AIP | Applied Physics Letters

Highly efficient green organic light-emitting diodes from single exciplex emission

Dan Wang, Wenlian Li, Bei Chu, Zisheng Su, Defeng Bi et al.

Citation: Appl. Phys. Lett. **92**, 053304 (2008); doi: 10.1063/1.2841060
View online: http://dx.doi.org/10.1063/1.2841060
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v92/i5
Published by the American Institute of Physics.

Highly efficient green organic light-emitting diodes from single exciplex emission

Dan Wang,[1,2] Wenlian Li,[1,2,a)] Bei Chu,[1,2] Zisheng Su,[1,2] Defeng Bi,[1,2] Dongyu Zhang,[1,2] Jianzhuo Zhu,[1,2] Fei Yan,[1,2] Yiren Chen,[1,2] and Taiju Tsuboi[3]
[1]*Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 16-Dong NanHu Road, Changchun 130033, People's Republic of China*
[2]*Graduate School of the Chinese Academy of Sciences, Beijing 100039 People's Republic of China*
[3]*Faculty of Engineering, Kyoto Sangyo University, Kamigamo, Kyoto 603-8555, Japan*

(Received 16 November 2007; accepted 15 January 2008; published online 5 February 2008)

Spectral single and stable green exciplex emission was demonstrated from organic light-emitting diodes (OLEDs) with 4,4′,4″-tris[3-methylphenyl(phenyl)amino] triphenylamine and 4,7-diphenyl-1,10-phenanthroline that function as electron donor (D) and acceptor (A), respectively. As 8-hydroxyquinoline aluminum (Alq_3) was attached to the acceptor layer, electroluminescent (EL) properties of the two exciplex-type OLEDs with D/A-bilayer and D:A mixture layer configurations were markedly improved, i.e., a peak current efficiency of 7.6 cd/A at 2.38 mA/cm^2 in three-layer device and a maximum luminance of 6620 cd/m^2 at 8.7 V in blend layer device were obtained, respectively, without changing the peak position (535 nm) and the shape of EL spectrum. Discussion is given on the harvest of the pure green exciplex emission and enhancement of luminance which is obtained by inserting Alq_3 layer. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2841060]

Two types of electroluminescence (EL) have been observed from multilayer organic light-emitting diodes (OLEDs) since the first success of OLED by Tang and Van Slyke.[1] One is EL from single molecule such as tris-(8-hydroxyquinoline) aluminum (Alq_3). This is called monomer emission, hereafter. The other is EL from two molecules in the excited state. When two molecules are the same or different, they give emission called excimer or exciplex emission, respectively. The exciplex is formed at the interface of multilayer OLEDs by charge transfer from electron-donor molecule to electron-acceptor molecule.[2–4]

When compared with monomer EL from single molecule, the EL of exciplex is weaker, resulting in poor EL performance in the OLEDs. When OLEDs generate both the monomer and exciplex emissions, the EL spectra change with increasing applied voltage. Therefore, several methods have been used to eliminate exciplex emission in multilayer structure OLEDs to obtain only EL from monomer.[5–7] However, the exciplex emission is exploited to improve double-functional device with both photovoltaic and EL performances,[8,9] to tune the OLED emission color,[10,11] and to be a green, yellow, or red emissive component for fabricating white OLED.[11]

Taking into account such an importance of exciplex emission, it is necessary to make OLEDs which give high EL intensity from exciplex and whose EL spectra never change by changing driving bias voltage. The present study was undertaken to find OLEDs which show high performance of exciplex emission. In this letter, we report high exciplex luminance from multilayer OLED devices where exciplex is formed using 4,4′,4″-tris[3-methylphenyl(phenyl)amino] triphenylamine (m-MTDATA) as donor and 4,7-diphenyl-1,10-phenanthroline(bathophenanthroline or Bphen) as acceptor.

Three types of OLED devices were fabricated to obtain a single green emission. The first is bilayer device of indium tin oxide (ITO)/m-MTDATA/Bphen/LiF/Al, the second is three-layer device of ITO/m-MTDATA/Bphen/Alq_3/LiF/Al, and the third is four-layer device of ITO/m-MTDATA/m-MTDATA:Bphen(1:1)/Bphen/Alq_3/LiF/Al. The third device is called blend device, hereafter. In these devices, Alq_3 is used as electron-transporting (ET) material. The layer thickness of m-MTDATA was fixed to 40 nm in all the devices, while the thickness was changed variously for the other layers.

