Electro-generated Chemiluminescence Mechanism of Polymer Solution Light-Emitting Devices

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The traditional polymer light-emitting device is a solid-state device in which the polymer thin film is sandwiched between two electrodes. Recently, we reported a different type of device: the polymer solution light-emitting device (SLED), in which the light-emitting medium is a thin layer of polymer solution sandwiched between two electrodes. In this article, we studied the light-emission mechanism of the SLEDs by cyclic voltammetry, transient electroluminescence measurement, current–light–voltage (I–L–V) measurement, and the optical microscopy observation on a surface cell SLED. The turn-on speed of the light-emission of the SLED with 1 μm gap was found to be ca. 40 ms, which is similar to that of the dye ECL cells. The voltage for charge injection of the SLED devices agrees with the potential difference between the onset potentials of the oxidation for radical cation formation and the reduction for radical anion formation. However, the light emission turns on at a higher voltage, and the turn-on voltage depends on the thickness of the SLED solution layer and the operation temperature. In the surface cell SLEDs, light emission occurs at the cathode side when the solution used is BDOH-PF in DCB, while it is at the anode side when the solution is MEH-PPV in cyclohexanone. For the SLEDs with the addition of dye molecules, the light emits from the luminescent molecules with lower exciton energy (lower energy gap). On the basis of the experimental results, we conclude that the device mechanism is due to electro-generated chemiluminescence.

Introduction

The traditional polymer light-emitting diode is a solid-state device consisting of a thin polymer film, typically 100 nm in thickness, sandwiched between an anode and a cathode.1 Upon application of a suitable bias, electrons and holes are injected into the polymer from the cathode and the anode, respectively. Some of the injected carriers subsequently undergo radiative recombination within the polymer thin film, giving rise to an electroluminescence emission. To achieve good device performance, disordered organic or polymeric materials are required. Maximum disorder in organic and polymeric materials can be found in the solution and gel phases; hence, it is of great interest to investigate polymer light-emitting devices having polymer solutions and gels as the active medium.

Recently, we demonstrated the concept of the polymer solution light-emitting device (SLED)2 and gel light-emitting device (GLED).3 In the SLED, a polymer solution was sandwiched between two transparent indium tin oxide (ITO)/glass substrates, with a solution thickness ranging from 1 to 2 μm. Upon the application of a suitable bias, the onset of a strong luminescence was observed. On the basis of very limited evidence we suggested that the mechanism of SLED is perhaps due to the electrogenerated chemiluminescence (ECL) effect.4 However, several critical questions remained unanswered during that time. For example, how does conjugated polymer, with its high molecular weight and bulky shape, participate in the device operating mechanism of SLED? What is the role of organic solvent in SLED? In this manuscript, systematic investigations were carried out to carefully prove that the mechanism is indeed due to the ECL effect, and we have cleared several important questions related to the device-operating mechanism of the polymer SLED.

Experimental Section

The following solvents were chosen for our characterizations of SLED: 1,2-dichlorobenzene (Aldrich, anhydrous, 99%), cyclohexanone (Aldrich, 99%+, ACS grade), tetrahydrofuran (Aldrich, anhydrous, 99.9% inhibitors free). The salt of tetra-n-butylammonium hexafluorophosphate was obtained from Fluka (electrochemical grade). They were used as received in an inert atmosphere drybox (Vacuum Atmospheres Corp.). Two polymers were used in this experiment: poly(2-methoxy-5(2′-ethyl-hexoxy)-p-phenylene vinylene) (MEH-PPV) which is easily p-doped,5 and poly [9,9-bis(3,6-dioxoheptyl)-fluorene-2,7-diyl] (BDOH-PF) which is easily n-doped.6

