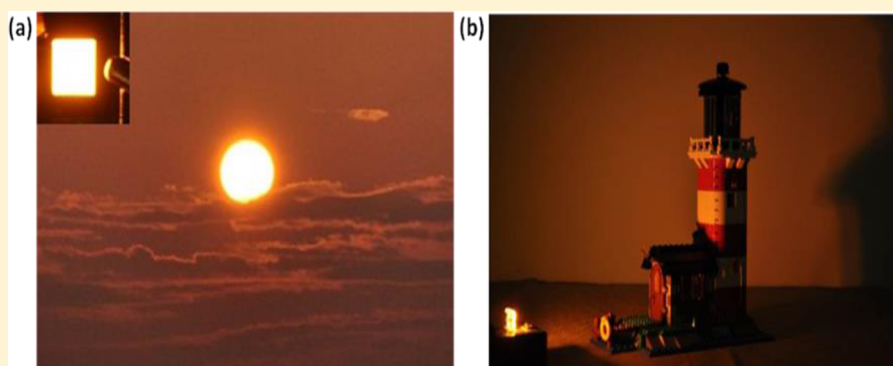


Artificial Dusk-Light Based on Organic Light Emitting Diodes

Jwo-Huei Jou,^{*,†} Ri-Zhong Wu,[†] Hui-Huan Yu,[†] Chieh-Ju Li,[†] Yung-Cheng Jou,[†] Shiang-Hau Peng,[†] Yu-Lin Chen,[†] Chien-Tien Chen,^{*,‡} Shih-Ming Shen,[†] Peter Joers,[§] and Chun-Yu Hsieh[†]

Departments of [†]Materials Science and Engineering and [‡]Chemistry, National Tsing Hua University, Hsin-Chu, Taiwan, 30013, Republic of China

[§]Department of Chemical Engineering, Iowa State University of Science and Technology, Ames, Iowa, United States



ABSTRACT: We demonstrate the feasibility of bringing the sunset hue indoors via a dusk-light-style organic light emitting diode that exhibits a color temperature ranging between 1500 and 3000 K, covering that of sunset hue within the last 30 min before sunset. Like the sunset, the device chromaticity changes from yellowish white to reddish orange, with illuminance decreasing by 60-fold as the color temperature decreases from 2900 to 2100 K. The artificial dusk hue at 2745 K, for example, shows a 92 color rendering index with an 87% luminance spectrum resemblance with the sunset hue. The very high color rendering character is obtained by depositing phosphorescent red and yellow dyes in one emission layer and a fluorescent green dye doped into a fluorescent blue light emitting host in another, separated by a nanoscale carrier modulation interlayer to harvest the ultimate color rendering index and minimize the color temperature.

KEYWORDS: OLED, dusk-light, low color temperature, sunlight

Sunset hue emits diurnally the most charming chromaticity, captivating numberless attention and stirring endless motion as poets have been depicting unceasingly.^{1–3} Sunset hue also affect profoundly the behaviors of animals, such as the migration of birds,^{4–7} birds' chorus at dusk,^{8,9} mating of crabs¹⁰ and moths,¹¹ and so on.

Although it is still not totally clear to the science regarding how the sunset hue imposes such a profound effect on human and the animals, the sunlight at dusk is known to compose an emission weakest in blue and strongest in red. In terms of color temperature, sunset hue exhibits a color temperature that is the lowest during the daytime. Lesser melatonin secretion would be suppressed at night if the employed lighting source is lower in color temperature or lesser in blue emission, as pointed out by many medical studies.^{12–14} The generation of melatonin would help people relax after dusk and sleep well at night, besides being an oncogenic hormone. The myth and functions of sunset hue are hence exploring-worthy.

However, the emersion of sunset hue is uncertain and brief, making the corresponding studies difficult. Moreover, the charming sunset hue is too prompt and too difficult to bring indoors. Devising a dusk hue-style light source has become crucial.

Over the past decades, achieving higher efficiency white light, such as white light emitting diodes (LED)^{15–19} and white organic light emitting diodes (OLED),^{20–24} had been the focal point in light source research. In 2009, a sunlight-style OLED with color temperature tunability was first reported.²⁵ Some low color temperature OLEDs were then reported.^{26–28} High quality light sources with very-high color rendering indexes^{29–31} had become possible and had also brought to the attention of the fields. However, achieving low-color temperature, high color rendering index, and meanwhile high power efficiency has been one major critical issue currently.

