

# White Light Emission From DBPPV and CdSe/ZnS Quantum Dots Dually Hybridized on InGaN Light-Emitting Diodes

Yan-Kuin Su\*, Ping-Chieh Tsai, Chun-Yuan Huang, and Ying-Chih Chen

Institute of Microelectronics, Department of Electrical Engineering, Advanced Optoelectronic Technology Center  
yksu@mail.ncku.edu.tw

IEEE Electron Device Letters 29, 575 (2008)

## Abstract

We have demonstrated the white light emission from the novel hybrid light-emitting diodes. With a polymer/QD composite film thickness of  $0.61 \mu\text{m}$ , the Commission Internationale de l'Éclairage chromaticity coordinates of the emitting light from the device attain (0.33, 0.36). The coordinates are shifted to (0.43, 0.46) as the thickness is further increased. Meanwhile, the luminescence spectrum shows that more than 90% of the blue light is effectively energy transferred to green and red lights. For a long-term operation, the luminescence intensity from the polymer is decreased by 62% within 5 h due to the photooxidation effect.

Index Terms-CdSe/ZnS quantum dots (QDs), GaN, hybrid light-emitting diode (LED), white light emission, 2,3-dibutoxy-1,4-poly (phenylene) (DBPPV).

## I. INTRODUCTION

By using white light emitting diodes (WLEDs) as the solid-state lighting has attracted much attention worldwide because of their benefits including energy saving, environment protection, safety, and reliability. It is estimated that solid-state lighting can reduce 50% of the global electricity consumption for illumination, and within the next five years, it is expected the LED-based white light sources will completely replace conventional incandescent and fluorescent lamps<sup>1</sup>. In fact, the techniques of fabrication of WLEDs have come a long way and been matured for commercialization. Nowadays, several methods are developed to achieve white light emission from LEDs, including multichip integration, multiple quantum wells or impurities doping in the monolithic chip, and phosphors for color conversion<sup>2,3</sup>. Among them, the color-conversion WLEDs are the easiest and the most practical for mass production. In particular, with the mature development of solid-state LEDs, the optically pumped emissions from polymer phosphors have avoided the electrically induced degradation suffered by polymer LEDs during operation<sup>4,5</sup>, which indicates that the hybrid polymer/solid-state WLEDs are more reliable white light sources. Quite a few studies have been reported for individual polymer or QD hybrid devices.<sup>3</sup> However, rare investigations have dually hybridized the polymer and QDs on blue or UV LEDs. Demir *et al.*<sup>6</sup> recently demonstrated the dual hybridization of QDs and polyfluorene on near-UV LEDs without further discussion about the reliability of their hybrid devices. In this letter, we have



demonstrated that the white light emission can be achieved via the dual hybridization of the 2,3-dibutoxy-1,4-poly(phenylene vinylene) (DBPPV) and CdSe/ZnS QDs on an InGaN LED with proper composite film thickness.