The indium tin oxide (ITO)/glass substrates underwent a rigorous cleaning process by sonicated washings in acetone and alcohol (Fisher, ACS grade). The cleaned substrates were then baked at 100 °C for several hours. The electrode separation of two ITO/glass electrodes was determined by using silicate beads (Duke Scientific Inc.) ranging from 1 to 100 μm. The preparation of the polymer solution and the device fabrication were carried out in an inert nitrogen environment. The optical and electrical properties of the SLEDs were characterized by current–brightness–voltage (I–L–V) measurements, emission spectra, and cyclic voltammetric measurements. The I–L–V curves were measured by a HP 4145A semiconductor parameter analyzer along with a calibrated silicon photodiode functioning...
as an optical sensor. The emission spectrum was measured with an Ocean Optics spectrometer [model PC2000-UV-Vis-ISA]. The cyclic voltammetric measurement was performed in an electrolyte solution consisting of a 0.1 mol/L tetrabutylammonium hexafluorophosphate (TBAPF6) tetrahydrofuran solution using a Bioanalytical Systems 100B analyzer at a potential scan rate of 20 mV/s. The working electrode for the cyclic voltammetric measurement was a glassy carbon disk electrode (3 mm diameter). A platinum wire served as the counter electrode, and Ag/Ag⁺ was utilized as the reference electrode. All the potential values quoted in this paper are in reference to the Ag/Ag⁺. The transient electroluminescent measurement was performed by sending a square-wave voltage signal, generated from an HP 3245A universal source power supply, to the SLED; the emitted light signal and the square wave signal were collected by a Tektronix TDS 400A digitized oscilloscope.

An SLED in the surface cell configuration was also fabricated using a planar interdigitated gold electrode (Abtech Scientific Inc.) with a 15 μm-wide electrode line and electrode space on the quartz substrate. The emission from the SLED surface cell was observed using a Nikon optical Eclipse E800 microscope.

Results and Discussion

One of the major differences between the polymer SLED and the ECL cell using organic dye molecules pioneered by Bard’s group is that the polymer has a rather high molecular weight and bulky structure. For the traditional ECL cells, positively charged radical cations and negatively charged radical anions move freely in the solution. But for the SLED, it is not clear how charge transportation occurs in the device. The ECL mechanism proposed previously needs to be verified. Therefore, we have carried out several experiments in this work to gain a better understanding of the mechanism of the polymer SLED.

**Transient Measurement.** The transient electroluminescence measurement is first performed. A square wave signal higher than the device turn-on voltage is applied to an SLED with a 1–2 μm thick active layer of 5% BDOH-PF polymer solution in 1,2-dichlorobenzene (DCB). The result, shown in Figure 1, indicates that the turn-on speed of the device is about 40 ms. This speed, believed to be dominated by the charge transport process, is far slower than that of the traditional PLED, but it is similar to that of the dye solution ECL cell. The slower rise time indicates that the charge transport may be dominated by diffusion and the electric-field drift process of the radical ions, rather than the electronic hopping process as found in the PLED.

**Surface Cell SLED.** The transient measurement mentioned above indicates that the motions of the species play an important role in the light emission of the SLED. However, it is still not clear how the large, bulky, charged polymer molecules move within the highly concentrated polymer solution (5%). To answer this question, a second investigation using a surface cell configuration is conducted in order to observe the light-emission process and its light-emitting location. A surface cell with inter-digitated electrodes is illustrated in Figure 2a. The lateral configuration of electrodes allows the direct observation of light-emission under an optical microscope. We placed one drop of BDOH-PF solution on top of the surface cell and a transparent cover glass was placed on the top of the polymer solution to prevent the vaporization of the organic solvent. When the surface cell SLED is biased, two phenomena are observed. First, the emissive light is near the cathode. Second, a flow of polymer solution parallel to the electrode is observed. Due to the low brightness of the device, a picture of the operating device could not be taken. The phenomena are depicted in Figure 2b. However, the cause of this flow of polymer solution is still unclear and remains under study.