We present in this report a novel dusk-light-style light source based on OLED lighting technology. The light source obtained can exhibit dusk hue like chromaticity with a color temperature ranging from 1500 to 3000 K, covering that of dusk-light at different times before sunset, by noting which is 2800 K 30 min before sunset and 1500 K 3 min before sunset. The resulting dusk-light-style OLED can also show a very high color rendering index, such as 92, and a high degree of spectral

Received: August 20, 2013

Published: December 4, 2013

resemblance, such as 87% resemblance in luminance spectrum with that of sunset hue at 2745 K.

EXPERIMENTAL SECTION

The device structure was composed of a 125 nm indium tin oxide (ITO) anode layer, a 35 nm poly(3,4-ethylene-dioxythiophene)-poly(styrenesulfonate) (PEDOT/PSS) hole injection layer, a 22 nm single or double EML(s), a 32 nm 1,3,5-tris(*N*-phe-nylbenzimidazol-2-yl)benzene (TPBi) electron transporting layer, a 0.8 nm lithium fluoride (LiF) electron injection layer, and a 150 nm aluminum cathode layer. The dusk-light-style emission was obtained by using six dusk-hue complementary emitters. They were red light-emitting dye bis(1-phenylisoquino-line)(acetylacetonate)iridium(III) [Ir(piq)₂(acac)], yellow light-emitting dye iridium(III) bis(4-phenylthieno[3,2-*c*]pyridinato-*N,C* 2')acetylacetonate (PO-01), green light-emitting dye tris(2-phenylpyridine)iridium(III) [Ir(ppy)₃] and bis[(*p*-isopropylphenyl)(*p*-tolyl)amino]-10-10-phenanthracene (BPTAPA), sky-blue light-emitting host 3,7-bis(4-*N,N*-diphenylamino)-5,5-spirofluorenyl-5*H*-benzo[*a,d*]cycloheptene (Ph₂N-STIF-NPh₂),³² and deep-blue, light-emitting host 2,7-bis-2[phenyl(*m*-tolyl)amino]-9,9-dimethyl-fluorene-7-yl-9,9-dimethyl-fluorene (MDP3FL), dispersed in two different emissive layers (EMLs). The first EML was designated to yield an energy-efficient orange emission obtained by doping 1 wt % Ir(piq)₂(acac), 5 wt % PO-01, and 5 wt % Ir(ppy)₃ in a host of 4,4'-bis(carbazol-9-yl)biphenyl (CBP), and the second EML to yield a mild bluish green emission obtained by doping 1 wt % BPTAPA in mixing hosts of Ph₂N-STIF-NPh₂ and MDP3FL with 1:1 weight. Device I contains a single orange EML, and device II contains a single bluish-green EML. Devices III and IV contain both the bluish green and orange EMLs with a respective interlayer of CBP and TPBi. The EMLs were thermally deposited at an evaporation rate of 0.5–1 Å/s using solution-premixed molecular targets. The vacuum level was 3×10^{-5} Torr. All devices were measured under atmospheric condition without encapsulation. The luminance, spectrum, and CIE chromatic coordinates results were measured by using a Minolta CS-100A luminance-meter, a PR-655 spectroradiometer, and a Keithley 2400 electrometer was used to measure the current–voltage (*I*–*V*) characteristics. The spectra of dusk hue at from 108 to 1 min before sunset were measured by using a PR-655 spectroradiometer collocated with a Marumi DHG 49 mm to dim the intensive sunlight. The dusk-light illuminance in terms of lux was measured by using a digital illumination meter, TES-1339. All these measurements were carried out at 24°48' N, 120°58' E, located in Hisn-Chu Harbor, Hsin-Chu, Taiwan.

RESULTS AND DISCUSSION

It is noteworthy that the chromaticity, color temperature, and luminance of the sun changes continuously and promptly with time approaching sunset. The sunlight changes its color from yellowish white, to orange yellow, to orange, and to reddish orange at time intervals from 108 to 1 min before sunset (Figure 1a). Due to the absorption by the atmosphere, the locus of the dusk hue deviates from the blackbody radiation locus.

