

Pure red emission of dye-doped organic molecules from microcavity organic light emitting diode

Dong-ming Cheng^{a,*}, Feng-ying Ma^a, Xing-yuan Liu^{b,c}

^a*School of Physics and Engineering, Zhengzhou University, Zhengzhou 450052, PR China*

^b*Laboratory of Excited State Processes, Chinese Academy of Sciences, Changchun 130033, PR China*

^c*Changchun Institute of Optics and Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130022, PR China*

Received 13 December 2005; received in revised form 24 March 2006; accepted 29 March 2006

Available online 16 May 2006

Abstract

Organic red emitting diode was fabricated by using 4-dicyanomethylene-2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[*ij*]quinolizin-8-yl)vinyl]-4H-pyran (DCM)-doped tri-(8-quinololato) aluminum (Alq₃) as emitter with the structure of G/ITO/NPB(25 nm)/DCM:Alq₃(55 nm)/Alq₃(20 nm)/LiF (1.2 nm)/Al(84 nm), (glass/indium–tin-oxide/4,4-bis-[*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl, G/ITO/NPB), the wavelength of the maximal emission of which is 615 nm. By introducing cavity to Organic light emitting diode (OLED), we got pure red emitting diode with wavelength of the maximal emission of 621 nm and full-width at half-maximum (FWHM) of 27 nm. As far as we know, it is the best result in the dye-doped organic red emitting diode. We also made a device of G/ITO/NPB(25 nm)/DCM:Alq₃(29 nm)/DCM:PBD(26 nm)/Alq₃(20 nm)/LiF(1.2 nm)/Al(84 nm), in order to compare the performance of Alq₃ with that of 2-(4-biphenyl)-5-(4-*t*-butylphenyl)-1,3,4-oxadiazole (PBD) as host material. It was found that the performance of device A is better than that of C both in brightness and color purity, as well as in EL efficiency.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Microcavity; Organic light emitting diode; DCM doping

Since Tang and Vanslyke [1], reported an organic light emitting diode (OLED) with high efficiency in 1987, OLEDs have been intensively investigated driven by their potential applications in the fields of flat-panel displays and lighting. The OLED display features a wider viewing angle, faster response, high brightness, low power consumption and thin design. The pure red, green and blue emissions of OLEDs are necessary to fabricate the full color display. Now, organic green and blue OLEDs with high efficiency of the luminescence, good color characteristics and long lifetime have been realized using other materials and tri-(8-quinololato) aluminum (Alq₃), which exhibits high quantum efficiency, excellent film formation and stability [2]. However, we are faced with difficulties to achieve full color display, because the efficiency of the luminescence of organic red LEDs is still very low and furthermore, obtaining pure emission colors from organic molecules is

difficult because their emission spectra typically have a full-width at half-maximum (FWHM) of 50–200 nm due to both vibronic sidebands and strong inhomogeneous broadening of the transitions [3]. In order to eliminate these obstacles, many methods were adopted, including use of an emitting-assist dopant [4], introducing a new device structure [5] or developing an original host material [6] to improve energy transfer from host to guest. Although there are a lot of red fluorescent dyes intensively researched by many groups, DCM is still the most efficient material among them. Since energy transfer can be very efficient over distances of 5–10 nm [7], it is necessary to have a small percentage by volume of the dye. Therefore, the host material is introduced to both dilute guest molecules and minimize concentration quenching. Because in such systems the emission centers are spatially separated, Alq₃, which has a good stability and charge-transporting ability, is often chosen for the host material. Recently, Qiao et al. [6] reported pure electroluminescence (EL) by using a new host material Ga₂(saph)₂q₂ instead of Alq₃, and a red dye

*Corresponding author.

E-mail address: Chengdm11@163.com (D.-m. Cheng).

material DCJTb. The doped $\text{Ga}_2(\text{saph})_2\text{q}_2$ device gave pure red emission and the color coordinates in the Commission Internationale del' Eclairage (CIE, 1931) chromaticity chart were $x = 0.675$ and $y = 0.322$. However, the FWHM is 80 nm, higher than that of rare earth complex. Some difficulties were encountered when utilizing organic rare earth complex in OLEDs, one being poor film-forming ability of organic rare earth complex and the other being its low EL efficiency [8]. In addition to the chemical tuning of the emission color, a microcavity cannot only realize the tenability of the wavelength, but can also increase the emission intensity at resonance wavelength in the forward direction of the microcavity plane, due to the fact that microcavity can change the mode density within the cavity, thus increasing the spontaneous emission rate at resonance wavelength and suppressing those at off-resonance wavelength [9]. In this article, we introduced microcavity to dye-doped OLED to realize pure red emission, and the FWHM was only 27 nm.