The first phenomenon observed above indicates that the radiative recombination occurs near the cathode. In other words, the radical cations must travel from the anode to the cathode and transfer its charge to the reduced BDOH-PF molecules. The energy is released in the form of photons. This can be further understood by the cyclic voltammetric measurement of both BDOH-PF in 0.1 M TBAPF6/THF and 0.1 M TBAPF6/DCB, as shown in Figure 3, parts a and b, respectively. In comparison
of the reduction and oxidation onset potentials of BDOH-PF and DCB in the solution, when the applied voltage across the SLED reaches a certain level, the BDOH-PF molecules are reduced near the cathode forming radical anions, while the DCB solvent molecules are oxidized at the anode to form radical cations. The cations produced at the anode and the anions produced at the cathode are both expected to migrate toward cathode and anode, respectively, under the influence of the electric field of the bias voltage. However, due to the cation’s lower molecular weight and thus its higher mobility with respect to the polymer anions, it is found that the migration of the cations occurs more readily than that of the anions. In contrast, both the anions and the cations move toward each other in the dye molecule ECL devices in Bard’s work.

When the radical anions and radical cations encounter each other within the charge hopping distance, energy transfer between them will occur. The transfer direction depends on the values of the excited-state energy (\(E_{\text{ex}}\)) of BDOH-PF and DCB. Since \(E_{\text{ex}}(\text{BDOH-PF}) < E_{\text{ex}}(\text{DCB})\), the radical cation of DCB will transfer its positive charge to the radical anions of BDOH-PF to form the excited state of BDOH-PF. Blue light emission will take place when the excited state relaxes to its ground state. The electrogenerated chemiluminescent spectrum is nearly identical to the photoluminescent spectrum of BDOH-PF, indicating that the energy transfer indeed occurs from the DCB radicals to the BDOH-PF radicals. Thus, the mechanism can be expressed as the following:

**Cathode:** \(\text{BDOH-PF} + e^- \rightarrow \text{BDOH-PF}^-\)

**Anode:** \(\text{DCB} - e^- \rightarrow \text{DCB}^+\)

**Recombination:**

\[
\text{BDOH-PF}^- + \text{DCB}^+ \rightarrow \text{DCB} + \text{BDOH-PF}^* \\
\rightarrow \text{DCB} + \text{BDOH-PF} + h\nu
\]

where DCB is the solvent molecule, and \(h\nu\) is the emitted photon from BDOH-PF.

To further prove this is indeed the operating mechanism, we also fabricated surface cell SLED using MEH-PPV as the active media dissolved in cyclohexanone (CHO). Examination of the surface cell experiment shows that light is emitted from the anode side of the cell. In addition, the electroluminescence is identical to the photoluminescence spectrum from the MEH-PPV solution. Again, the mechanism can be explained by the ECL mechanism on the basis of the redox potentials of MEH-PPV and CHO. The electrochemical properties of MEH-PPV have previously been studied in the literature; the onset potential of p-doping (oxidation) is ca. 0.15 V vs Ag/Ag\(^+\) and that of n-doping is ca. \(-2.10\) V vs Ag/Ag\(^+\). The cyclic voltammogram of 0.1 M TBAPF\(_6\)/CHO measured in this work is shown in Figure 3c. The onset potential of its oxidation is higher than 1.0 V vs Ag/Ag\(^+\) and that of its reduction is ca. \(-2.20\) V vs Ag/Ag\(^+\). When the applied voltage across the MEH-PPV (CHO) SLED is high enough, MEH-PPV will oxidize forming radical cations at the anode. This will occur because the oxidation potential of MEH-PPV is much lower than that of CHO. The reduction reaction at the cathode is more complicated in comparison with the oxidation at the anode because the reduction potentials of MEH-PPV and CHO are quite close. The reduction reaction of both MEH-PPV and CHO probably takes place to form radical anions on the cathode. But high-molecular-weight MEH-PPV radical anions are difficult to move. Only the low-molecular-weight CHO radical anions move from the cathode toward the anode under bias voltage. Near the anode, the negative charge species of the CHO radical anions will transfer to the radical cations of MEH-PPV to form the excited state of MEH-PPV since \(E_{\text{ex}}(\text{MEH-PPV}) < E_{\text{ex}}(\text{CHO})\). The orange light emission occurs near the anode when the excited-state MEH-PPV decays to its ground state.

