

Temperature Dependence of the Electroluminescence and the Photoluminescence of A Silyl-Disubstituted Poly(p-phenylenevinylene) Derivative

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We have studied the temperature dependences of the current-voltage ($I - V$) characteristics, the electroluminescence (EL), and the photoluminescence (PL) of light-emitting diodes fabricated with poly(2,5-bis(dimethyloctylsilyl)-1,4-phenylenevinylene) (BDMOS-PPV). The ITO/BDMOS-PPV/Al devices show green light emission under both forward and reverse biases. The $I - V$ characteristics under both biases fit the Fowler-Nordheim tunneling formula at high fields, and the current and the EL intensity under a constant bias are independent of temperature below about 270 K, indicating that the tunneling of charge carriers is an important injection process. The EL spectra under both biases are very similar to the PL spectra and are narrower compared than the optical absorption spectrum. These results and a red-shift of the transient PL spectra with time imply that excitons migrate towards longer conjugated segments prior to recombination.

I. INTRODUCTION

Light-emitting diodes (LEDs) fabricated with conjugated polymers have attracted considerable interest due to their potential applications in flat-panel displays [1,2] and solid-state laser diodes [3,4]. High luminance efficiency in the full range of the visible spectrum and lasing properties in the neat film upon optical pumping have demonstrated the tremendous potential of light-emitting polymers [1-4]. However, it is still necessary to further improve the stability and the brightness of the polymeric LEDs. Improvement of the electroluminescence (EL) efficiencies is very much dependent on enhancement of the charge carrier injection into the polymer layers and efficient radiative recombination of the injected electrons and holes. Although considerable progress has been achieved in polymer LED performance, many fundamental electrical and optical properties in these materials are not fully understood. Thus, there is a need for a detailed study of the EL and the photoluminescence (PL) of light-emitting polymers, which will provide not only a better understanding of the operating mechanisms of the polymer LEDs but also a direction for improvements in the

quality of the materials and in the device structures.

In this research, we have studied the temperature dependences of the $I - V$ characteristics, the EL and the PL of a new soluble silyl-disubstituted PPV derivative, poly(2,5-bis(dimethyloctylsilyl)-1,4-phenylenevinylene), BDMOS-PPV. As will be demonstrated, the LED with the structure of ITO/BDMOS-PPV/Al shows rectifying $I - V$ characteristics with a bright green light emission from about +6 V and -10 V under forward and reverse bias, respectively. The current and the EL intensity under a constant bias voltage are independent of temperature below about 270 K, and the $I - V$ characteristics fit the Fowler-Nordheim tunneling formula at high fields, indicating that tunneling of the charge carriers is an important injection process in this device. The PL and the EL spectra under both biases are observed to be very similar, but narrower than the optical absorption spectrum, implying that excitons are generated in a distribution of conjugation lengths and migrate to lower energy regions with longer conjugated segments.

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II. EXPERIMENT

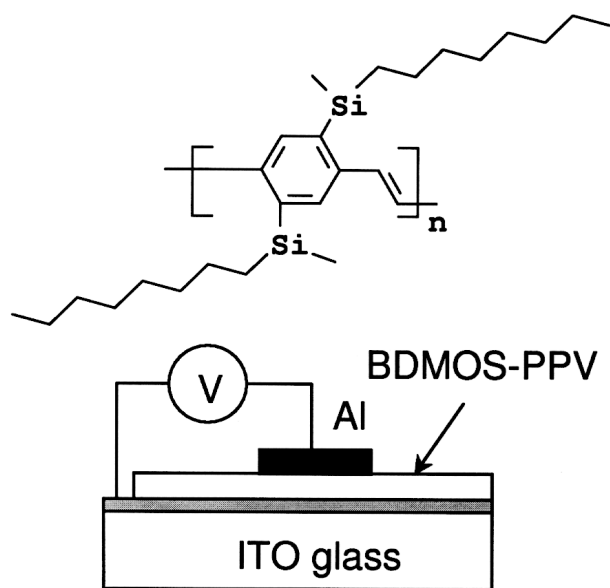


Fig. 1. The chemical structure of BDMOS-PPV and the EL device structure.