The DBR was evaporated on the glass substrates. The structure of the DBR is $G(\text{HL})^6\text{H}$, where H stands for high-refractive material ZnS ($n = 2.35$) and L stands for low-refractive material MgF_2 ($n = 1.38$), and the Bragg wavelength is 620 nm. The microcavity was sandwiched between a DBR and a metal Al reflective mirror. Indium–tin-oxide (ITO) was coated on the top of the DBR as the anode and Al acted as cathode as well as another reflector of the microcavity. 4,4-bis-[*N*-(1-naphthyl)-*N*-phenyl-amino] biphenyl (NPB) served as the hole transporter, whereas Alq_3 was the electron transporter as well as host material. 2-(4-biphenyl)-5-(4-*t*-butylphenyl)-1,3,4-oxadiazole (PBD) also served as the host material. All the organic materials and Al were deposited by vacuum deposition in a vacuum of 1×10^{-5} Torr. The deposition rate of the NPB was 0.5 \AA/s . DCM-doped Alq_3 and PBD were deposited by coevaporation of the two source materials. The proper ratios of the evaporation rates of the DCM and Alq_3 , PBD were 1:50 and 1:250, respectively.

In this experiment, we made three devices, whose structures were as follows:

- device A: Glass/ITO/NPB(25 nm)/DCM: Alq_3 (55 nm)/ Alq_3 (20 nm)/LiF(1.2 nm)/Al(84 nm),
- device B: Glass/DBR/ITO/NPB(25 nm)/DCM: Alq_3 (55 nm)/ Alq_3 (20 nm)/LiF(1.2 nm)/Al(84 nm),
- device C: Glass/ITO/NPB(25 nm)/DCM: Alq_3 (29 nm)/DCM:PBD(26 nm)/ Alq_3 (20 nm)/LiF(1.2 nm)/Al(84 nm); the thickness of which was detected by a ZMK-III detector.

The EL emission spectra were recorded on a Hitachi spectrophotometer F4000 and the brightness was determined by using a ST-86LA luminance meter.

Fig. 1 shows the absorption and PL spectra of PBD, Alq_3 and DCM. It shows that the fairly good overlap between the emission spectra of Alq_3 and that of PBD, and

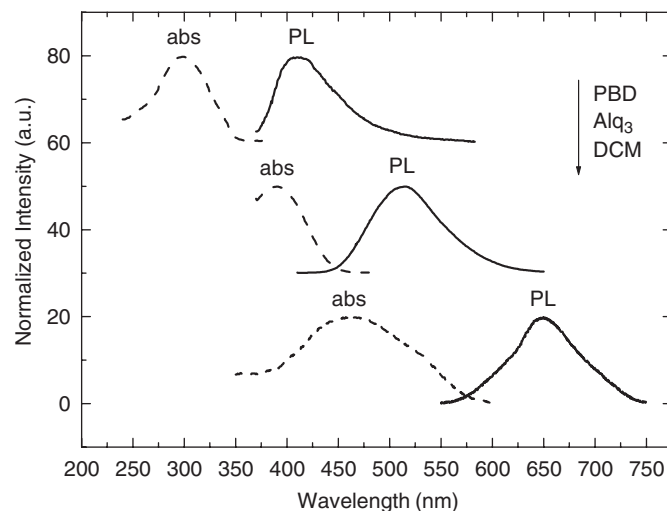


Fig. 1. Absorption and PL spectra of PBD, Alq_3 and DCM.

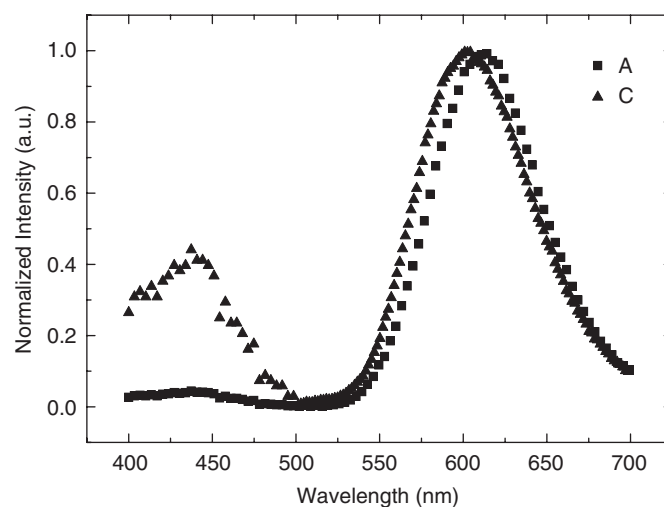


Fig. 2. EL spectra of devices A and C.

