

Very broad white-emission spectrum based organic light-emitting diodes by four exciplex emission bands

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White light is emitted by an organic light-emitting diode by inserting two blend layers of m-MTDATA: Al(DBM)₃ and TPD:Bphen between an m-MTDATA hole-transporting layer and a Bphen electron-transporting layer, where m-MTDATA, TPD, Al(DBM)₃, and Bphen are 4,4',4''-tris[methylphenyl(phenyl)amino]-triphenylamine, *N,N'*-bis(3-methylphenyl)-*N,N'*-diphenylbenzidine, tris(dibenzoyl methane)-aluminum, and 4,7-diphenyl-1,10-phenanthroline molecules, respectively. The white-light spectrum consists of four broad bands that arise from blue-emitting TPD/Bphen, green-emitting m-MTDATA/Bphen, orange-emitting TPD/Al(DBM)₃, and red-emitting m-MTDATA/Al(DBM)₃ exciplexes, respectively, and strongly overlap at 400–760 nm. Any monomer emission is not generated. A high-color rendering index of 94.1, Commission Internationale de l'Eclairage-1931_{x,y} coordinates of (0.33, 0.35), and correlated color temperature of 5477 K were obtained at 10 V. Discussion is given for the formation mechanism of the four exciplexes. © 2009 Optical Society of America

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Electroluminescence (EL) of organic light-emitting diodes (OLEDs) is generated from an molecular exciton that is formed by recombination of an electron and a hole at the same single molecule. In addition to such a monomer exciton emission, there is another EL emission due to exciplexes [1–3]. Exciplex emission is caused by the radiative electron transition from the lowest unoccupied molecular orbital level of the electron acceptor molecule to the highest occupied molecular orbital of the electron donor molecule. Earlier studies on exciplexes in OLEDs were focused mainly on avoiding its formation because of its low EL efficiency [4,5]. Recently, several favorable properties of exciplexes have been paid attention, because exciplexes give a broader emission band than the monomer emission band, and we can change OLEDs with low efficient emitters to highly emissive OLEDs by forming exciplexes [6]. The broad orange-red exciplex emission band is used for white OLEDs (WOLEDs) by combining a monomer emission band [7–9], but such a white color has a lower color-rendering index (CRI). If we want to obtain high CRI using monomer emissions, many kinds of emitting components are needed in the WOLED. This leads to complications of device structure, including an increase in the number of emitting layers.

In this Letter, we present a WOLED with high CRI using only exciplex emissions, without monomer emission. In this WOLED, the blue, green, orange, and red emissions are generated by exciplexes of TPD/Bphen, m-MTDATA/Bphen, TPD/Al(DBM)₃, and m-MTDATA/Al(DBM)₃, respectively, where m-MTDATA, TPD, Al(DBM)₃ and Bphen denote 4,4',

4''-tris[methylphenyl(phenyl)amino]-triphenylamine, *N,N'*-bis(3-methylphenyl)-*N,N'*-diphenylbenzidine, tris(dibenzoyl methane)-aluminum, and 4,7-diphenyl-1,10-phenanthroline, respectively. A wide spectral band with high CRI is obtained at the 400–760 nm region, which consists of four exciplex emission bands without any monomer emission.

The Al(DBM)₃ was synthesized in our laboratory, and the other materials were commercially available. Detailed processes of the fabrication for OLEDs and the measurement methods of photoluminescence (PL) and EL characteristics were described in our previous paper [6]. We first fabricated the following four monochromatic-emitting OLEDs: EL-1, indium-tin-oxide (ITO)/TPD (40 nm)/Bphen (40 nm)/LiF (1 nm)/Al (200 nm); EL-2, ITO/m-MTDATA (40 nm)/Bphen (40 nm)/LiF (1 nm)/Al (200 nm); EL-3, ITO/TPD (40 nm)/Al(DBM)₃ (30 nm)/LiF (1 nm)/Al (200 nm); and EL-4, ITO/m-MTDATA (40 nm)/Al(DBM)₃ (30 nm)/LiF (1 nm)/Al (200 nm) to check the appearance of a single-exciplex EL in each OLED. The WOLED has a structure of ITO/m-MTDATA (40 nm)/m-MTDATA:Al(DBM)₃(*R*,*x*)/TPD:Bphen (10 nm)/Bphen (40 nm)/LiF (1 nm)/Al (200 nm), where *R* denotes the molar ratio of m-MTDATA-to-Al(DBM)₃ and *x* denotes its layer thickness. *R* was changed from 1:1 to 1:2 to 1:3, while *x* was changed among 2, 3, 4, and 5 nm. The layer of m-MTDATA:Al(DBM)₃ is called ML-1 and TPD:Bphen (molar ratio of 1:1) is called ML-2 hereafter. The schematic level diagram and chemical structure of Al(DBM)₃ are shown in Fig. 1(a).