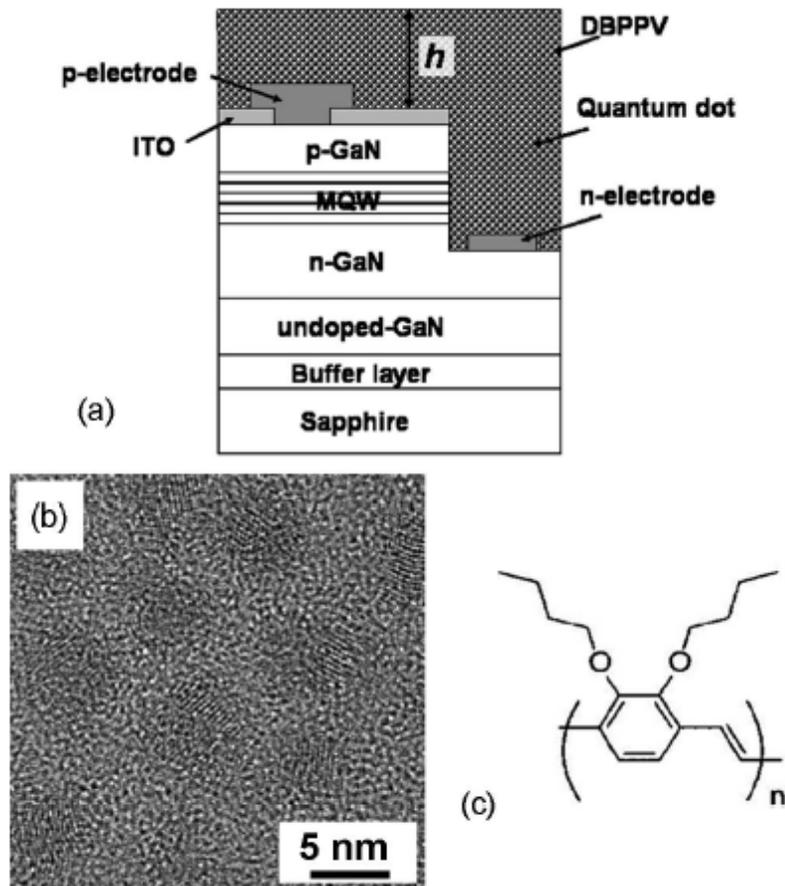


Fig. 1. Schematic structure of our hybrid LEDs, (b) a TEM image of CdSe/ZnS core/shell QDs, and (c) the chemical structure of DBPPV.

## II. EXPERIMENTS

The device structure is shown in Fig. 1(a). CdSe/ZnS core/shell QDs and DBPPV composite film were spin coated on a fabricated InGaN blue LED chip. The QDs and DBPPV were chosen since they had been demonstrated to be excellent candidates for polymer-QD LEDs<sup>7</sup>. The transmission electron microscopy image of the QDs is shown in Fig. 1(b). The QDs with an average diameter of 5.5 nm were well dispersed in toluene first with a concentration of 10 mg/ml and have a photoluminescence (PL) emission peak at 610 nm as well as a full width at half maximum (FWHM) of 32 nm. Meanwhile, the DBPPV powder [the chemical structure is shown in Fig. 1(c)] was solved in toluene 1.5 wt. % and further blended with the QD solution in a volume ratio of 4:1 for more than 24 h to complete the DBPPV/QD composite. The InGaN LED consists of a 30-nm-thick GaN buffer layer, a 2- $\mu$ m-thick undoped GaN layer, a 1- $\mu$ m-thick Si-doped GaN layer, an InGaN/GaN multiple-quantum-well active layer, and a 200-nm-thick Mg-doped GaN layer. It has a peak wavelength  $\lambda_p$  of 436 nm and an FWHM of 15 nm. Afterward, to precisely control the thickness of composite film, four spin speeds—4000, 3000, 2000, and 1000 r/min—were used to optimize the light characteristics, which resulted four thicknesses of the composite film  $h$ —0.22, 0.30, 0.61, and 0.87  $\mu$ m. They were thus marked as devices A, B, C, and D, respectively.

