

Color-tunable multilayer light-emitting diodes based on conjugated polymers

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Wide-range low-voltage continuous color tuning is achieved in multilayer light-emitting diodes based exclusively on the commonly used high-efficiency electroluminescent conjugated polymers. There are three layers for red, green, and blue emission, and one extra layer for electron blocking. The color of the emitted photon depends on the position of the electron-hole recombination. Due to the stronger field dependence of the electron mobility relative to the hole mobility, the recombination zone is pushed away from the cathode and concentrated in different emissive layers as the voltage increases. © 2004 American Institute of Physics. [DOI: 10.1063/1.1645983]

Conjugated polymers have been used as the emissive materials for efficient light-emitting diodes (LED),¹ which cover the whole visible spectral range. The emission color is fixed by the band gap of the particular polymer. Poly(*p*-phenylene vinylene) (PPV) and polyfluorene (PF) are the two most important families of conjugated polymers used in LED. PPV derivatives cover the red to green spectral range, while PF derivatives cover the whole visible range. It will be highly desirable if one single LED can emit light with a wide range of color, continuously tuned by the applied voltage. Such tunable LED can be applied in the full-color display, signaling, and illumination. There is currently a tremendous amount of effort on the PPV and PF display. In order to achieve a full-color pixel, ink-jet and other techniques are being developed to deposit accurately three different kinds of polymers for red, green, and blue in small areas.^{2,3} In addition to technical difficulties, such approaches sacrifice one great advantage of the conjugated polymers, namely, ease of direct spin-coating to form large-area uniform films. It will be much simpler if the polymer film is uniformly formed while the color of each pixel is controlled by the voltage. Apparently the capability of such continuous color tuning will also be highly desirable for solid-state illumination in the future. There have been reports of organic color-tunable LED involving small molecules,⁴ a combination of polymers and small molecules,⁵⁻⁷ CdSe nano-particle/polymer composites,^{8,9} dye-doped polythiophene,¹⁰ polythiophene blends,^{11,12} and *n*-type polymers.¹³ In this letter, we propose a mechanism which enables wide-range color-tuning for multilayer polymer LED based on PPV and PF with tuning voltage as low as 4 V.

Color-tuning can be realized in a multilayer LED if the electron-hole recombination zone is controlled by the voltage. Due to the presence of electron traps in most conjugated polymers including PPV and PF, the electron mobility μ_e is much smaller than the hole mobility μ_h . So the holes can easily move away from the anode while the electrons hardly move far from the cathode. The carrier mobility depends on the electric field E in the Poole-Frenkel form: $\mu = \mu_0 \exp(\gamma\sqrt{E})$. The parameter γ determines how rapidly the mobility increases with E . As the voltage bias increases, the electron traps are gradually filled by the injected current and μ_e increases strongly.¹⁴ This corresponds effectively to a larger γ for μ_e than for μ_h .¹⁵ For the typical case of poly [2-methoxy-5 (2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV), it is shown that $\mu_h = 37\mu_e$ at zero field, while $\mu_h = 2.2\mu_e$ at $E = 2 \times 10^8$ V/m.¹⁵ Light emission is due to the recombination of the holes and electrons. At low bias, the electron distribution concentrates near the cathode, while the hole distribution is more extended from the anode due to the higher mobility. So most of the recombination takes place near the cathode. As the bias increases, the electron distribution become more extended, and the recombination moves from the cathode toward the anode.¹⁴ In single-layer LED, such motion of the recombination zone does not alter the emission color. However, the color does vary due to such zone motion in multilayer LED whose layers emit with different colors. At low bias, recombination occurs only in the layer nearest to the cathode. As bias increases, electrons become able to move out of the nearest layer and recombination takes place in other layers successively. An electron blocking layer is needed to enhance the electron density and recombination in the farthest layer from the cathode at high bias by confining the electrons near the interface with the

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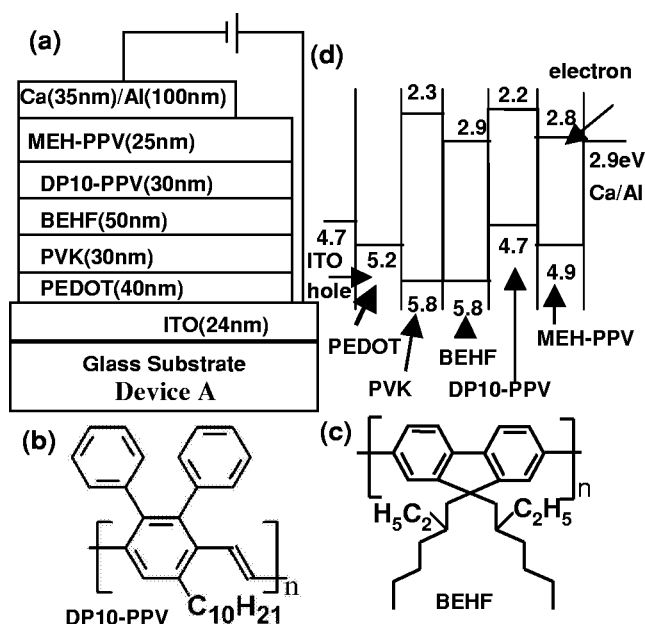