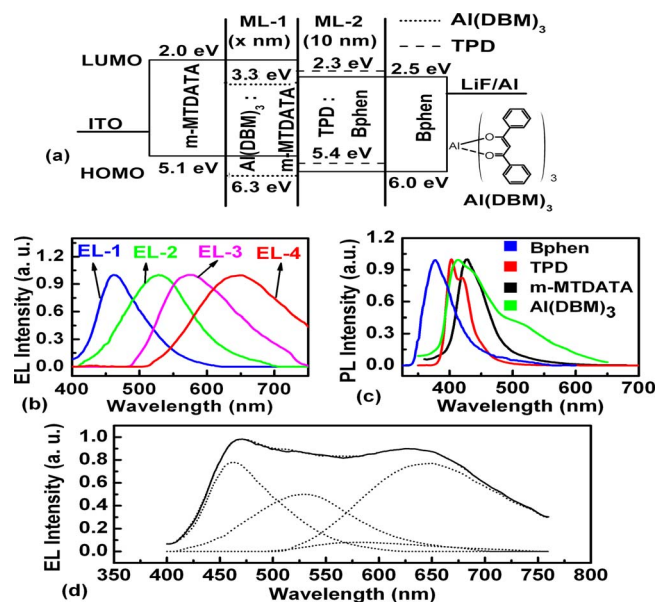


Fig. 1. (Color online) (a) Energy-level diagram of the WOLEDs and the chemical structure of $\text{Al}(\text{DBM})_3$. (b) EL spectra of four OLEDs: EL-1, EL-2, EL-3, and EL-4. (c) PL spectra of m-MTDATA, TPD, Bphen, and $\text{Al}(\text{DBM})_3$ films excited at 360 nm. (d) EL spectrum of the WOLED with $x = 3$ nm and $R = 1:2$ at 9 V (solid), the fitted EL spectrum (dashed), and four decomposed bands corresponding to the four exciplex emissions (dashed).

Figure 1(b) shows the EL spectra of the EL-1, EL-2, EL-3, and EL-4 OLEDs, where emission band peaks appear at about 463, 528, 572, and 650 nm, respectively. Figure 1(c) shows the PL spectra of neat films of m-MTDATA, TPD, Bphen, and $\text{Al}(\text{DBM})_3$, which give a monomer (i.e., bulk exciton) emission band with peaks at about 375, 401, 413, and 425 nm, respectively. Each of the EL spectra does not correspond to any monomer emission, indicating that it arises from intermolecular exciplex. Figure 1(d) shows the EL spectrum, at 9 V, of the WOLED with $x = 3$ nm and $R = 1:2$. The EL spectrum seems to consist of three broad bands with peaks at about 470, 520, and 630 nm and a weak shoulder at 570 nm. If monomer emissions due to Bphen, TPD, $\text{Al}(\text{DBM})_3$, and m-MTDATA would be responsible for the EL spectrum, sharp bands would appear at 375, 401, 413, and 425 nm, respectively. Such sharp bands, however, are not observed in Fig. 1(d). The spectral line shapes at 400–500 nm and 600–750 nm are quite similar to the 463 and 650 nm exciplex emission bands of TPD/Bphen and m-MTDATA/ $\text{Al}(\text{DBM})_3$, respectively. The peak at 520 nm and shoulder at 570 nm are close to the exciplex emission band peaks of m-MTDATA/Bphen and TPD/ $\text{Al}(\text{DBM})_3$, respectively. Therefore we assume that the observed EL spectrum consists of these four exciplex emission bands. We decomposed the EL spectrum into the four bands under this assumption. Good fitting was obtained between the observed EL spectrum and the sum of the four decomposed bands, as shown in Fig. 1(d). This indicates that our assumption is reasonable, i.e., the EL of the WOLED arises from only exciplexes but does not arise from any monomer.