## III. RESULTS AND DISCUSSION

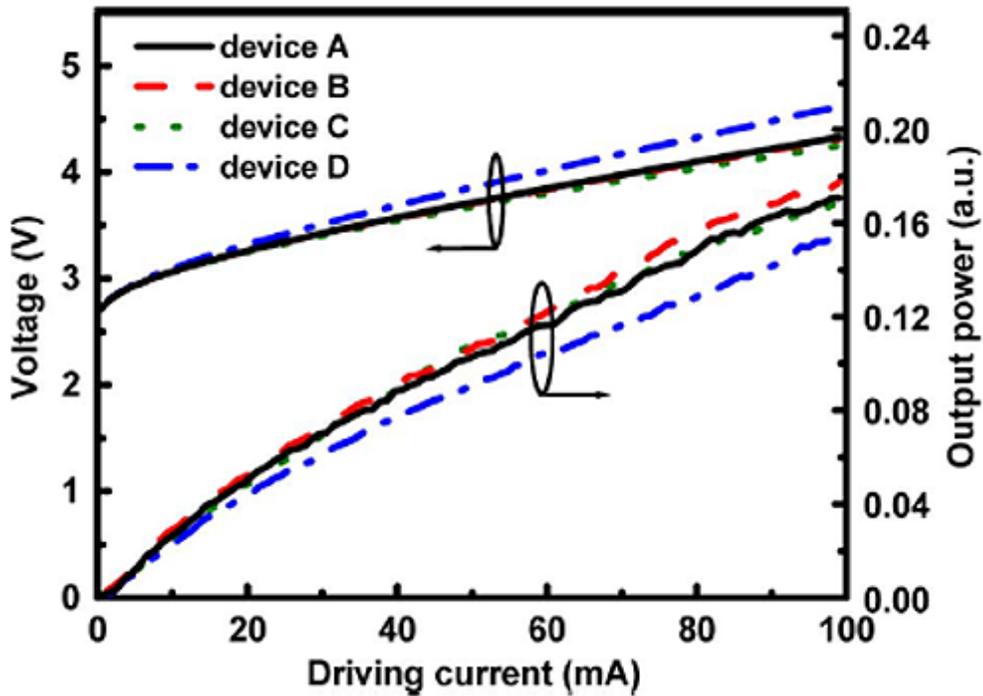


Fig. 2.  $I$ - $L$ - $V$  curves of the hybrid devices with composite film thicknesses of 0.22, 0.30, 0.61, and 0.87  $\mu\text{m}$ , respectively.

The voltage-current ( $V$ - $I$ ) and light-current ( $L$ - $I$ ) curves of hybrid LEDs are shown in Fig. 2. The devices are turned on at 2.8 V, and the forward voltages (the biased voltage at 20 mA) are around 3.25, 3.25, 3.24, and 3.31 V for devices A, B, C, and D, respectively. The increase of forward voltage for device D should be resulted from the incomplete removal of the electrically resistive DBPPV/QD composite between probe tips and metal pads, i.e., the series resistance of about  $3\Omega$ . From the difference of that between device D and the others. On the other hand, the  $L$ - $I$  possesses the same condition that is less luminance intensity in device D. Since the output light was measured by a silicon detector whose spectral responsivity was not corrected according to the human eye sensitivity function, the measured data could definitely be influenced by both the color-conversion efficiency of composite and the responsivity of the detector.

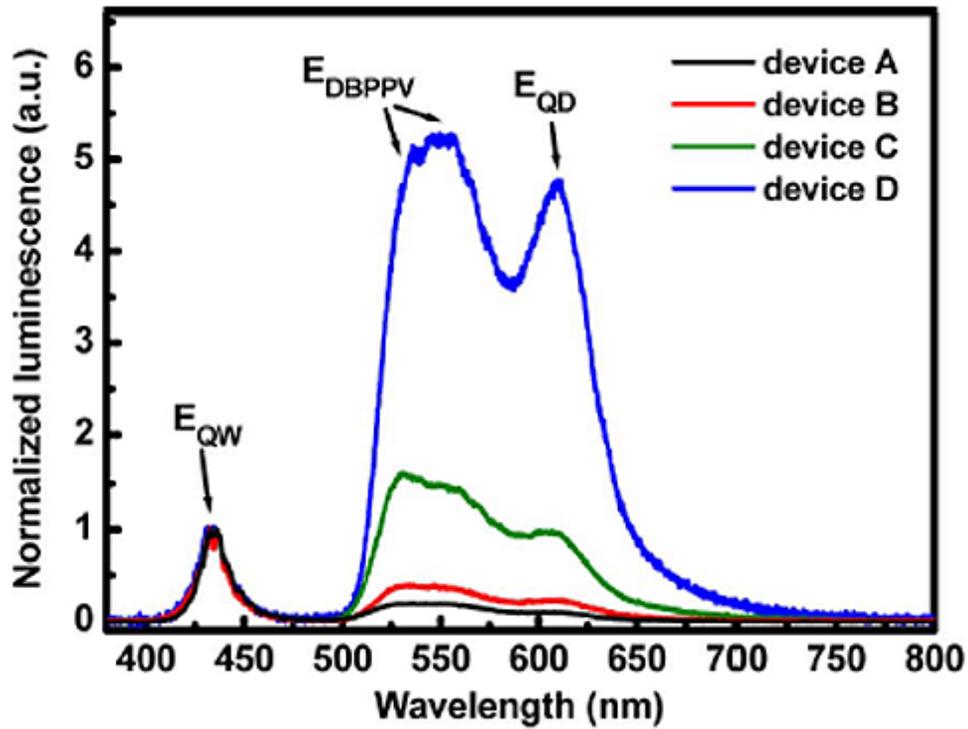


Fig. 3. Room temperature luminescence spectra of devices measured at 20 mA. For easy comparison, the spectra are normalized to the peak at 436 nm.