The chemical structure of BDMOS-PPV and the EL device structure are shown in Fig. 1. The details of the synthesis and the characterization of BDMOS-PPV were reported elsewhere [5]. Thin films of BDMOS-PPV were prepared by spin coating from a xylene solution onto quartz substrates for the PL study. For the EL measurement, BDMOS-PPV was spin cast onto an ITO

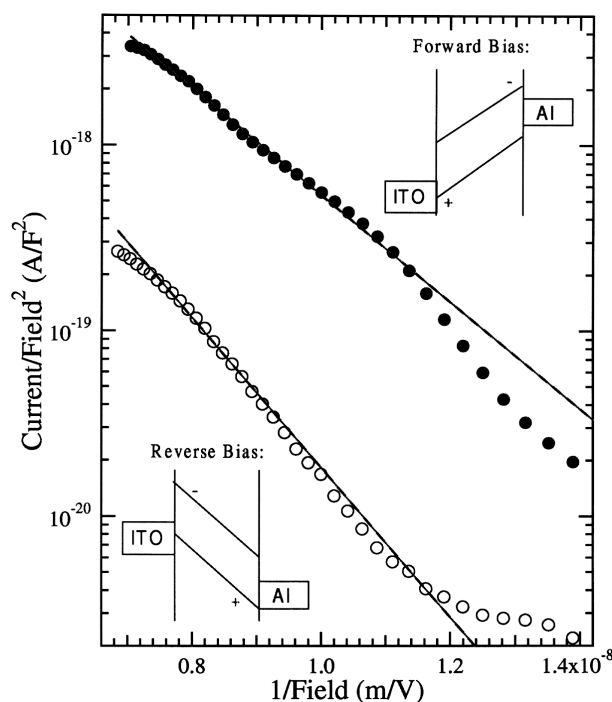


Fig. 3. Fowler-Nordheim plot for an ITO/BDMOS-PPV/Al device with a 100-nm-thick polymer layer under forward bias (solid circle) and reverse bias (open circle). The solid lines through the data are fits to the Fowler-Nordheim tunneling formula. The inset shows the schematic energy level diagram for the device under both biases.

glass substrate, and an aluminum electrode with a size of 2 mm² was deposited. The samples were mounted in a cryostat under vacuum. The *I* – *V* characteristics and the EL intensity were measured with a Keithley 487 picoammeter/voltage source and PMT, respectively. The

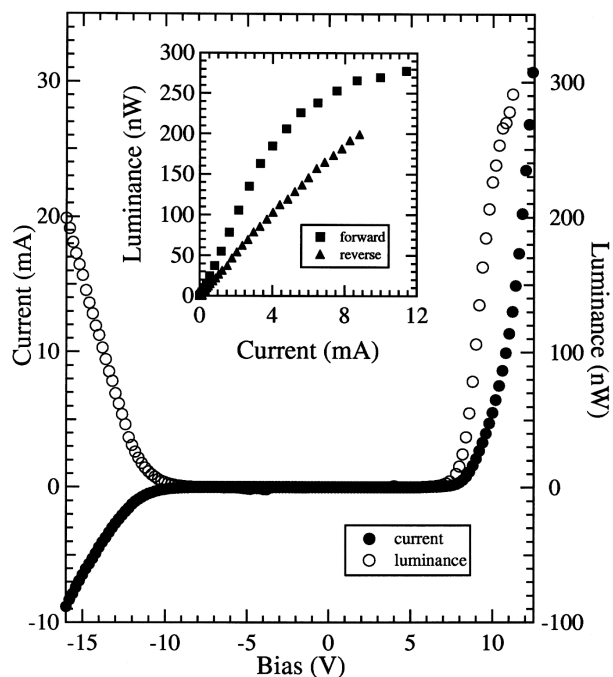


Fig. 2. *I* – *V* and *L* – *V* characteristics of ITO/BDMOS-PPV/Al at room temperature. The inset compares the *L* – *I* dependence for forward and reverse biases.

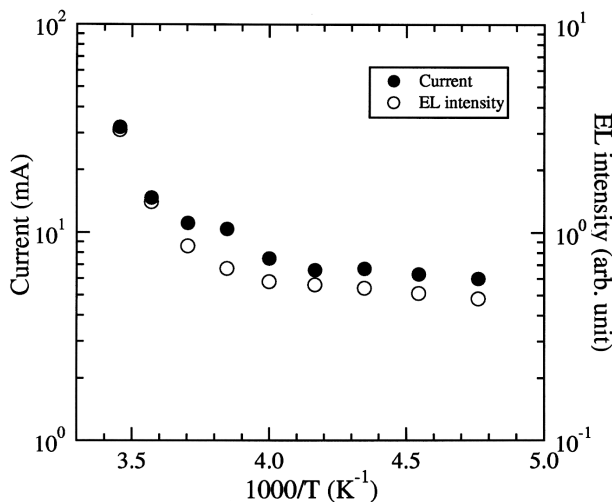


Fig. 4. Temperature dependence of the current (solid circle) and the EL intensity (open circle) of an ITO/BDMOS-PPV/Al device under a forward bias of 12 V.

