S M and Chen S Z, *Org. Electron*, **24**, 254 (2015).

[26] Jou J H et al., *Appl. Phys. Lett.* **96**, 143306 (2010).

[27] Su S J, Gonmori E, Sasabe H. and Kido J, *Adv, Mater*. **20**, 4189 (2008).