The EL spectra of devices measured at 20 mA are shown in Fig. 3. To clearly observe the variations, the spectra are normalized to peak at 436 nm, the emission from InGaN QWs ( $E_{QW}$ ). Aside from this peak, three additional peaks can also be observed as expected. Namely, the broader band located at about 550 nm is the emission from DBPPV ( $E_{DBPPV}$ ), which consists of two peaks at 525 and 563 nm, respectively. As previously reported, the peak at shorter wavelength ( $E_1$ ) is from the single polymer chain (or intrachain) exciton emissions, whereas the other peak ( $E_2$ ) is related to the emissions from the interchain species such as excimers or aggregates<sup>8</sup>. At lower spin speeds (thicker thicknesses), most of the polymer chains are stuck and less extended, which results in the less aggregated morphology and  $E_1$  dominant spectra<sup>9</sup>. Since the QDs are with higher absorption coefficient at shorter wavelength, the emission from QDs at 610 nm ( $E_{QD}$ ) is mainly excited by the blue light. With the increase of composite film thickness, the color of emission light is gradually changed, and the white light emission can be obtained for device C. The corresponding Commission Internationale de l'Eclairage (CIE) chromaticity coordinates are (0.33, 0.36), and the correlated color temperature (CCT) is about 5300 K. After calibration, the luminous flux of device C at 20 mA is 0.5 lm, which corresponds to a luminous efficiency of 8.7 lm/W. However, the coordinates are shifted to the yellow region (0.43, 0.46) as the thickness is further increased to 0.87  $\mu$ m. Meanwhile, the luminescence spectrum showed that more than 90% of the blue light is energy transferred to green and red lights.

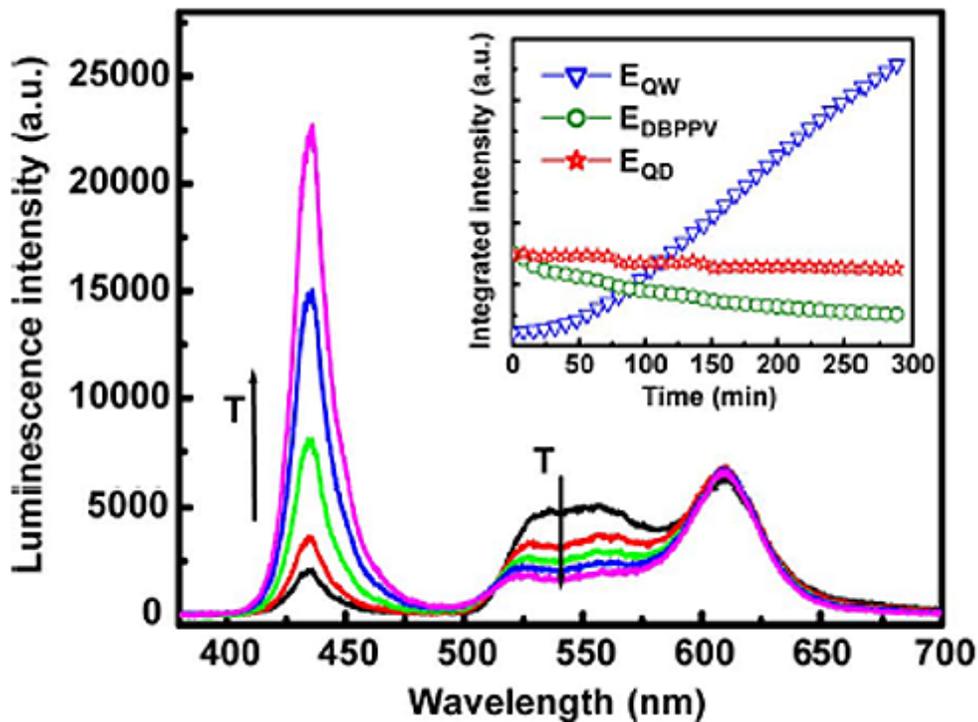


Fig. 4. Variation of luminescence spectrum of device D biased at 20 mA for 5 h. Inset is the variations of integrated intensity from InGaN QWs ( $E_{QW}$ ), DBPPV ( $E_{DBPPV}$ ), and QDs ( $E_{QD}$ ) with time increasing.