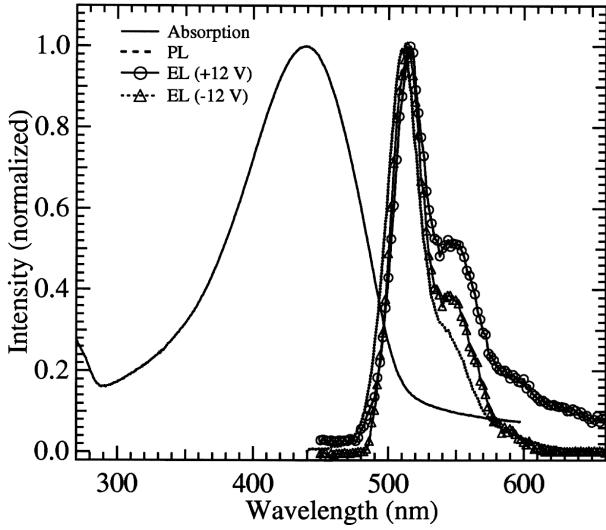


Fig. 5. The optical absorption (solid line), the PL (dotted line) and the EL spectra under +12 V (open circle) and -12 V (open triangle) biases with respect to the ITO electrode at room temperature.

temporal decay and the spectral evolution of the PL was investigated in the temperature range between 12 and 300 K by using a *ps* laser system with an average power of about 40 mW at 400 nm. A streak camera detection system was used to collect time-resolved PL data, and the overall time resolution of the detection system was about 15 ps.

III. RESULTS AND DISCUSSION

Figure 2 shows the $I - V$ and the luminance (L) - V characteristics of ITO/BDMOS-PPV/Al. Interestingly, the device exhibits rectifying $I - V$ characteristics with a bright green light emission from about +6 V and -10 V under forward and reverse bias, respectively. The forward bias is defined as the positive voltage on the ITO electrode. The inset compares the $L - I$ dependence for forward and reverse biases. The luminance is proportional to the current through the device under both biases. The luminous efficiency, the slope of the $L - I$ curve, is about 2-times larger for forward bias, but decreases at high current injection.

Although most single-layer polymer LEDs show EL emission only under forward bias, the EL emission operated in reverse bias was first reported in ITO/poly(3-octylthiophene)/Al device by F. Garten *et al.* [6]. The ITO/poly(3-octylthiophene)/Al device was reported to show different carrier injection mechanisms—thermionic emission under forward bias and tunneling under reverse bias. However, we find that under both biases, the Fowler-Nordheim tunneling formula fits the current well in the high-field region where EL occurs, as shown in Fig. 3 which displays the Fowler-Nordheim plot,

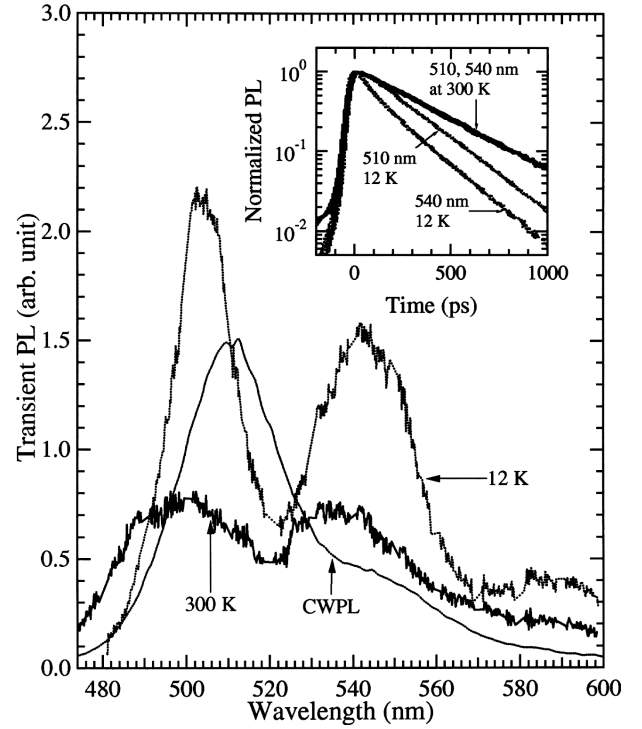


Fig. 6. The transient PL spectra of a BDMS-PPV film observed at 12 and 300 K, compared with the steady-state PL spectrum (CWPL) at room temperature. Inset shows the time-resolved PL decay at 510 and 540 nm observed at 300 and 12 K under the photoexcitation by a ps pulse at 400 nm with a fluence of about 1 W/cm².

