

## Polymer solution light-emitting devices

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Traditional conjugated polymer electroluminescent devices are thin-film solid-state devices consisting of a thin polymer film sandwiched between two electrodes. In this letter, we demonstrate the generation of luminescence from polymer solutions in a compact polymer solution configuration. This unique polymer solution light-emitting device (SLED) consists of a thin layer of a polymer solution sandwiched between two transparent indium-tin-oxide/glass substrates. When biased, the device turns on at slightly above the band-gap energy and emits bright luminescence. The emission spectrum is consistent with the photoluminescence spectrum obtained from the polymer solution. We suggest that the mechanism of the SLED is due to the electrogenerated chemiluminescence effect. The SLED combines the advantages of low operating voltage, and easy and low-cost fabrication. The SLED is also a highly transparent emissive device when transparent materials are used for the electrodes and the substrates. © 1999 American Institute of Physics. [S0003-6951(99)02414-6]

Traditional polymer light-emitting diodes are thin-film solid-state devices consisting of a thin polymer film with a typical thickness of about 100 nm, sandwiched between an anode and a cathode.<sup>1</sup> On the application of a suitable bias, electrons and holes are injected from the cathode and the anode, respectively, into the polymer. Some of the injected carriers subsequently undergo radiative recombination within the polymer thin film with the resulting release of energy in the form of an electroluminescence emission. In this letter, we present a polymer solution-based light-emitting device (SLED) for the generation of luminescence. In the SLEDs, polymer solutions were sandwiched between two transparent indium-tin-oxide (ITO)/glass substrates with the thickness of the solution layer ranging from 1 to 2  $\mu\text{m}$ . The onset of a strong luminescence was observed slightly above the band-gap energy on the application of a suitable bias.

Previously, the application of organic dye solutions as the active medium for light emission was demonstrated more than a decade ago in closed-cell<sup>2</sup> and circulated-cell<sup>3</sup> configurations. The active media were organic dye molecules dissolved in organic solvents. It was proved that electrogenerated chemiluminescence (ECL) was responsible for the generation of the light. More recently, Horiuchi, Niwa, and Hatakenaka reported the observation of electrically pumped laser action from a circulation cell employing an organic dye solution inside a resonant cavity.<sup>4</sup> Although the polymer ECL has been demonstrated before, it was done in the solid-state format, i.e., conjugated polymer was coated on the surface of one of the electrodes.<sup>5</sup> On the other hand, our SLED consists of a thin polymer solution layer sandwiched between two ITO/glass substrates in a closed-cell configuration. The fabrication process of the SLED is fairly simple and typically consists of three steps. In the first step, several drops of the polymer solution are deposited on top of a pre-cleaned ITO/glass substrate. Next, another pre-cleaned ITO/

glass substrate is placed on top of the first ITO/glass substrate with the two ITO electrodes facing each other and the polymer solution situated in between the two substrates. In the third step these two substrates are pushed against each other by the application of an external force resulting in the simultaneous ejection of the extra polymer solution from the sides of the SLED. On drying, this extra polymer solution forms a nature seal around the edge, thereby preventing the solvent vaporization from the sandwich structure. The thickness of the polymer solution layer is controlled by embedding glass beads, ranging from 1 to 2  $\mu\text{m}$ , within the polymer solution.

The pre-cleaned ITO/glass substrates were baked at 100 °C for several hours before they were used. The polymer solution preparation process and device fabrication were carried out in a nitrogen environment. Due to its simplicity, the device fabrication process can be completed within a few minutes. We have examined polymer solutions of poly [9,9-bis(3,6-dioxahexyl)-fluorene-2,7-diyl] (BDOH-PF) (Ref. 6) prepared in different concentrations, ranged from 1% to 20%, using dichloro-benzene as the solvent. BDOH-PF has a very high photoluminescent quantum efficiency, 77% for the solution and 73% for the thin film. The completed devices were then characterized by optical and electrical measurements. The current-voltage ( $I$ - $V$ ) and brightness-voltage ( $L$ - $V$ ) characteristics were measured using a HP 4145A semiconductor parameter analyzer along with a calibrated silicon photodiode functioning as an optical sensor. The photoluminescent (PL) and ECL spectra were measured using an Ocean Optics spectrometer. The absorption spectra were measured using a HP 8453 diode array spectrometer. The absolute brightness was determined by using a Photo Research PR650 spectroradiometer.