Figure 1b shows the entire spectrum of the sun in the visible range that varies with the time approaching sunset. The spectrum initially peaks at a comparatively shorter wavelength, that is, 600 nm, at 108 min before sunset. The main peaks shift

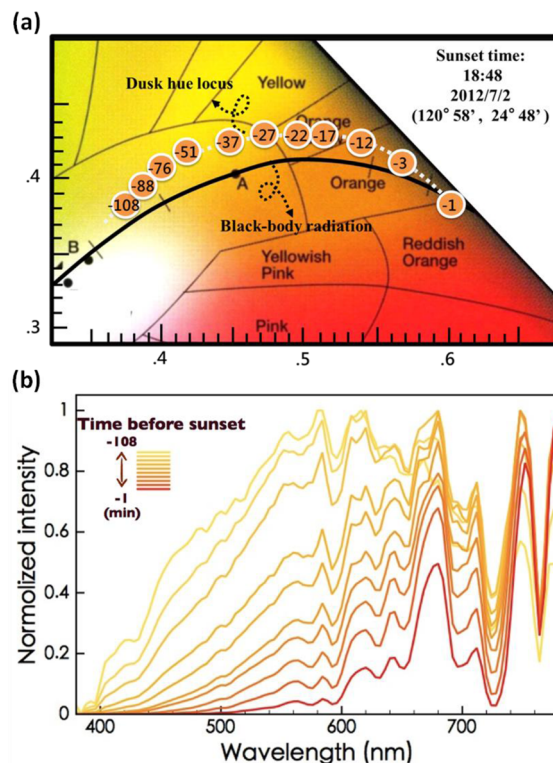


Figure 1. (a) Experimentally measured chromaticity of the sunset hue within the last 108 min before sunset, which changes from yellowish white (–108 min), through orange yellow (–22 min), to orange (–12 min), and to reddish orange (–1 min). (b) Corresponding spectra of the sunset hue, which initially peaks at a comparatively shorter wavelength, that is, 600 nm, and shift toward the long wavelength side at time closer to the sunset, which explains why the sun becomes redder toward sunset.

toward the long wavelength side at time closer to the sunset, which explains why the sun becomes redder.

The uneven absorption by the atmosphere, especially the strong red absorption by the ozonosphere, explains why the emissive spectrum of sunset hue is significantly different from that of blackbody radiation at the same color temperature. The spectra disparity may also explain why sunlight does not show a 100 color rendering index (CRI) especially at the time near sunset. For example, the CRI is 95 at 3000 K, 84 at 2000 K, and 46 at 1500 K.

Figure 2 shows the color temperature of the sun to decrease from 4160 to 1400 K at from 108 to 1 min before sunset. Its corresponding intensity, on the other hand, drastically decreases from 80000 to 520 lx, a near 160-fold decrement. In contrast to the sun, the sky shows a much higher color temperature, which decreases from 12800 to 8760 K, with a much lower brightness, which decreases from 32000 to 480 lx, correspondingly.

However, the sky is still glowing with a greater than 100 lx intensity and its color temperature remains greater 8000 K within the first 10 min after sunset, while no luminance or color temperature can then be observed directly from the sun. In other words, the low color temperature reddish orange sunset hue is rapidly vanishing after sunset, and the ambience is dominated by the high color temperature bluish-white sky light. Further studies would be interesting regarding whether it is the changing chromaticity, color temperature, and luminance of the

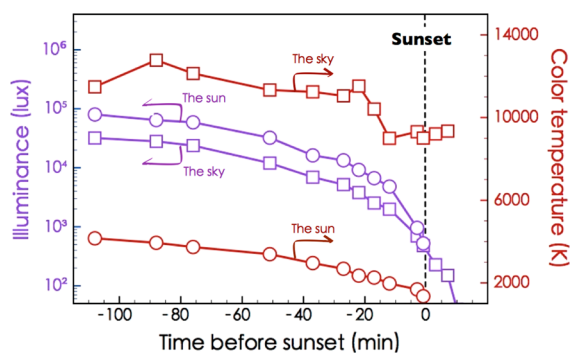


Figure 2. Color temperature of the sunset hue that decreases from 4200 to 1400 K with its corresponding intensity drastically decreasing from 80000 to 500 lx, a near 160-fold decrement, at from 108 to 1 min before sunset. In contrast, the sky shows a much higher color temperature that decreases from 12800 to 8800 K with a much lower brightness decreasing from 32000 to 480 lx, correspondingly. Importantly, the sky is still glowing with a greater than 100 lx intensity and its color temperature remains greater 8000 K within the first 10 min after sunset, while no luminance or color temperature can then be observed directly from the sun.

sun or the sky that plays a major role in affecting the behaviors of animals mentioned above.