Chemical materials used in the present study were purchased from chemical companies. All organic layers and LiF were evaporated onto precleaned and plasma-treated ITO glass substrate (25 Ω/□) in a vacuum at 4×10^{-4} Pa without breaking vacuum. Thermal deposition rates were ~1, 1, and 10 Å/s for organic materials, LiF, and Al, respectively. The emitting area was 6 mm^2 in all devices. Neat films of m-MTDATA and Bphen were evaporated onto quartz substrates for the absorption and photoluminescence (PL) measurements, while a film of mixture of m-MTDATA and Bphen was fabricated by co-evaporating from separate heating sources. The absorption, PL, and EL spectra and luminance-current-voltage (*L-I-V*) curves were measured by the same methods reported previously.[11] The highest occupied molecular orbital (HOMO) and lowest unoccupied MO (LUMO) energies were obtained from literatures.[12–14] All the measurements were performed at room temperature under ambient laboratory conditions.

Figure 1(a) shows PL spectra of m-MTDATA, Bphen, and m-MTDATA:Bphen (1:1) composite, together with EL spectrum of the bilayer device. The neat m-MTDATA and Bphen films exhibit emission band with peaks at 430 and 380 nm, respectively. The m-MTDATA:BPhen composite

a)Electronic mail: wllioel@yahoo.com.cn.

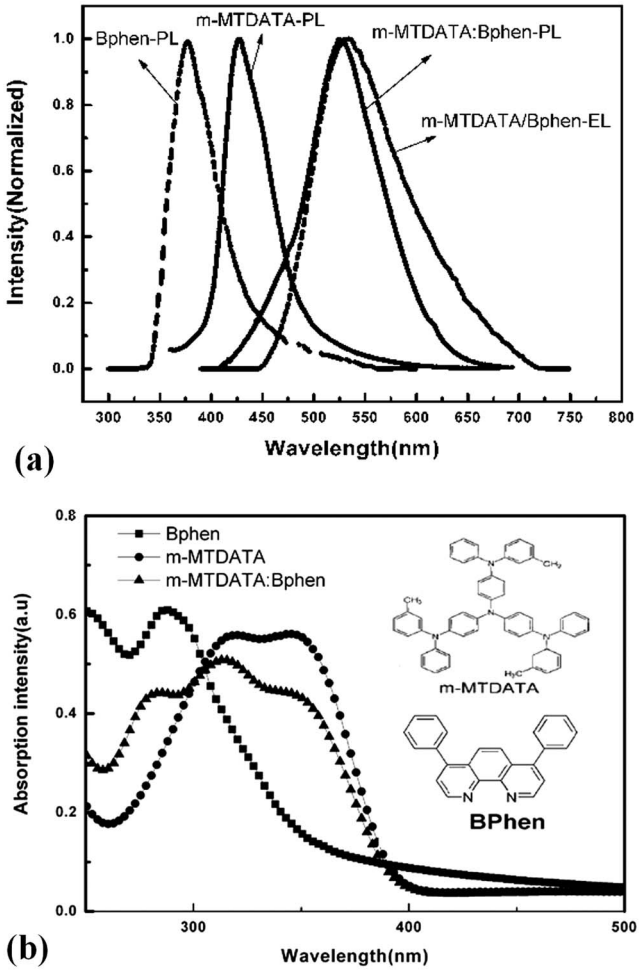

FIG. 1. (a) PL spectra of neat m-MTDATA and Bphen films, and film of mixture of m-MTDATA:Bphen (1:1), which were excited at 360 nm, and EL spectrum of bilayer OLED of m-MTDATA/Bphen. (b) Absorption spectra of neat m-MTDATA and Bphen films, and m-MTDATA:Bphen (1:1) composite. Inset shows the chemical structures of these molecules.

exhibits a green PL band with a peak at 530 nm, which is similar to the EL band of the bilayer device. These green emission bands are completely different from emission bands of m-MTDATA and Bphen and redshifted from these PL bands from monomer, indicating that it is caused by exciplex as is confirmed below. Figure 1(b) shows absorption spectra of neat m-MTDATA and Bphen films, and blend film, together with the chemical structures of m-MTDATA and Bphen. No additional band is observed in the spectrum of the blend film, indicating that two molecules have never been covalent to each other in the ground state and coexist independently in the blend film.