The absorption, PL, and electrogenerated luminescent spectra of the SLED made of BDOH-PF solutions are shown in Fig. 1. Both the luminescent spectra are nearly identical, thereby indicating that the electrogenerated luminescence

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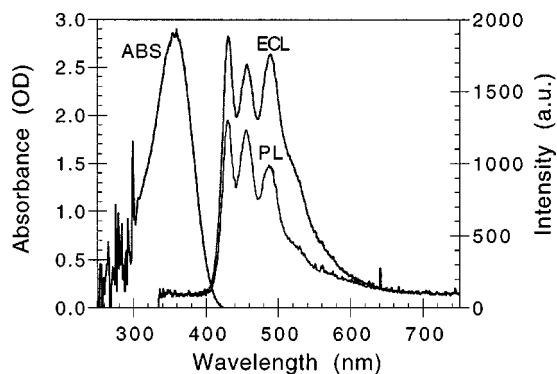


FIG. 1. Absorption, photoluminescence, and electrochemiluminescence spectra of a SLED using BDOH-PF solution as the active material.

from the SLED is indeed from the polymer solution. In addition, the higher-wavelength emissions (around 550 nm) due to the polymer interchain interaction that is prominent in BDOH-PF thin film are not observed in our SLEDs.<sup>6</sup> The  $I$ - $V$  and  $L$ - $V$  curves for the SLED are shown in Fig. 2. The voltage scan rate is about 5 V/s. The  $I$ - $V$  curves indicate that significant charge injection occurs around 3.5 V, which is consistent with the band-gap energy. (The band-gap energy is taken as the measured energy of the edge of the absorption spectra of BDOH-PF, which is consistent with the values obtained from the difference of the oxidation and reduction potentials of this material.<sup>6</sup>) However, the voltage for the onset of photon emission is around 6 V, which is higher than that required for the injection of electrical current. The quantum efficiency is estimated to be  $\sim 1\%$  (photons/electron). The operating mechanism of the SLED is believed to be due to ECL, similar to the reported dye solution cells.<sup>2</sup> The onset of charge injection in the SLED at 3.5 V is probably indicative of the initiation of the oxidation and reduction process of BDOH-PF. The lifetime is about 30 min under the continuous driving condition around 10 V. The major failure mechanism is the vaporization of the organic solvent during the device stress test. The device lifetime can be significantly prolonged if the edges of the device can be hermetically sealed. We also observed the device turn-on speed could be enhanced after several times of prebiases. Once the SLED

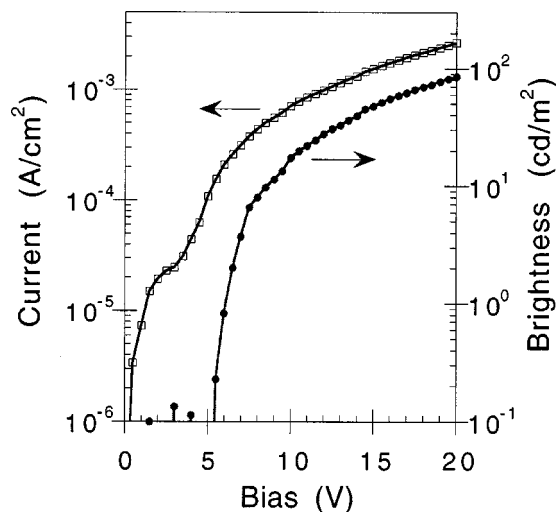


FIG. 2. Current-brightness-voltage curves for the SLED using BDOH-PF solution as the active material.

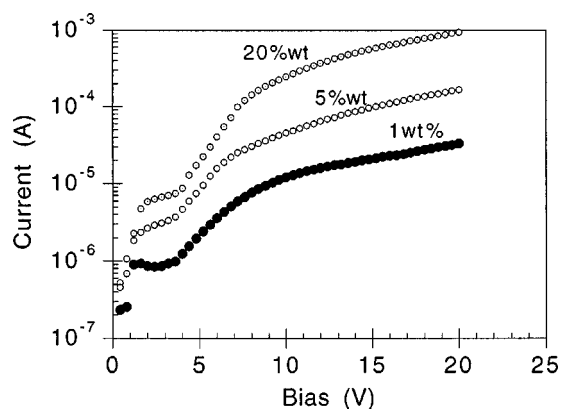


FIG. 3. Current-voltage curves for the SLED with different BDOH-PF concentrations.

has been prebiased, the device turn-on time is about 20–40 ms; depending on the solvent and polymer concentration, this switching time is comparable to liquid-crystal displays.