Figure 3a shows the photograph of the dusk-light-style OLED device with a 2760 K color temperature, comparing with

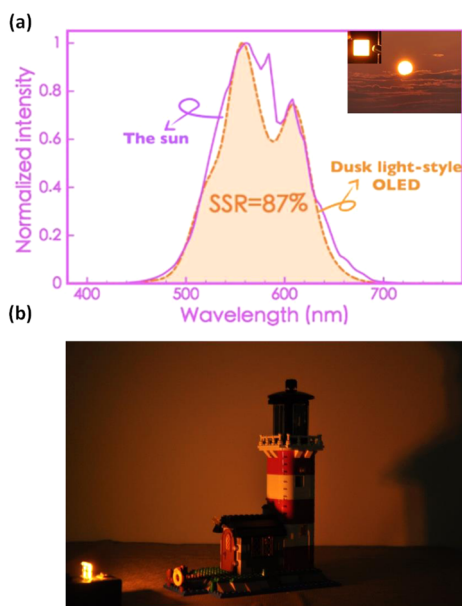


Figure 3. (a) Direct comparison of the dusk hue-style OLED (2760 K) with the sunset hue at 2600 K in terms of spectral luminosity distribution. The dusk-light-style OLED shows an 87% similarity with the sun by comparing their spectral luminance distributions convoluted from their power spectra with luminosity function. (b) Photograph of a miniature lighthouse under the illumination of a dusk-light-style OLED (2200 K).

that of the sunset hue at 2600 K. The inset shows that the two lights have an 87% similarity in their luminance spectra, with the major emissions peaking at around 580 nm, where the luminance spectrum are obtained by convoluting the experimentally determined power spectra with the luminosity function. The high luminance spectrum similarity coupling with a mingling emission peaking at 580 nm explains why they both

emit the extremely similar orange yellow dominant color. Figure 3b shows the photograph of a miniature lighthouse shone under the illumination of the dusk-light-style OLED. The scene mimics that under the sunset hue. These demonstrate the feasibility of bringing the charming sunset hue indoors by employing the dusk-light-style OLED.

Figure 4a shows the device structures of the dusk-light-style OLEDs and their corresponding energy level diagrams. The