We changed the layer thickness of Bphen in the bilayer device. A maximum luminance of 2870 cd/m^2 and a peak

TABLE I. Dependence of EL performance in bilayer OLED devices on Bphen layer thickness (under a fixed m-MTDATA layer thickness of 40 nm).

Bphen layer thickness (nm)	Maximum luminance (cd/m^2)	Maximum current efficiency (cd/A)
20	1354	0.41
40	2376	2.02
60	2870	2.78
80	1618	1.72

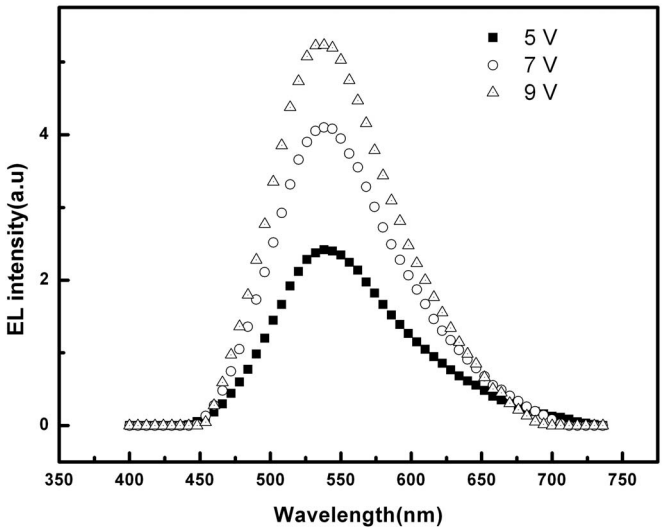

FIG. 2. EL spectra from bilayer OLED device of ITO/m-MTDATA (40 nm)/Bphen (60 nm)/LiF/Al at different driving bias voltages.

current efficiency of 2.8 cd/A were obtained in the device with 60 nm thick Bphen layer, as shown in Table I. Figure 2 shows the EL spectra of the bilayer device. The 535 nm exciplex emission is observed and the EL line shape never changes with increasing voltage. The same EL spectra were observed in the three-layer device and also in the blend device. This indicates that the EL emission is caused by the exciplex formed at the interface between the m-MTDATA