The formation of the four exciplexes is understood as follows. The exciplex of m-MTDATA/ $\text{Al}(\text{DBM})_3$ is formed at the interface between m-MTDATA hole-transporting and ML-1 layers, exciplexes of TPD/ $\text{Al}(\text{DBM})_3$ and m-MTDATA/Bphen are at the interface between ML-1 and ML-2 layers, and the exciplex of TPD/Bphen is at the interface between ML-2 and Bphen electron-transporting layers. Besides such an exciplex, which is formed at the interface between two distinct layers [hereafter called a layer-boundary (LB) exciplex], another type of exciplex is possible, i.e., an exciplex formed by two distinct molecules in the same layer [hereafter called an intralayer (IL) exciplex]. The IL exciplexes of m-MTDATA/ $\text{Al}(\text{DBM})_3$ and TPD/Bphen are formed in ML-1 and ML-2 layers, respectively. Presence of the IL exciplex is consistent with the observation of exciplex formed in a blend film of m-MTDATA:Bphen [6] and in a blend film of TPD:STO [8,9].

Figure 2(a) shows the EL spectra of the WOLED with various ML-1 thicknesses (x). The 650 nm emission band enhances relative to the 455 nm band with an increase in thickness. In the decomposed bands of Fig. 2(a), no big change occurs for green and orange emission bands with an increase in thickness, while a large increase occurs for the red emission band. This increase is understood as follows. The m-MTDATA/ $\text{Al}(\text{DBM})_3$ exciplex is formed not only at the interface between m-MTDATA hole-transporting and ML-1 layers, i.e., the LB exciplex, but also in ML-1 layer, i.e., the IL exciplex. Increase of ML-1 thickness gives rise to increase the volume of ML-1 and increase concentration of the IL exciplex, resulting in enhancement of red emission. The other exciplexes are not influenced by the ML-1 layer thickness; therefore no change was observed in blue, green, and orange emissions.

Figure 2(b) shows the EL spectra of the WOLED with $x = 3$ nm at different m-MTDATA-to- $\text{Al}(\text{DBM})_3$ ratios (R) in the ML-1 layer. When R decreases from 1:1 to 1:2 to 1:3, the intensities of red and green emissions decrease relative to blue emission. The decrease

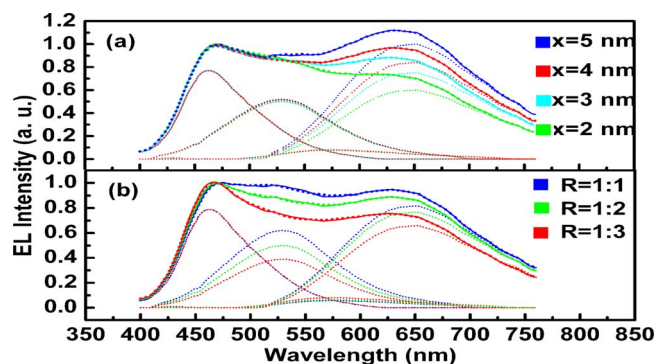


Fig. 2. (Color online) (a) EL spectra of the WOLED with $R = 1:2$ but at various thicknesses x (solid), the fitted EL spectra (dashed) and four decomposed bands corresponding to the four exciplex emissions (dashed) at 9 V. (b) EL spectra of the WOLED with $x = 3$ nm and different ratio R at 9 V (solid), the fitted EL spectra (dashed), and four decomposed bands corresponding to the four exciplex emissions (dashed). The measured, fitted, and decomposed spectra are normalized at the peak height of blue emission.

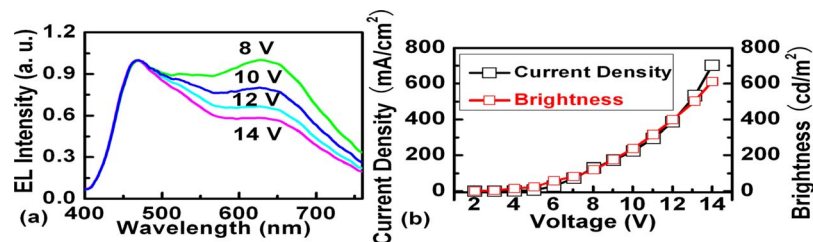


Fig. 3. (Color online) (a) Normalized EL spectra and (b) B-J-V characteristics of the WOLED with $x = 3$ nm and $R = 1:2$.

of green emission is easily understood by the decrease of relative concentration of m-MTDATA. With the decrease of R , the number of m-MTDATA and $\text{Al}(\text{DBM})_3$ molecules decreases and increases, respectively, resulting in low contacting probability for m-MTDATA and $\text{Al}(\text{DBM})_3$ in ML-1; therefore red emission is expected to decrease. Unlike the cases of green and red emission bands, the intensity of orange emission increases with decreasing R value. This is due to enhancement of exciplex formation between $\text{Al}(\text{DBM})_3$ in ML-1 and TPD in ML-2 with the increase of $\text{Al}(\text{DBM})_3$ molecules.