In addition to the redox potentials of the polymer and organic solvent, another important issue is the energy level and stability of the redox states of the radical ions. We illustrated this point by dissolving BDOH-PF in CHO and MEH-PPV in DCB as active media, and found device performances were worse than the two cases mentioned above. Judging the cyclic voltammograms, the oxidation potential of CHO is lower than that of DCB, suggesting that CHO should be easier to be oxidized than that of DCB. However, better device performance was observed while BDOH-PF in DCB is employed as an active medium. This interesting observation could be explained based on the energy level of the cation radicals. The energy level of CHO\(^+\) is lower than that of DCB\(^+\) because of the lower oxidation potential of CHO, and the energy level of DCB\(^+\) is close to that of BDOH-PF. Thus the energy transfer to BDOH-PF is easier from DCB\(^+\) than from CHO\(^+\), so that the device performance of the SLED with BDOH-PF in DCB is better than that of the SLED with BDOH-PF in CHO.

For MEH-PPV SLED, devices fabricated from MEH-PPV in CHO obtain better device performance than those from MEH-PPV in DCB. Due to rather lower oxidation potential, MEH-PPV can be easily oxidized when DCB or CHO is chosen as the solvent. For the reduction reaction, the reduction potentials of DCB and CHO are closed, implying that similar device performance is expected. However, our results shows that CHO yielded better device performance than DCB. It can be interpreted by the following equations: Upon reduction, a DCB
molecule obtains an electron to be a radical anion D2 and then the decomposition of D2 might occur before the recombination of radical cations and radical anions occurs. This may be the reason that devices performance was worse when using MEH-PPV/DCB as the active medium.

Therefore, we conclude that it is not only the oxidation and reduction potentials are related to the device performance, but also the energy level and the stabilities of radical cations and radical anions are pertinent to the device performance.

I–L–V Curves. From microscopic observations, we conclude that the liquid solution in the thin-layer cell moves under the bias voltage. The radical ions produced at the electrodes move toward their counter-electrode. The ECL light emission cannot be observed before the smaller radical ions contact their bulky counterpart radical ions. Hence, the emission turn-on voltage should be delayed in comparison with the charge-injection voltage. If we scan the operation voltage of the SLED device at a constant speed, then the device turn-on voltage is expected to be influenced by the thickness of the solution layer of the SLED as well as the device operation temperature. To confirm this, we measured the current–light–voltage (I–L–V) curves of the SLED under different electrode separations and at different temperatures. Figure 4a shows the L–V curves of the SLED using the 5% BDOH-PF solution in DCB as the active media under 1 μm, 10 μm, and 100 μm electrode separations at a constant voltage scan rate. Obviously, the device turn-on voltage should be increased with the decrease of operation temperature. This is again in agreement with the ECL mechanism, because the radical cations move slower at lower temperatures.

The I–V curves of the devices consisting of 5% BDOH-PF in DCB as shown in Figure 4b show that the current decreases with the increase of solution layer thickness due to higher device resistance for thicker devices. Similarly, Figure 5b shows that the current decreases with the decrease of operation temperature due to lower radical ion mobility at lower temperatures. In addition, the voltage for the charge injection is almost independent of the device thickness. However, it depends on the difference between the onset potentials of oxidation and reduction, producing the radical cations and anions, respectively. For example, in the BDOH-PF-DCB case, the charge injection voltage is more or less identical to the potential difference calculated from the cyclic voltammograms of BDOH-PF in Figure 3a and DCB in Figure 3b.