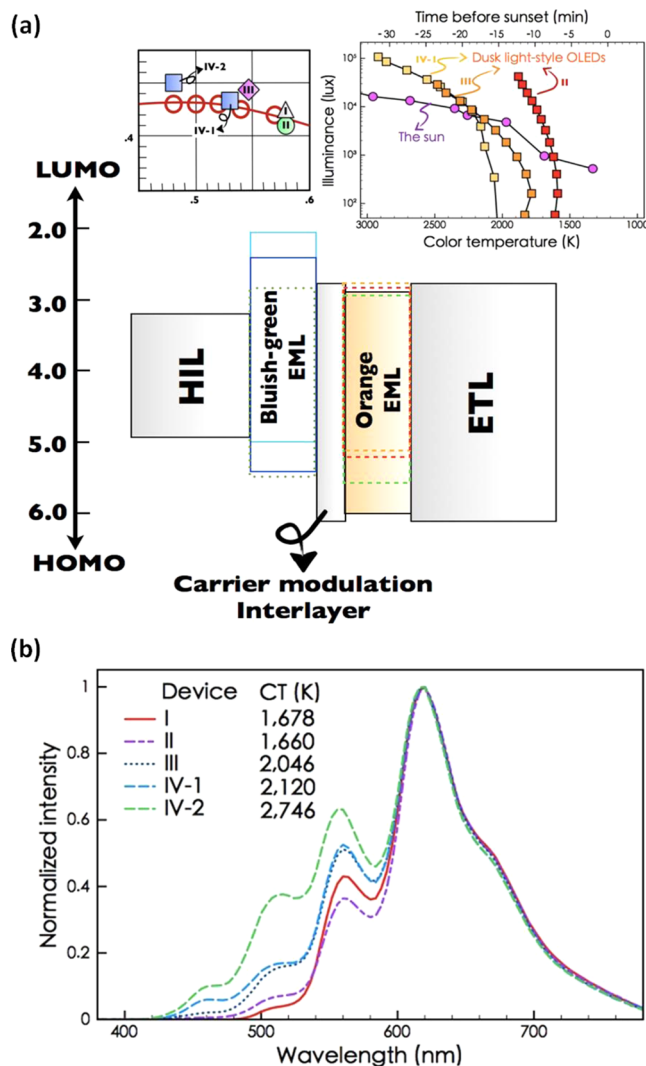


Figure 4. (a) Schematic illustration of the dusk-light style OLED device in terms of energy level. The artificial dusk-light is formed by mingling the emission of a bluish green and an orange emissive layers (EMLs). Top-left inset shows that the color of the dusk-light-style OLED can easily be tuned along the dusk hue locus (in red open circle) via device engineering using different EMLs or carrier modulation interlayers. Top-right inset shows that every dusk-light-style OLED device can easily tune its color temperature along with a changing illuminance mimicking that of sunset hue. (b) Experimentally measured electroluminescent spectra of the dusk-light-style OLEDs with different color temperature.

color temperature of the dusk-light-style OLED can be tuned lower and the chromaticity redder to yield a warmer sensation by engineering the device with different emissive layers and different carrier modulation interlayers etc. As shown in the inset (left), the color temperature decreases from 2745 K for device IV to 1660 K for device I, and the corresponding color

changes from yellow to orange. Even in a single device, such as device IV-1, the chromaticity can change gradually from yellowish white to orange yellow accompanying with an illuminance decreasing from 17000 lx to 1500 lx (right-inset), a 60-fold variation, as the color temperature is decreased from 2900 to 2100 K.

Figure 4b shows the corresponding emissive spectra of the dusk-light-style OLED devices (devices I–IV). The color temperature can be tuned to as low as 1500 K as the blue emissive layer is removed (device I). The device shows a 78% sunlight spectrum resemblance with a 66 CRI. The color temperature is increased to 1700 K and the CRI 74 as a bluish green emissive layer is incorporated (device II). As a 4 nm interlayer of CBP is incorporated between the two emissive layers (device III), the sunlight spectrum resemblance becomes 84% and CRI 86, with a color temperature of 2046 K. By changing the interlayer to a 1 nm TPBi (device IV-1), the sunlight spectrum resemblance becomes 83% and CRI 90, with 2120 K. As the TPBi interlayer is increased to 2 nm (device IV-2), the sunlight spectrum resemblance increases to 87% and CRI to 92, with 2746 K.

To conclude, we demonstrate the feasibility of bringing the sunset hue indoors via the fabrication of a dusk-light-style OLED with a color temperature tunable between 1500 and 3000 K, covering that of dusk hue within the last two hours before sunset. Like the sunset, the dusk-light-style OLED can yield a varying chromaticity that changes gradually from yellowish white to reddish orange accompanying with an illuminance decreasing by 60-fold as the color temperature is decreased from 2900 to 2100 K. The artificial dusk hue at 2745 K for example can also show very high luminance spectrum resemblance with the sunset hue, such as 87% with a 92 CRI.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: jjou@mx.nthu.edu.tw.

*E-mail: ctchen@mx.nthu.edu.tw.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to acknowledge the support from the Energy Fund of Ministry of Economics Affairs and National Science Council, Taiwan. This work was financially supported in part by Grants MEA 102-EC-17-A-07-S1-181, NSC 102-3113-E-007-001, NSC 100-2119-M-007-011-MY3.

REFERENCES

- (1) Lu, Z. h. English Translation of “Tian Jing Sha Autumn”. *J. Chiz. Teac. Col.* **2001**, *2*, 95–97.
- (2) Shu, J. X.; Xu, Y. J. Translator’s subjectivity and english translation of Tang poems-case studies of the English versions of Li Shangyin’s poems. *Jiangsu Univ. Sci. Technol.: Social Sci. Ed.* **2007**, *4*, 54–61.
- (3) Harris, D. *Just Beyond the Sunset and Other Poems*; Lulu Enterprises, UK Ltd.: U.K., 2008.
- (4) Able, K. P.; Able, M. A. Manipulations of polarized skylight calibrate magnetic orientation in a migratory bird. *J. Comp. Physiol., A* **1995**, *177*, 351–356.
- (5) Able, K. P.; Able, M. A. The flexible migratory orientation system of the Savannah sparrow (*Passerculus sandwichensis*). *J. Exp. Biol.* **1996**, *199*, 3–8.