FIG. 1. (a) Device structure of multi-layer LED, (b) chemical structures of the emissive polymers DP10-PPV, and (c) BEHF. (d) The EA and IP are also shown.

blocking layer. It is expected that in such multilayer LEDs the motion of the recombination zone through different layers causes a continuous change in the weighting of the emission from each layer. The overall color can therefore be controlled by the voltage.

Four multilayered LEDs (devices A–D) are studied with various combinations of red (R), green (G), and blue (B) layers. The device structure for A is shown in Fig. 1(a). We use MEH-PPV for R, poly(2,3-diphenylphenylene vinylene) (DP10-PPV) [Fig. 1(b)] for G1, Dow Chemical LUMATION¹⁶ Green-B polyfluorene (DPF) for G2, and poly[9,9-di-(2-ethylhexyl)-fluorenyl-2,7-diyl] (BEHF) [Fig. 1(c)] for B. MEH-PPV and DP10-PPV are synthesized,^{17,18} DPF is from Dow Chemical Company,¹⁹ and BEHF is from Aldrich. The peaks of photoluminescence (PL) for the polymers are 592 nm (R), 500 nm (G1), 540 nm (G2), and 424 nm (B). Poly(3,4-ethylenedioxythiophene) doped with polystyrene sulphonated acid (PEDOT:PSS) is used as the hole transport layer. A layer of poly(*N*-vinyl carbazole) (PVK) is added between PEDOT:PSS and the emissive layer in order to block the electrons. The electron affinity (EA) and ionization potential (IP) are indicated in Fig. 1(d). All the emissive polymers are dissolved in toluene with weight percentages 0.3 wt. % for R, 0.5 wt. % for G1, 1.2 wt. % for G2, and 1.5 wt. % for B. The concentration for R and G is lower than what is normally used for LED in order to have a thinner film. The layer thicknesses for the devices are as follows. Device A (B/G1/R): PEDOT/PVK (50 nm)/BEHF (70 nm)/DP10-PPV (20 nm)/MEH-PPV (20 nm)/Ca; device B (B/G2/R): PEDOT/PVK (30 nm)/BEHF (50 nm)/DPF (30 nm)/MEH-PPV (30 nm)/Ca; device C (B/G2): PEDOT/PVK (50 nm)/BEHF (70 nm)/DPF (30 nm)/Ca; device D (G2/B): PEDOT/PVK (50 nm)/DPF (70 nm)/BEHF (30 nm)/Ca. Each polymer layer is baked at 120 °C for 60 minutes in vacuum (10^{-3} torr) after spin-coating. It is crucial that the spin coating of the subsequent layer does not dissolve the previous layer. To check this, pure toluene is spin-cast on

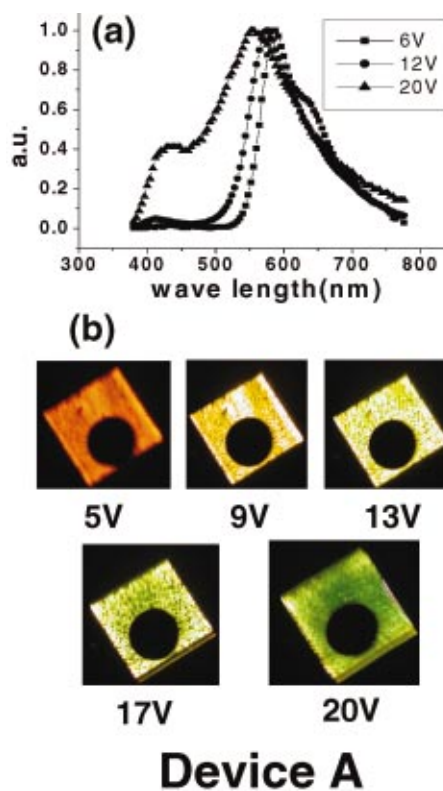


FIG. 2. (Color) (a) Normalized spectra and (b) pictures of triple-layer device A (BGR) at various voltages.

baked film and we found that the film thickness is reduced by no more than 5%. The Ca/Al cathode is evaporated and packaged in a glove box.