the absorption spectrum of DCM meets the needs of efficient energy transfer. Fig 2 shows the EL spectra of devices A and C. It can be seen from the figure that the spectrum of device A has one peak located at 615 nm, while the spectrum of device C has two peaks, with the strong peak located at 604 nm and the weaker one at about 430 nm, which probably comes from PBD. That can be explained from the different structures between devices A and C. Using the reported energy levels for the organic materials used in this experiment, we have shown the relationship of the energy levels for device C in Fig 3. Here, a thin inorganic LiF layer was used as a buffer layer, which can bend the energy level of Alq_3 , and thus reduce the barrier between organic layer and cathode. The holes injected the Alq_3 layer and recombined with electrons from the cathode. The surplus holes would travel to the interface of Alq_3 and PBD, and then recombine with electrons. The doping concentration being very low, a lot of PBD molecules were excited and then emitted light. Fig. 4 shows

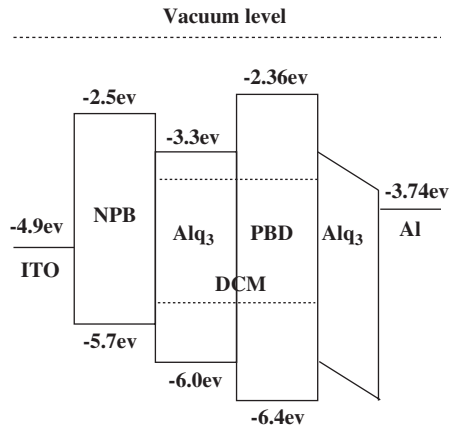


Fig. 3. The energy diagrams of the doping system of device C.

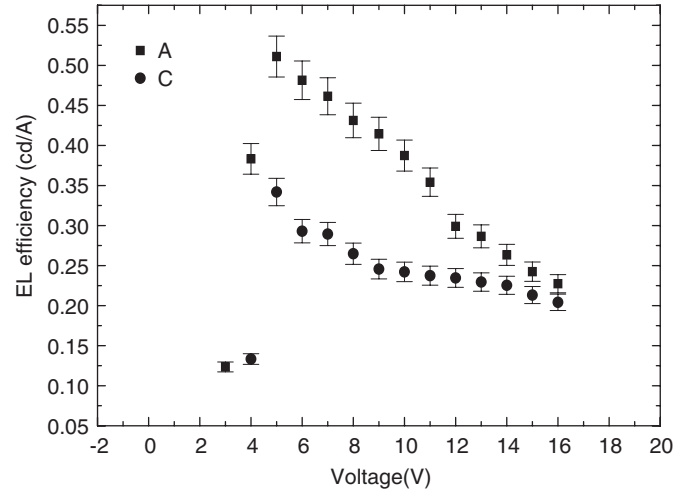


Fig. 5. EL efficiency–voltage characteristics for devices A and C.

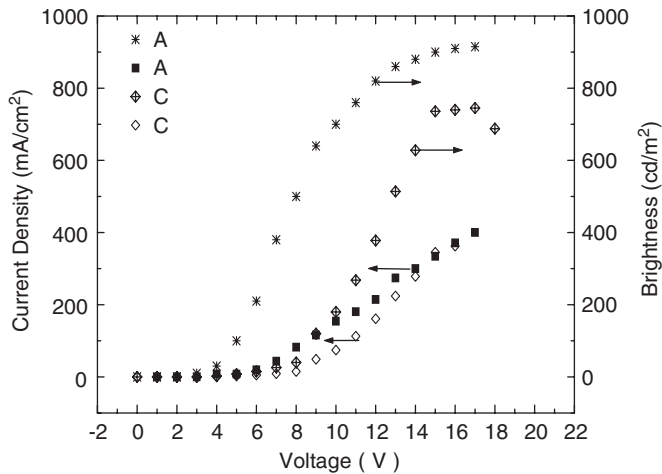


Fig. 4. L–J–V characteristics for devices A and C.