To investigate the stability of the DBPPV/QD composite, device D was steadily operated at an injection current of 20 mA at room temperature, and the luminescence spectra were constantly analyzed. The integrated luminescence intensities of  $E_{QW}$ ,  $E_{DBPPV}$ , and  $E_{QD}$  were also separately recorded as a function of operation time. The time-dependent EL spectra are shown in Fig. 4, and the inset shows the variations of intensities of  $E_{QW}$ ,  $E_{DBPPV}$ , and  $E_{QD}$ . Obviously,  $E_{DBPPV}$  ( $E_1 + E_2$ ) is decreased by 62% within 5 h, whereas  $E_{QW}$  is rapidly increased and  $E_{QD}$  is almost constant. Since the reliability test was in the air environment, the simultaneous oxygen penetration and photoexcitation lead to the well-known photooxidation effect, which is one of the main causes of the photodegradation in PPV derivatives<sup>10</sup>. Accordingly, the chain scission of the vinylene double bond originated from the oxygen-related photochemical reaction gradually reduces the excitons and causes the peak blue shift (bandgap widening)<sup>11</sup>. The PL efficiency of DBPPV is decreased, and the composite film becomes transparent, which results in the rapid increase of  $E_{QW}$ .

The current-dependent emission colors of devices biased from 6 to 60 mA are shown in Fig. 5. With the increase of composite thickness, the variations of current-dependent CIE coordinates are decreased, and no observable fluctuation is measured when the film is thicker than 0.61  $\mu\text{m}$ . Also shown are the time-dependent CIE coordinates of device D derived from Fig. 4. Within the first 30 min, the coordinates are shifted toward the pink region. After the blue component becomes dominant, they are monotonously shifted toward the blue region and eventually turn to be the purple light.

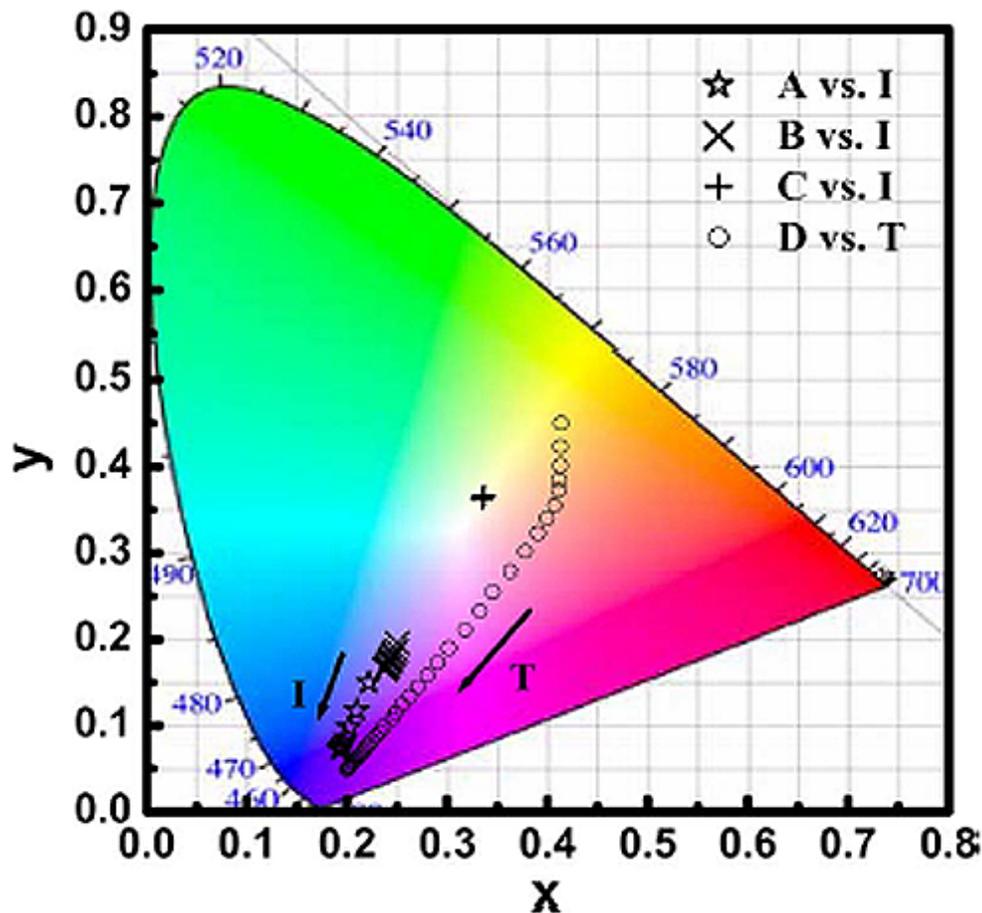


Fig. 5. CIE coordinates of devices A, B, and C as a function of driving current from 6 to 60 mA. Also shown are the coordinates of device D as functions of aging time.