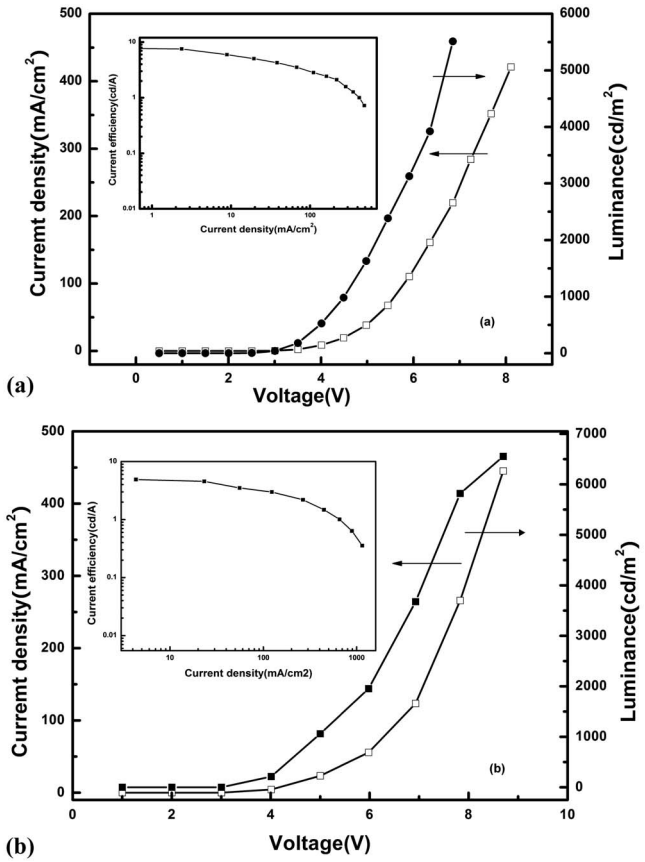

FIG. 3. The *L-I-V* and current efficiency–current density (inset) curves of (a) m-MTDATA (40 nm)/Bphen (60 nm)/Alq_3 (20 nm) three-layer OLED device and (b) m-MTDATA (40 nm)/m-MTDATA:Bphen(1:1) (30 nm)/Bphen (30 nm)/Alq_3 (20 nm) blend device.

TABLE II. Dependence of EL performance in three-layer OLED devices on Alq_3 layer thickness (under fixed m-MTDATA and Bphen layer thicknesses of 40 and 60 nm, respectively).

Alq_3 layer thickness (nm)	Maximum luminance (cd/m^2)	Maximum current efficiency (cd/A)
10	3520	4.3
20	5512	7.6
30	4130	5.3
40	3080	4.1

and Bphen layers, and Alq_3 layer works efficiently as the electron transporting layer because emission from Alq_3 (at 520 nm) is not observed in the three-layer and blend devices.

After the optimal layer thickness is determined as 60 nm for the Bphen layer from the bilayer devices, we measured the *L-I-V* curves in the three-layer devices with 60 nm thick Bphen layer by changing thickness of Alq_3 layer variously. A peak current efficiency of 7.6 cd/A at current density of 2.38 mA/cm^2 and a maximum luminance of 5512 cd/m^2 at 6.8 V were obtained in the device with 20 nm thick Alq_3 layer, as shown in Table II. An example of *L-I-V* plot is shown in Fig. 3(a). As shown in Fig. 3(b), the blend layer based device behaves with a maximum luminance of 6620 cd/m^2 at 8.7 V, although its peak current efficiency is a little bit lower (4.9 cd/A at 4.33 mA/cm^2) but still markedly higher than the bilayer.

The electron mobility of Bphen is 5×10^{-4} cm^2 V^{-1} s^{-1},[13] which has the same order as the hole mobility of m-MTDATA (10^{-4} cm^2 V^{-1} s^{-1}),[14] indicating that a good charge balance is maintained in the bilayer device. Only the exciplex emission is observed in EL from the bilayer, three-layer, and blend devices, and EL due to monomer is not observed. The HOMO and LUMO energies were obtained from literatures.[12–14] The offset between the LUMO levels of m-MTDATA and Bphen is 0.6 eV, while the offset between the HOMO levels is 0.9 eV. Such a high gap not only in LUMO but also in HOMO gives rise to confinement of electrons in the Bphen layer at the interface with m-MTDATA and to confinement of holes in the m-MTDATA layer at the interface with Bphen. These confined electrons and holes have difficulties in overcoming the barrier and entering the m-MTDATA and Bphen layers, respectively. Even if these carriers can enter these layers, fluorescence from each of m-MTDATA and Bphen would be very weak because m-MTDATA and Bphen are well-known as low efficient PL and EL materials. Therefore, the OLEDs with m-MTDATA/Bphen layers generate only EL emission from exciplex which is formed at the interface.

Since ITO forms an approximately Ohmic contact to m-MTDATA layer,[13,15] holes are easily injected from ITO to m-MTDATA layer. On the other hand, it is difficult to inject electrons from Al cathode into Bphen layer directly because of high barrier of about 1.5 eV in the bilayer device. When Alq_3 layer is inserted between Bphen layer and cathode, electrons are more easily injected to Bphen layer because of stepwise transporting process from cathode to Bphen layer via the LUMO level of Alq_3 layer (see Fig. 4). Additionally, more electrons are injected because Alq_3 is known as a good

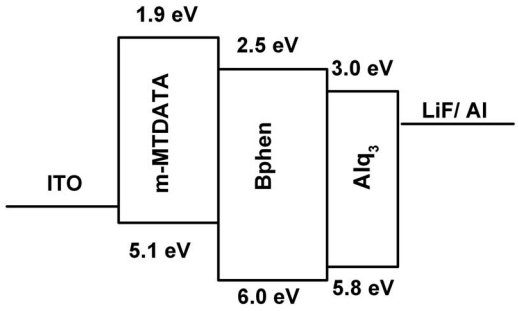

FIG. 4. Schematic LUMO and HOMO energy level diagram of three-layer OLED device.