Traditionally, the dye solution ECL cell involves the movement of the electrically charged dye molecules under the influence of the applied electrical field. When biased, some of the dye molecules are oxidized near the anode side and some of them are reduced near the cathode side. Under the influence of the applied electric field, the oxidized molecules migrate toward the cathode while the reduced molecules migrate toward the anode. The photons are generated by the radiative recombination of the encountering oppositely charged dye molecules. For the SLED, it was originally thought that the high molecular weight of the conjugated polymers used in this research would hinder such a motion, thereby making this operating mechanism improbable. However, the observation of the fluid motion within a biased SLED under an optical microscope seems to confirm that ECL is indeed the operating mechanism for these devices. In addition, the delay of photon emission observed in the  $L$ - $V$  curve could be probably due to the higher field required to enable the migration of the charged polymer from one electrode to the other. The injection current and device brightness can be significantly enhanced when a higher concentration of polymer solution is used. Figure 3 shows the  $I$ - $V$  curves of SLEDs with three different BDOH-PF concentrations, 1%, 5%, and 20%. (The  $L$ - $V$  curves, not shown here, follow the  $I$ - $V$  curves and have a similar pattern as the  $L$ - $V$  curve shown in Fig. 2.) The enhancement of injection current is obviously due to the higher concentration of polymer available for the ECL process. It is interesting to note that the turn-on voltages of the injection current and photon emission are more or less the same, even the concentration of BDOH-PF has increased by a factor of 20. Meanwhile, the magnitude of the injection current (and emission photons) has increased by  $\sim 40$  times. This nonlinear enhancement of the injection current and emission photons is currently under investigation.

It can be also suspected that the device operates by an electrochemical process similar to the polymer light-emitting electrochemical cells (LECs). This is because of the devices' injection current turn on at the band-gap energy, a special feature which is also observed in the LECs.<sup>7</sup> However, we did not add any salt to our SLEDs, which is necessary for the



FIG. 4. Picture of an unbiased SLED, showing the transparent devices. The transmittance is higher than 90%.

formation of polymer LECs. (The chemical element analysis indicated that the ion concentrations of BDOH-PF are below the detectable level.) Furthermore, on the addition of a small amount of lithium-triflate salt to the SLED, in a ratio of 1:1000 of lithium-triflate to BDOH-PF, we observed an enhancement of the electrical current and the device was able to turn on more uniformly in the beginning. The quantum efficiency of the SLED remains unchanged. The increase of electrical current and brightness is perhaps due to the presence of ions enhancing the charge injection from the electrode to the BDOH-PF polymer. This enhancement of charge injection can also be reproduced by adding polar molecules, such as laser dye DCM, into the BDOH-PF solution. However, adding lithium-triflate salt into the BDOH-PF solution significantly quenched the photoluminescence after the device operation, indicating that the applied voltage induces the doping process of BDOH-PF. We further widened the spacing between the anode and the cathode using 2  $\mu\text{m}$  diam glass beads into the SLED device structure. We observed that the injection current was significantly reduced and the luminescence from the device nearly disappeared. All these observations are inconsistent with the LECs.

There are many advantages associated with SLEDs. The most significant advantages are the simplicity of the process of device fabrication, its large-area processing capability, and its pinhole-free nature. The SLED is also a self-encapsulated device since it does not require a capping layer; the top ITO/glass plate serves as the device capping layer. The edge sealing can also be done by the regular fusion of glass and by taking care to include orifices in the edges for the introduction and removal of the polymer solution. Due to the use of dual ITO/glass substrates, the SLED is a highly transparent device. The transparency is above 90% for nearly the entire visible spectrum. Figures 4 and 5 show the pictures of the transparent SLED without and with bias, respectively. Therefore, vertically stacked, transparent light-emitting devices with high contrast can also be easily achieved by SLEDs.<sup>8</sup> Finally, the low cost of fabrication and minimal wastage of the polymer solution will be attractive features for future practical applications. Although polymer SLEDs have many advantages, there are still many technical issues that need to be resolved. Major challenges for the future practical applications of the polymer SLEDs are the en-



FIG. 5. Picture of a biased SLED, showing a strong blue electrochemiluminescence emission.

hancement of device efficiency, turn-on speed, and device lifetime.

In summary, we have demonstrated a novel type of polymer emissive device, the polymer solution light-emitting device. The device operating mechanism is believed to be similar to the regular electrochemiluminescent cell fabricated by the organic dye solutions proved earlier.<sup>2-4</sup> The SLEDs demonstrated in this letter are transparent devices with two ITO/glass substrates sandwiching a thin layer of polymer solution. The active material used in this letter is BDOH-PF. When biased, the device turns on slightly above the band-gap energy and emits a bright electrochemiluminescence. The emission spectrum is consistent with the photoluminescence spectrum obtained from the polymer solution. Based on the data collected, we suggest that the mechanism of the SLED is probably due to the ECL effect. The SLED combines the advantages of low operating voltage, and easy and low-cost fabrication. It is anticipated that the SLED will open a new direction for the fabrication of future polymer luminescent devices with the potential of creating electrically generated polymer lasing.<sup>4</sup>

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