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Efficient Blue and Green Electroluminescent Devices from Conjugated Polymers

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1. Introduction

Conjugated polymers offer many advantages as materials for use in light-emitting diodes (LEDs). [1-9] They are mechanically flexible, they can be fabricated in large areas and patterned with relative ease by casting the semiconducting and luminescent polymer from solution, and the color of the emitted light can be tailored by chemical modification of the molecular structure. Among various emission colors, blue and blue-green electroluminescence are of great interest to many practical applications, from simple indicating lights to high-end flat panel displays. In this summary, we will introduce two approaches of fabricating efficient blue emission polymer electroluminescent devices: the polymer light emitting diodes and polymer light-emitting electrochemical cells.

2. Efficient Blue Poly (paraphenylene) LEDs

Among the blue emitting materials, poly-(paraphenylene) (PPP) and its derivatives are promising because of their high photo-luminescence (PL) efficiency. We have recently demonstrated an efficient PPP derivative: the DO-PPP as an efficient conjugated polymer as the active material for the blue polymer LED. The chemical structure, absorption, and emission spectra of DO-PPP are shown in Figure 1. The PL quantum efficiency is about 85% for DO-PPP solution, and 35% for spin-casted thin film. DO-PPP thin films show small crystalline structure under cross-polarized microscope.

For this study, ITO was used as the anode and Ca was used as the cathode. The LEDs fabricated from DO-PPP were double-layer devices; a hole transport layer, poly(N-vinylcarbazole) (PVK), was introduced between the DO-PPP and the ITO to enhance hole injection and to serve as an electron blocking layer. [10] The measured external quantum efficiency is ~3% for double-layer devices. The LED turned on at approximately 15 volts, and reached a brightness of 490 cd/m^2 at ~30 volts. The highest external quantum efficiency obtained is about 3%, which is equivalent to ~5.4% internal quantum efficiency. Typical quantum efficiencies of DO-PPP double layer devices ranged between 2.0% -2.5%. The blue-violet light was uniform and bright. The device operating voltage varies with the thickness of the PVK and PPP films., with thicker films always requiring a higher operating voltage. This thickness dependence of the operating voltage is typical of polymer LEDs and has been explained in terms of Fowler-Nordheim tunneling injection.

Although, the device performance of DO-PPP is among the best of the blue polymer LEDs, the operating voltage of DO-PPP LEDs is still too high. Such high voltage is not practical for real world application, particularly for portable electronics. In addition, the use of low work function metals such as calcium, is also problematic for future device fabrication. In order to overcome these problems, a new type of light-emitting device has been developed.

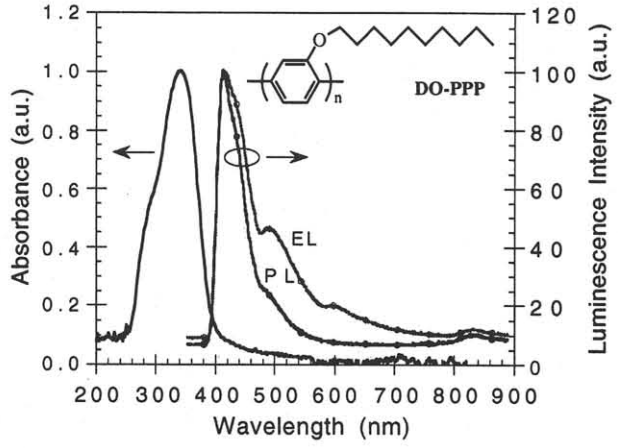

Figure 1. Absorption and photoluminescence spectra for solid films of pure DO-PPP, and electroluminescence spectrum obtained from an ITO/PVK/DO-PPP/Ca device.