ET material. As a result, excellent EL performance was achieved in the three-layer and blend device. We used other ET materials such as 2-(4-biphenyl)-5-(4-butylphenyl)-1,3,4-oxadiazole and 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene. These materials, however, did not give high efficiency.

In conclusion, we obtained a single and pure 535 nm green exciplex emission from OLEDs with m-MTDATA and Bphen. The EL performance was improved by inserting an Alq_3 layer with thickness of 20 nm between the Bphen layer and cathode. A peak current efficiency of 7.6 cd/A at 2.38 mA/cm^2 and a maximum luminance of 5512 cd/m^2 at 6.8 V were obtained from the three-layer device, while high luminance of 6620 cd/m^2 at 8.7 V and a little bit lower of peak current efficiency (4.9 cd/A at 4.33 mA/cm^2) were obtained in blend device. The EL peak position and line shape of the green emission were never changed with increasing applied voltage. High EL performance is obtained not only by a carrier balance and easy electron injection but also by the following reason. Both m-MTDATA and Bphen are too efficiently low to emit their monomer EL. Therefore, no competition of the electronic transition occurs between exciplex and monomer, resulting in high efficient exciplex emission.

[1] C. W. Tang and S. A. Van Slyke, Appl. Phys. Lett. **51**, 913 (1987).
[2] Y. Shirota, M. Kinoshita, T. Noda, K. Okumoto, and T. Ohara, J. Am. Chem. Soc. **122**, 11021 (2000).
[3] H. Doi, M. Kinoshita, K. Okumoto, and Y. Shirota, Chem. Mater. **15**, 1080 (2003).
[4] T. Noda, H. Ogawa, and Y. Shirota, Adv. Mater. (Weinheim, Ger.) **11**, 283 (1999).
[5] C. J. Liang, D. Zhao, Z. R. Hong, D. X. Zhao, X. Y. Liu, and W. L. Li, Appl. Phys. Lett. **76**, 67 (2000).
[6] D. Y. Wang, W. L. Li, B. Chu, C. J. Liang, Z. R. Hong, M. T. Li, H. Z. Wei, Q. Xin, J. H. Niu, and J. B. Xu, J. Appl. Phys. **100**, 024506 (2006).
[7] J. Thompson, R. I. R. Blyth, M. Mazzeo, M. Anni, G. Gigli, and R. Cingolani, Appl. Phys. Lett. **79**, 560 (2001).
[8] S. W. Cha and J. I. Jin, J. Mater. Chem. **13**, 479 (2003).
[9] K. Okumoto and Y. Shirota, J. Lumin. **87-89**, 1171 (2000).
[10] M. T. Li, W. L. Li, L. L. Chen, Z. G. Kong, B. Chu, B. Li, Z. Z. Hu, and Z. Q. Zhang, Appl. Phys. Lett. **88**, 091108 (2006).
[11] D. Wang, W. L. Li, Z. S. Su, T. L. Li, B. Chu, D. F. Bi, L. L. Chen, W. M. Su, and H. He, Appl. Phys. Lett. **89**, 233511 (2006).
[12] S. Naka, H. Okada, H. Onnagawa, and T. Tsutsui, Appl. Phys. Lett. **76**, 197 (2000).
[13] S. W. Tsang, S. K. So, and J. B. Xu, J. Appl. Phys. **99**, 013706 (2006).
[14] Q. Xin, W. L. Li, W. M. Su, T. L. Li, Z. S. Su, B. Chu, and B. Li, J. Appl. Phys. **101**, 044512 (2007).
[15] C. Giebeler, H. Antioniadis, D. D. C. Bradley, and Y. Shirota, Appl. Phys. Lett. **72**, 2448 (1998).