$\log(I/F^2)$ vs $1/F$, for an ITO/BDMOS-PPV/Al device with a 100-nm-thick polymer layer. The inset shows the schematic energy-level diagram under both biases. Fowler-Nordheim tunneling of electrons or holes through a triangular barrier predicts [7]

$$I \propto F^2 \exp(-\kappa/F), \quad (1)$$

$$\kappa = \frac{4(2m^*)^{\frac{1}{2}}}{3\hbar e} \phi^{\frac{3}{2}}, \quad (2)$$

where I is the current, F is the electric-field strength, m^* is the effective mass of charge carriers, and ϕ is the barrier height. A linear relationship is observed in the Fowler-Nordheim plot as can be seen in Fig. 3, indicating that tunneling injection is dominating at high field for both biases [7]. The deviation from linearity at lower field is considered to be due to a thermionic emission contribution [7,8]. The barrier height obtained from the Fowler-Nordheim analysis is about 0.21 and 0.27 eV for forward and reverse bias, respectively.

Further evidence for carrier injection by tunneling is observed in the temperature dependence of the current and the EL intensity of the ITO/BDMOS-PPV/Al device under a forward bias of 12 V, as shown in Fig. 4. Both the current and the EL show a weak temperature dependence below 270 K, consistent with the tunneling mechanism for carrier injection. However, the slight,

activated temperature dependence above 270 K implies that thermally assisted tunneling plays some role for carrier injection at high temperature.

Figure 5 shows the optical absorption and the steady-state PL spectra of the BDMOS-PPV film along with the EL spectra of ITO/BDMOS-PPV/Al under ± 12 V biases at room temperature. The PL spectrum and the EL spectra under both biases are very similar, with a strong emission peak at about 510 nm and a vibronic shoulder at about 550 nm, implying that excited states that decay radiatively are independent of the way in which carriers are injected. As can be seen in Fig. 5, the PL and the EL spectra are much narrower than the optical absorption spectrum. It is thought that a broad optical absorption band indicates a distribution of conjugation lengths and narrower PL and EL spectra imply an exciton migration towards lower energy regions with longer conjugated segments [9,10]. Further evidence for exciton migration is observed by the red-shift of the PL spectra. Figure 6 compares the steady-state PL spectrum (CWPL) at room temperature with the transient PL spectra measured at 12 and 300 K after photoexcitation by a ps pulse at 400 nm. The transient PL emission peaks show a red-shift of about 10 nm compared with the peaks in the CWPL spectrum. We also observed that the transient PL spectra in the short-wavelength region below about 500 nm decay faster compared with those in the longer-wavelength region in the subnanosecond time region which is consistent with exciton migration [11].

The transient PL spectra in Fig. 6 show that, compared with the PL spectra at 300 K, the PL intensity at 12 K increases and the PL spectrum becomes narrower with a red-shift. In addition, the main PL emission peak at 510 nm becomes stronger than the vibronic shoulder at 12 K. These observations suggest that the conjugation lengths increase due to the prevention of phenylene-ring rotation at lower temperatures.

The inset of Fig. 6 displays the PL temporal decay at 510 and 540 nm for both 12 and 300 K. The transient PL at all wavelengths at 300 K shows a single exponential decay with a decay time of about 350 ps. Although the PL decay time increases at lower temperatures in most conjugated polymers, the transient PL of BDMOS-PPV at 12 K shows shorter decay times with different decay dynamics at different wavelengths. The PL at 12 K shows a single exponential decay with a decay time of about 245 ps at 510 nm and a non-exponential decay at 540 nm. We also observed that the PL decay times at 12 K decrease slightly as the excitation intensity increases, implying that the exciton-exciton collision plays a role in the decay processes.

IV. CONCLUSIONS

We have presented the temperature dependences of

the $I - V$ characteristics, the EL, and the PL of light-emitting diodes fabricated with BDMOS-PPV. The ITO/BDMOS-PPV/Al devices exhibit rectifying $I - V$ characteristics with bright green light emission under both forward and reverse biases. The $I - V$ characteristics under both biases fit well the Fowler-Nordheim tunneling formula at high fields, and the current and the EL intensity under a constant bias are observed to be independent of temperature below about 270 K, indicating that tunneling of charge carriers is an important injection process. The narrower PL and EL spectra compared with the optical absorption spectrum, as well as a red-shift of the transient PL emission with time, imply that excitons are generated in a distribution of conjugation lengths and migrate towards longer conjugated segments. The PL spectrum becomes narrower with a red-shift at lower temperature, suggesting that the conjugation lengths increase due to the prevention of phenylene-ring rotation at lower temperatures.

ACKNOWLEDGMENTS

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