Efficient Blue-Green Polymer Light-Emitting Electrochemical Cells

The light-emitting electrochemical cell (LEC) which combines the novel electrochemical properties of conjugated polymers with the ionic conductivity of polymer electrolytes has recently been invented. [11-14] The LEC is a bipolar p-n junction device; when biased, the *p*- and *n*-doping regions, adjacent to the anode and cathode, are electrochemically induced respectively. A dynamic *p-n* junction is therefore created between the *p*- and *n*-doped regions. Confirmation of the LEC operating mechanism came from the direct observation of the p-n junction in an LEC with planar electrode configuration. [11] The active layer of an LEC is a blend of luminescent conjugated polymers and solid electrolytes. Since an LEC is a *p-n* junction device, it has the following advantages: low operating voltage, high quantum efficiency, high power efficiency, and the use of air stable electrodes. In this section, we present a very efficient blue-green LEC made of poly[9,9-bis(3,6-dioxaheptyl)-fluorene-2,7-diyl] (BDOH-PF). This device reaches 4% of external quantum efficiency with 12 lumen/watt luminous efficiency at 3.1V bias.

Figure 2 displays the chemical structure the optical absorption, and PL spectra of both a solution of BDOH-PF in THF (1mg/100ml) and of a thin film spin-cast from a concentrated solution (20mg/ml). The absorption spectrum of the dilute solution has a relatively sharp peak at 385 nm, with an onset of absorption at 430 nm. The absorption spectrum of the thin film is similar except that the peak is broader.

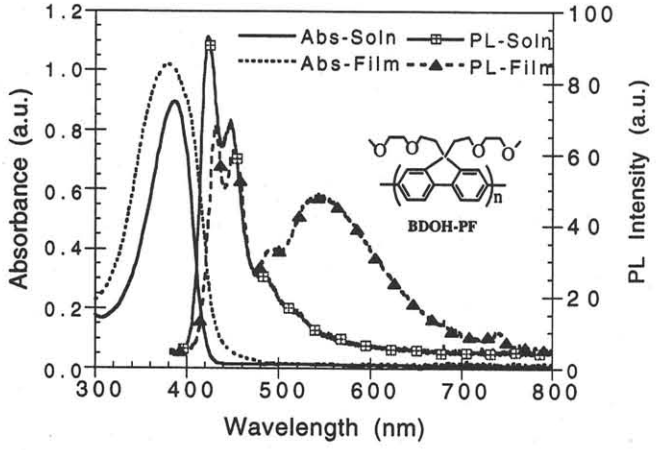

Figure 2. Optical absorption and PL spectra of BDOH-PF in a dilute solution in THF (1mg/100mL) and in a thin film spin-cast from a solution in THF (20mg/mL).

LECs were fabricated using a blend of BDOH-PF with lithium triflate, at a weight ratio of 5.6:1, as the emissive material. A thin film of this blend (1500 Å thick) was sandwiched between an ITO coated glass and a vacuum-evaporated aluminum film (400 Å thick). When a bias of 3.1V was applied between the two electrodes, the device slowly turned on and emitted a bright blue-green light. The initial EL is blue, similar to the PL, however, EL slowly changes to blue-green color as the biasing continued. Compared to the PL, the 430nm and 450 nm peaks were dramatically decreased. At 3.1V, the emission intensity reached a maximum brightness of 190 cd/m^2. The external quantum efficiency was 4% photons/electron, and the power efficiency was 12 lumens/watt. This is the highest reported data from any organic or polymeric LEDs with a single layer device structure. The device brightness increase to near 1000 cd/m^2 at 3.5 volts. However, the device lifetime is still short, only a few hours. The failure of these devices are still under investigation.

4. Conclusions:

Two efficient polymer electroluminescent devices, with blue and blue-green emission respectively, have been demonstrated. The DO-PPP LED has achieved the highest efficiency, 3% external efficiency, in blue polymer light-emitting diodes. The BDOH-PF LEC, with blue-green EL emission, has achieved the highest efficiency in single layer polymer devices. Both of these devices have relatively short lifetimes and the failure mechanisms are still under investigation.

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