The EL spectra of the WOLED under various bias voltages are shown in Fig. 3(a). The red-emission-band intensity decreases relative to the blue emission with increasing bias voltage. It is suggested that this phenomenon is due to a shift of the recombination zone from ML-1 layer to ML-2 layer. The brightness-current density-voltage (B-J-V) characteristics are plotted in Fig. 3(b). The WOLED exhibits a CRI of 94.1, Commission Internationale de l'Eclairage-1931 (CIE) coordinates of (0.33, 0.35) at 10 V, and correlated color temperature (CCT) between 3376 and 6571 K, as listed in Table 1. The current efficiency was about 0.1 cd/A, because usually the efficiency of OLEDs using exciplex emission is smaller [2,7]. Although the efficiency of our WOLED is low and luminance is not so high, the CRI is quite high and the CIE coordinate is close to the white-light equienergy point (0.33, 0.33). Such a high CRI and good CIE coordinates are obtained by the four overlapping broad emission bands owing to coexistence of four exciplexes.

Table 1. CIE Coordinates, CCT, and CRI of the WOLED with $x = 3$ nm and $R = 1:2$

Bias Voltage	CIE Coordinates (x, y)	CCT	CRI
8 V	(0.36, 0.37)	4593 K	94.0
10 V	(0.33, 0.35)	5477 K	94.1
12 V	(0.32, 0.35)	6100 K	93.6
14 V	(0.31, 0.35)	6571 K	92.5

In summary, a type of WOLED using four exciplexes was fabricated. A very broad white EL band with a half-width of about 270 nm was obtained by four emission bands that strongly overlap. The four bands were generated from four exciplexes of TPD/Bphen, m-MTDATA/Bphen, TPD/ $\text{Al}(\text{DBM})_3$, and m-MTDATA/ $\text{Al}(\text{DBM})_3$, which give rise to blue, green, orange, and red emission bands, respectively. No monomer emission is responsible for the EL. A CRI of 94.1, CIE coordinates of (0.33, 0.35), and CCT of 5477 K were obtained at bias voltage of 10 V. High CRI obtained from WOLED with four exciplexes will be useful for application to lighting.

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References

1. K. Itano, H. Ogawa, and Y. Shirota, *Appl. Phys. Lett.* **72**, 636 (1998).
2. K. Okumoto and Y. Shirota, *J. Lumin.* **87**, 1171 (2000).
3. J. Wang, Y. Kawabe, D. E. Shaheen, M. M. Morrell, G. E. Jabbour, P. A. Lee, J. Anderson, N. R. Armstrong, B. Kippelen, E. A. Mash, and N. Peyghambarian, *Adv. Mater.* **10**, 230 (1998).
4. C. Adachi, T. Tsutsui, and S. Saito, *Appl. Phys. Lett.* **56**, 799 (1990).
5. Z. R. Hong, C. J. Liang, R. G. Li, W. L. Li, D. Zhao, D. Fan, D. Y. Wang, B. Chu, F. X. Zang, L. S. Hong, and S. T. Lee, *Adv. Mater.* **13**, 1241 (2001).
6. D. Wang, W. L. Li, B. Chu, Z. S. Su, D. F. Bi, D. Y. Zhang, J. Z. Zhu, F. Yan, Y. R. Chen, and T. Tsuboi, *Appl. Phys. Lett.* **92**, 053304 (2008).
7. J. Feng, F. Li, W. Gao, S. Liu, Y. Liu, and Y. Wang, *Appl. Phys. Lett.* **78**, 3947 (2001).
8. J. Thompson, R. I. R. Blyth, M. Mazzeo, M. Anni, G. Gigli, and R. Cingolani, *Appl. Phys. Lett.* **79**, 560 (2001).
9. M. Mazzeo, D. Pisignano, F. Della Sala, J. Thompson, R. I. R. Blyth, G. Gigli, R. Cingolani, G. Sotgiu, and G. Barbarella, *Appl. Phys. Lett.* **82**, 334 (2003).