- (6) Able, K. P.; Able, M. A. Development of sunset orientation in a migratory bird: No calibration by the magnetic field. *Anim. Behav.* **1997**, *53*, 363–368.

- (7) Akesson, S.; Backman, J. Orientation in pied flycatchers: The relative importance of magnetic and visual information at dusk. *Anim. Behav.* **1999**, *57*, 819–828.

- (8) Erne, N.; Amrhein, V. Long-term influence of simulated territorial intrusions on dawn and dusk singing in the Winter wren: Spring versus autumn. *J. Ornithol.* **2008**, *149*, 479–486.

- (9) Penteriani, V.; Delgado, M. D. The dusk chorus from an owl perspective: Eagle owls vocalize when their white throat badge contrasts most. *Plos One* **2009**, *4*, 1–4.

- (10) Kosuge, T.; Murai, M.; Nishihira, M. Dusk-copulation of the rock-dwelling ocypodid, *Ilyoplax-integra* (Brachyura). *J. Ethol.* **1992**, *10*, 53–61.

- (11) Kan, E.; Kitajima, H.; Hidaka, T.; Nakashima, T.; Sato, T. Dusk mating flight in the swift moth, *Endoclita excrescens* (Butler) (Lepidoptera: Hepialidae). *Appl. Entomol. Zool.* **2002**, *37*, 147–153.

- (12) Brainard, G. C.; Richardson, B. A.; King, T. S.; Reiter, R. J. The influence of different light spectra on the suppression of pineal melatonin content in the syrian-hamster. *Brain Res.* **1984**, *294*, 333–339.

- (13) Lockley, S. W.; Brainard, G. C.; Czeisler, C. A. High sensitivity of the human circadian melatonin rhythm to resetting by short wavelength light. *J. Clin. Endocr. Metab.* **2003**, *88*, 4502–4505.

- (14) Pauley, S. M. Lighting for the human circadian clock: Recent research indicates that lighting has become a public health issue. *Med. Hypotheses* **2004**, *63*, 588–596.

- (15) Liu, W. R.; Yeh, C. W.; Huang, C. H.; Lin, C. C.; Chiu, Y. C.; Yeh, Y. T.; Liu, R. S. (Ba,Sr)Y₂Si₂Al₂O₇:Eu²⁺: A novel near-ultraviolet converting green phosphor for white light-emitting diodes. *J. Mater. Chem.* **2011**, *21*, 3740–3744.

- (16) Liu, W. R.; Huang, C. H.; Wu, C. P.; Chiu, Y. C.; Yeh, Y. T.; Chen, T. M. High efficiency and high color purity blue-emitting NaSrBO₃:Ce³⁺ phosphor for near-UV light-emitting diodes. *J. Mater. Chem.* **2011**, *21*, 6869–6874.

- (17) Kuo, T. W.; Huang, C. H.; Chen, T. M. Novel yellowish-orange Sr₈Al₁₂O₂₄S₂:Eu²⁺ phosphor for application in blue light-emitting diode based white LED. *Opt. Express.* **2010**, *18*, A231–A236.

- (18) Huang, C. H.; Chen, T. M. Novel yellow-emitting Sr₈MgLn(PO₄)₇:Eu²⁺ (Ln = Y, La) phosphors for applications in white LEDs with excellent color rendering index. *Inorg. Chem.* **2011**, *50*, 5725–5730.

- (19) Huang, C. H.; Chen, T. M. A novel single-composition trichromatic white-light Ca₃Y(GaO)₃(BO₃)₄:Ce³⁺, Mn²⁺, Tb³⁺ phosphor for UV-light emitting diodes. *J. Phys. Chem. C* **2011**, *115*, 2349–2355.