#### IV. SUMMARY

For achieving white light emission, synthesized red-emitting CdSe/ZnS QDs in combination with the green-emitting DBPPV were dually hybridized on the blue InGaN LEDs. With the thickness of the capped DBPPV/QD composite film reaching  $0.61 \mu\text{m}$ , the corresponding CIE chromaticity coordinates attain (0.33, 0.36), which are located within the white region of the diagram, and the CCT is about 5300 K. However, the coordinates are shifted to the yellow region (0.43, 0.46) as the thickness is further increased to  $0.87 \mu\text{m}$ . Meanwhile, the luminescence spectrum shows that more than 90% of the blue light is effectively energy transferred to green and red lights. Finally, for a long-term operation, the integrated luminescence intensity from the DBPPV is significantly decreased to be 38% of its original value within 5 h.

#### Reference

- [1] R. Peon, G. Doluweera, I. Platonova, and G. Irvine-Halliday, "Solid state lighting for the developing world—The only solution," *Proc. SPIE*, vol. 5941, pp. 594 10N.1–594 10N.15, Sep. 2005.
- [2] Y. J. Lee, H. C. Kuo, and S. C. Wang, "Dichromatic InGaN-based white light emitting diode by using laser lift-off and wafer-bonding schemes," *Appl. Phys. Lett.*, vol. 90, no. 16, p. 161 115, Apr. 2007.
- [3] Y. Li, A. Rizzo, R. Cingolani, and G. Gigli, "White-light-emitting diodes using semiconductor nanocrystals," *Microchim. Acta*, vol. 159, no. 3/4, pp. 207–215, Jul. 2007.
- [4] S. Y. Kim, K. Y. Kim, Y. H. Tak, and J. L. Lee, "Dark spot formation mechanism in organic light emitting diodes," *Appl. Phys. Lett.*, vol. 89, no. 13, pp. 132 108-1–132 108-3, Sep. 2006.

- [5] J. H. Park, J. Y. Kim, B. D. Chin, Y. C. Kim, and O. O. Park, "White emission from polymer/quantum dot ternary nanocomposites by incomplete energy transfer," *Nanotechnology*, vol. 15, no. 9, pp. 1217–1220, Sep. 2004.
- [6] H. V. Demir, S. Nizamoglu, T. Ozel, E. Sari, and N. Tian, "White light generation tuned by dual hybridization of nanocrystals and conjugated polymers," *New J. Phys.*, vol. 9, no. 10, pp. 362-1–362-13, Oct. 2007.
- [7] C. Y. Huang, Y. K. Su, T. C. Wen, T. F. Guo, and M. L. Tu, "Singlelayered hybrid DBPPV-CdSe-ZnS quantum-dot light-emitting diodes," *IEEE Photon. Technol. Lett.*, vol. 20, no. 4, pp. 282–284, Feb. 2008.
- [8] F. Kong, X. L. Wu, R. K. Yuan, C. Z. Yang, G. G. Siu, and P. K. Chu, "Optical emission from the aggregated state in poly [2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene vinylene]," *J. Vac. Sci. Technol. A, Vac. Surf. Films*, vol. 24, no. 2, pp. 202–205, Mar./Apr. 2006.
- [9] J. Liu, T. F. Guo, and Y. Yang, "Effects of thermal annealing on the performance of polymer light emitting diodes," *J. Appl. Phys.*, vol. 91, no. 3, pp. 1595–1600, Feb. 2002.
- [10] H. Y. Low, "Photo and photo-oxidative degradations of poly (phenylene vinylent)," *Thin Solid Films*, vol. 413, no. 1/2, pp. 160–166, Jun. 2002.
- [11] X. Y. Deng, K. Y. Wong, and Y. Q. Mo, "Three-color polymeric lightemitting devices using selective photo-oxidation of multilayered conjugated polymers," *Appl. Phys. Lett.*, vol. 90, no. 6, p. 063 505, Feb. 2007.

*Copyright 2008 National Cheng Kung University*