The normalized emission spectrum and picture of device A with triple emission layers is shown in Fig. 2. At 6 V, the spectrum is identical to the PL of MEH-PPV because the electron-hole recombination concentrates near the cathode. As the bias voltage increases, there is a significant blueshift. It is yellow at 9 V and green at 13 V. The emission becomes greenish blue after 17 V. In the spectrum one sees clearly the emergence of the peak around 424 nm due to BEHF. The spectrum is, however, never dominated by the blue emission up to 20 V. The main reason is that the efficiency of blue polymers is much weaker than red and green polymers. Better color-tuning at higher voltage could be realized if more efficient blue polymers (or less efficient red and green) are used. The highest brightness is around 400 cd/m^2 , reached at 14 V. Beyond 14 V, the brightness decreases and the current saturates at the same time (Fig. 4). This peculiar saturation behavior is reproduced in many triple-layer devices with similar structures. One possible reason is that as the voltage increases, a large amount of electrons are accumulated at the barrier between R and G, which screen the electric field effectively in the very thin R layer and cause an effective increase in the injection barrier from the cathode to R.²⁰ The green polymer is replaced by DPF in device B. The spectrum shown in Fig. 3(a) starts to shift rigidly from red to green for voltage as low as 6 V. The blue emission is weaker, presumably due to the larger barrier between G2 and B. The current saturation at high voltage is even more pronounced than device A.

Figure 3(b) shows the results for double-layer device C.

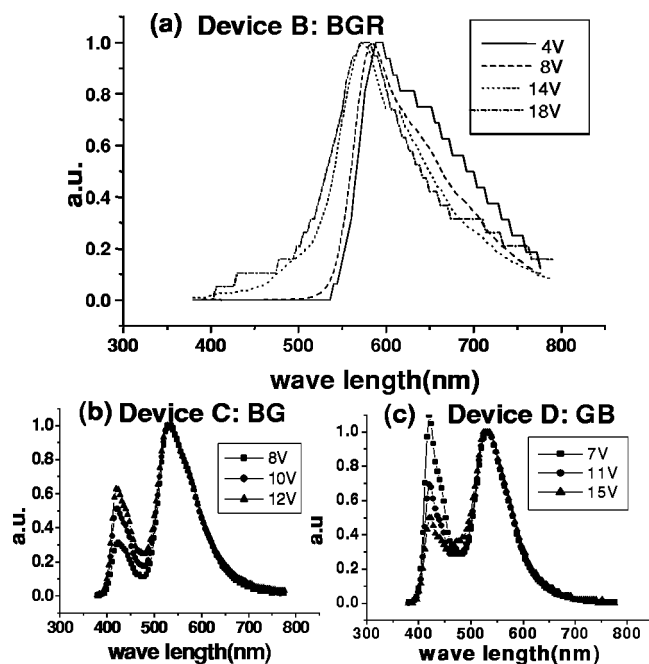


FIG. 3. (a) Normalized spectra of triple-layer device *B*(BGR) and of (b) double-layer devices *C*(BG) and (c) *D*(GB). Green emission is normalized.

As expected, there is an emergence of the blue emission as the voltage increases. Without the broad R emission, the B and G emission are well separated. Significant color-tuning occurs between 8 and 12 V. In order to test the mechanism of color-tuning further, we study device *D*, which has a reversed order or G and B layers. As expected, from the stronger field dependence of electron mobility, the spectrum has a redshift instead of a blueshift as the voltage increases [Fig. 3(c)]. At low voltage, the recombination concentrates in the B layer, which is next to the cathode. The strong G emission at 7 V is due to the PL of the G layer excited by the B emission. There is no such effect in the other devices in which layers with larger band gaps are closer to the transparent ITO. The redshift of device *D* is a clear confirmation that the recombination zone is controlled by the mobility difference. The current and luminance are plotted in Fig. 4 as functions of voltage. In general, the double-layer devices are much brighter than the triple-layer devices. Perhaps the layer junctions introduce exciton quenching centers and the efficiency decreases with more junctions. The color is determined by the field and the luminance is determined by the current. They change simultaneously in our LED's. Many applications require independent control of the color and luminance. One may add a base layer between PEDOT:PSS and PVK to make a device similar to a bipolar junction transistor,²⁰ in which color is controlled by the base-collector (Ca/Al) bias while current is controlled by the emitter (ITO) base bias.

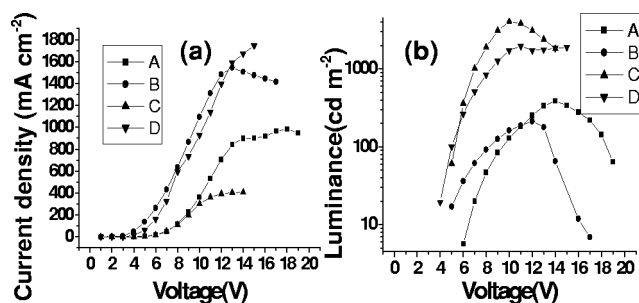


FIG. 4. (a) Current-voltage and (b) luminance-voltage relations for devices *A*–*D*.

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