- (20) Reineke, S.; Lindner, F.; Schwartz, G.; Seidler, N.; Walzer, K.; Lüssem, B.; Leo, K. White organic light-emitting diodes with fluorescent tube efficiency. *Nature* **2009**, *459*, 234–238.

- (21) Su, S. J.; Gonmori, E.; Sasabe, H.; Kido, J. Highly efficient organic blue-and white-light-emitting devices having a carrier- and exciton-confining structure for reduced efficiency roll-off. *Adv. Mater.* **2008**, *20*, 4189–4194.

- (22) Rosenow, T. C.; Furno, M.; Reineke, S.; Olthof, S.; Luessem, B.; Leo, K. Highly efficient white organic light-emitting diodes based on fluorescent blue emitters. *J. Appl. Phys.* **2010**, *108*, 113113–113115.

- (23) Chen, Y. H.; Chen, J. S.; Ma, D. G.; Yan, D. H.; Wang, L. X. Tandem white phosphorescent organic light-emitting diodes based on interface-modified C-60/pentacene organic heterojunction as charge generation layer. *Appl. Phys. Lett.* **2011**, *99*, 103304–103306.

- (24) Sasabe, H.; Takamatsu, J.; Motoyama, T.; Watanabe, S.; Wagenblast, G.; Langer, N.; Molt, O.; Fuchs, E.; Lennartz, C.; Kido, J. High-efficiency blue and white organic light-emitting devices incorporating a blue iridium carbene complex. *Adv. Mater.* **2010**, *22*, 5003–5007.

- (25) Jou, J. H.; Wu, M. H.; Shen, S. M.; Wang, H. C.; Chen, S. Z.; Chen, S. H.; Lin, C. R.; Hsieh, Y. L. Sunlight-style color-temperature

tunable organic light-emitting diode. *Appl. Phys. Lett.* **2009**, *95*, 013307–013310.

(26) Jou, J. H.; Chen, S. H.; Shen, S. M.; Jou, Y. C.; Lin, C. H.; Peng, S. H.; Hsia, S. P.; Wang, C. W.; Chen, C. C.; Wang, C. C. High efficiency low color-temperature organic light-emitting diodes with a blend interlayer. *J. Mater. Chem.* **2011**, *21*, 17850–17854.

(27) Jou, J. H.; Hwang, P. Y.; Wang, W. B.; Lin, C. W.; Jou, Y. C.; Chen, Y. L.; Shyue, J. J.; Shen, S. M.; Chen, S. Z. High-efficiency low color temperature organic light emitting diodes with solution-processed emissive layer. *Org. Electron.* **2012**, *13*, 899–904.

(28) Jou, J. H.; Tang, M. C.; Chen, P. C.; Wang, Y. S.; Shen, S. M.; Chen, B. R.; Lin, C. H.; Wang, W. B.; Chen, S. H.; Chen, C. T.; Tsai, F. Y.; Wang, C. W.; Chen, C. C.; Wang, C. C. Organic light-emitting diode-based plausibly physiologically-friendly low color-temperature night light. *Org. Electron.* **2012**, *13*, 1349–1355.

(29) Zhou, G.; Wang, Q.; Ho, C. L.; Wong, W. Y.; M D.; Wang, L. Duplicating “sunlight” from simple WOLEDs for lighting applications. *Chem. Commun.* **2009**, 3574–3576.

(30) Jou, J. H.; Chou, Y. C.; Shen, S. M.; Wu, M. H.; Wu, P. S.; Lin, C. R.; Wu, R. Z.; Chen, S. H.; Wei, M. K.; Wang, C. W. High-efficiency, very-high color rendering white organic light-emitting diode with a high triplet interlayer. *J. Mater. Chem.* **2011**, *21*, 18523–18526.

(31) Jou, J. H.; Shen, S. M.; Lin, C. R.; Wang, Y. S.; Chou, Y. C.; Chen, S. Z.; Jou, Y. C. Efficient very-high color rendering index organic light-emitting diode. *Org. Electron.* **2011**, *12*, 865–868.

(32) Wei, Y.; Chen, C. T. Doubly *ortho*-linked *cis*-4,4'-bis-(diarylamino)stilbene/fluorene hybrids as efficient nondoped, sky-blue fluorescent materials for optoelectronic applications. *J. Am. Chem. Soc.* **2007**, *129*, 7478–7479.