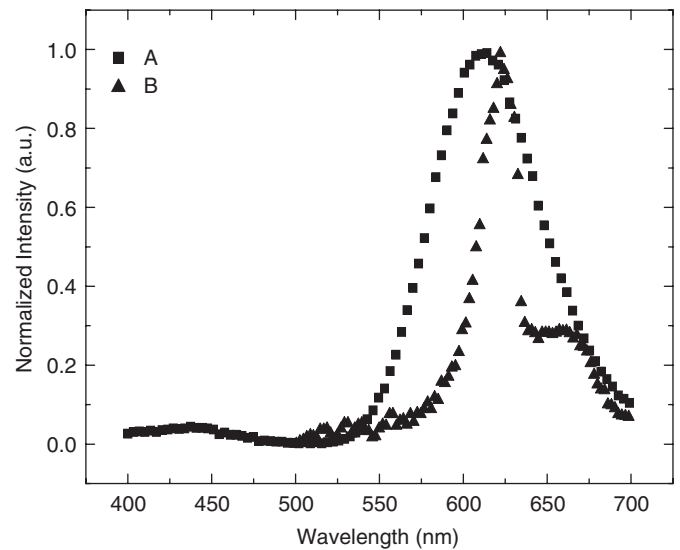


Fig. 6. EL spectra of devices A and B.

the L–J–V characteristics of devices A and C. The opening voltage of device A was 5 V, lower than that of device C, and at the same voltage, the current density and brightness were all higher than those of device C. It can also be explained using Fig 3. It can be found that the barrier between PBD and Alq₃ is much higher than that of Alq₃ and Al. Fig 5 shows the relationship between EL efficiency of applied voltage of devices A and C obtained from Fig 4. We can see that the performance of device A is better than C, both in brightness and in EL efficiency. Fig 6 shows the spectra of devices A and B. An effect of spectral narrowing of device B was clearly observed compared to device A. The FWHM of device A was 80 nm, much higher than that of device B (27 nm). Because of electron–vibration and particularly electron–vibration anharmonic interactions of the organic materials, the linewidths of OLEDs are around 100 nm, which affect the monochromatization of the device [10,11]. By introducing microcavity in OLEDs, the linewidth of the spectra was sharply reduced. So, the purity of the device was improved.

We made two kinds of organic red emitting devices. By using a larger band gap molecule as host material, we have

found that in addition to the film formation and stability, and the overlap between the absorption spectrum of dye and the PL spectrum of the host material, the band gap is also an important factor when choosing the host material. When LUMO and HOMO of the host material are close to those of the dye respectively, the host material is the best [6]. We also made a red emitting microcavity device and obtained pure red emission with peak at 621 nm and FWHM of 27 nm.

References

- [1] Tang CW, VanSlyke SA. Organic electroluminescent diodes. *Appl. Phys. Lett.* 1987;51:913–5.
- [2] Campos RA, Kovalev IP, Guo Y, Wakili N, Skotheim I. Red electroluminescence from a thin organometallic layer of europium. *J. Appl. Phys.* 1996;80:7144–50.

- [3] Bradley DDC, Weaver MS, Lidzey DG, Fisher TA, et al. Recent progress in polymers for electroluminescence: microcavity devices and electron transport polymers. *Thin Solid Films* 1996; 273:39–47.
- [4] Hamada Y, Kanno H, Tsujioka T, Takahashi H, Usuki T. Red organic light-emitting diodes using an emitting assist dopant. *Appl. Phys. Lett.* 1999;75:1682–4.
- [5] Xie ZY, Hung LS, Lee ST. High-efficiency red electroluminescence from a narrow recombination zone confined by an organic double heterostructure. *Appl. Phys. Lett.* 2001;79: 1048–50.
- [6] Juan Q, Yong Q, Liduo W, et al. Pure red electroluminescence from a host material of binuclear gallium complex. *Appl. Phys. Lett.* 2002; 81:4913–5.
- [7] Berggren M, Dodabalapur A, Slusher RE. Stimulated emission and lasing in dye-doped organic thin films with Forster transfer. *Appl. Phys. Lett.* 1997;71:2230–2.
- [8] Hu W, Matsumura M, Wang M, Jin L. Efficient red electroluminescence from devices having multilayers of a europium complex. *Appl. Phys. Lett.* 2000;77:4271–3.
- [9] Zhao J, Ma F, Liu X, et al. Effect of Emitter Position on Emission Intensity in an Organic Planar Microcavity. *Chin. Phys. Lett* 2002; 19:724–6.
- [10] Kościel E, Sanetra J, Gondek E, Jarosz B, Kityk IV. Optical poling of several halogen derivatives of pyrazoloquinoline. *Opt. Commun* 2004;242:401–9.
- [11] Makowska-Janusik M, Gondek E. Second-order optical effects in several pyrazolo-quinoline derivatives. *Chem Phys* 2004;306:265–71.