Color Tunability. According to this mechanism, the polymer SLED requires at least one low-molecular-weight species to form the mobile radical counterions. The species can then transfer charge to the radical ions of the luminescent material with a lower excited-state energy. This produces the excited-state molecule. The transportation of the low-molecular-weight ions is the dominant process of the polymer SLED. On the basis of this understanding, we are able to tune the emission color of an SLED by carefully selecting additive molecules (dopants).
in the SLED. For instance, we are able to demonstrate a transparent red-emission polymer SLED by blending BDOH-PF with a very small amount of platinum(II) 2,8,12,17-tetraethyl-3,7,13,18-tetramethylporphyrin (PtOX) dopant in DCB. The ratio of PtOX to BDOH-PF is 1 mg to 20 mg in a polymer solution consisting of 5% BDOH-PF in DCB. The photoluminescence (PL) and ECL spectra are shown in Figure 6. The PL spectrum is almost entirely from the emission of BDOH-PF with a very small amount of emission from PtOX. This is an indication that the physical separation distance between BDOH-PF (the host) and PtOX (the dopant) is so large that no energy transfer occurs. Under electric excitation, however, no ECL peak contributed from the emission of BDOH-PF is observed. The entire emission is from the PtOX species. This is identical to the electroluminescence (EL) of PtOX-doped OLED and PLED. From the cyclic voltammograms of PtOX (Figure 3d) and that of BDOH-PF (Figure 3a), PtOX is easily oxidized, while BDOH-PF is easily reduced. Upon application of a voltage, radical anions of BDOH-PF and radical cations of PtOX are generated near the cathode and anode, respectively. When these two species encounter each other during the operation of the SLED, energy transfer occurs. Since $E_{ox}(PtOX) < E_{ox}^-$ (BDOH-PF), the energy transfer is from BDOH-PF to PtOX. Thus, red emission from PtOX is observed. The mechanism for the two-component BDOH-PF and PtOX system is described as follows:

Cathode: BDOH-PF + e$^-$ → BDOH-PF$^*$

Anode: PtOX − e$^-$ → PtOX$^{++}$

Recombination:

BDOH-PF$^{++}$ + PtOX$^{++}$ → BDOH-PF + PtOX + hv

Due to the narrower band gap of PtOX and thus the energy transfer from the BDOH-PF to the PtOX, the emissive light (hv) is red. Figure 7 illustrates a typical I−L−V curve of the BDOH-PF:PtOX two-component SLED. Similar to the BDOH-PF in DCB case, the voltage of charge injection is more or less identical to the potential difference calculated from the cyclic voltammograms of PtOX in Figure 3d and BDOH-PF in Figure 3a. In addition, due to the two transparent ITO/glass substrates employed as the two electrodes, the SLED is a highly transparent device. Figure 8, parts a and b, shows pictures of the transparent SLED without and with bias, respectively. Without bias, the transparency of device is as high as up to 90%. Upon application of a voltage, red emissive light is observed. Due to
the different PL and ECL emission spectra, we can control independently the optical (PL and absorption) and electric properties (EL) of the device.

Conclusion

We have summarized the device-operating mechanism of the polymer solution LED through a careful and systematic study using surface cell experiments and the transient electroluminescent measurement. We conclude that the mechanism of SLED is due to the ECL process. Upon application of a bias, one species is reduced at the cathode and the other species is oxidized at the anode. The smaller molecules migrate toward the counter-electrode and recombine with the larger molecules. The characteristic light is emitted. In a one-component system, for example, BDOH-PF in DCB or MEH-PPV in CHO, solvent radicals move toward the counter-electrode where energy transfer and recombination occur. Therefore, the general mechanism of the SLED can be expressed as follows:

Cathode:  \[ A + e^- \rightarrow A^{\text{**}} \]

Anode:  \[ B - e^- \rightarrow B^{\text{**}} \]

Recombination:  \[ A^{\text{**}} + B^{\text{**}} \rightarrow A^* + B + A + B^* \rightarrow A + B + h\nu \]

where A and B are the species that are easily reduced and oxidized, respectively. When radical cations (B^{\text{**}}) and radical anions (A^{\text{**}}) recombine, the characteristic light (h\nu) is emitted from the species with the smaller band gap (lower \( E_{\text{ex}} \)). In a two-component case, such as the blend of BDOH-PF and PtOX, energy transfer occurs between the two species and different emitting colors can be achieved. Red light is emitted due to the smaller band gap of PtOX.

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References and Notes


