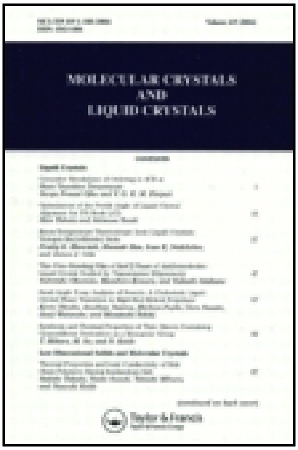

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Transition Phenomenon in Salt-Doped Organic Electroluminescent Devices at High Bias Voltage

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Transition Phenomenon in Salt-Doped Organic Electroluminescent Devices at High Bias Voltage

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Organic electroluminescent (EL) devices using molecularly dispersed poly(N-vinylcarbazole) (PVCz) exhibit an irreversible transition phenomenon with a simultaneous and remarkable improvement in carrier injection at high bias voltage by doping with ammonium salt. The device structure used in this study was an indium tin oxide anode/PVCz:2,5-bis(1-naphtyl)-1,3,4-oxadiazole:coumarin 6:tetra-n-butylammonium tetrafluoroborate/metal cathode. The altered devices require significantly lower driving voltage and exhibit higher EL intensity compared with undoped devices. Furthermore, the EL intensity-voltage characteristics of the altered devices are independent of the work function of the cathodes.

Keywords: organic electroluminescent device, poly(N-vinyl carbazole), tetra-n-butylammonium tetrafluoroborate

INTRODUCTION

Organic electroluminescent (EL) devices have been extensively investigated for use in the next generation of flat panel displays [1,2]. The basic structure of an organic EL device is a thin organic film sandwiched between a metal cathode and an indium-tin oxide (ITO) anode. When a bias voltage is applied to the electrodes, electrons and holes are injected from the electrodes into the organic layer and the resultant recombination generates light.

Undoped materials are usually used for the emissive layer of organic EL devices because doping introduces quenching sites and reduces the efficiency of the radiative relaxation of excitons. However, the EL of certain materials

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has been reported to be improved by doping, for example, poly(3-hexylthiophene) doped with $FeCl_3$ [3], poly(2-methoxy, 5-(-2′-ethyl-hexyloxy)-1, 4-phenylene-vinylene) (MEH-PPV) doped with I^2 [4], and light-emitting electrochemical cells (LEC) [5,6]. The emissive layer of LECs is a mixture of EL polymer such as poly(p-phenylene-vinylene) (PPV), an ionically conducting material such as poly(ethylene-oxide) (PEO), and an ionic salt such as $LiCF_3SO_3$.

The electron conductivity of EL materials can be improved by doping, with the result that the contact between the organic layer and the electrodes becomes close to ohmic. Hence, the driving voltage of EL devices using doped materials is not strongly dependent on the difference between the work-function of the electrodes and the highest or lowest occupied molecular orbital (HOMO/LUMO) level of the organic layer, compared with undoped devices.

Molecularly dispersed poly(N-vinylcarbazole) (PVCz) films are widely used in single-layer organic EL devices [7–11]. As PVCz itself is a hole-transport material, it is usually dispersed with electron-transport materials and luminescent dyes. Recently, we have reported that the carrier injection of EL devices using PVCz films can be improved by doping with ammonium salts [12]. In this paper, we report a unique transition phenomenon at high bias voltage in EL devices using ammonium salt-doped PVCz. This translation is irreversible, and the altered devices perform much better than undoped devices in terms of driving voltage and EL intensity. We investigated the characteristics of the altered devices for various cathode metals and salt concentrations.

EXPERIMENTAL

Figure 1 shows the chemical structures of the materials and the structure of the EL device used in this study. The electron transport material was 2,5-bis(1-naphtyl)-1,3,4-oxadiazole (BND). Coumarin 6 (C6) provides green emission. Tetra-n-butylammonium tetrafluoroborate (Bu_4NBF_4) is an additive that leads the transition. ITO glass with a sheet resistance of $8\Omega/\square$ was routinely cleaned by ultrasonic treatment in a detergent solution, deionized water, isopropanol, and methanol, and then dried with nitrogen gas. Organic compounds were mixed and dissolved in dichloroethane. Organic layers were spin coated from these solutions onto the cleaned ITO glass. The thickness of the organic layers was about 100 nm. Metal cathodes were fabricated by vacuum evaporation onto these organic layers. The diameter of the cathodes was 3 mm.

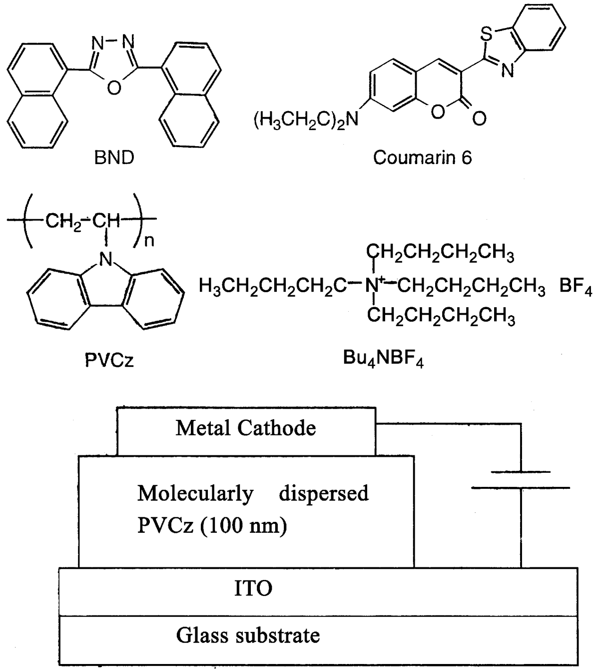

FIGURE 1 Chemical structures of materials and structure of EL device used in this study.

EL devices were operated using a Kenwood PSR-60M DC power supply. Current density was measured with an Advantest R5451 auto-ranging multimeter. EL intensity was measured with a Minolta LS-100 luminance meter, and EL spectra were measured with a Jasco FP-777 spectrometer. All measurements were carried out in air at room temperature.

RESULTS AND DISCUSSION

The unique transition examined in this paper takes place when a high bias voltage is applied to a doped device for a certain period of time. Under steady voltage, the current density and EL intensity of conventional undoped EL devices gradually decreases, as shown in Figure 2a. This undoped device has a Au cathode and operates at 17 V and emits a green light at low intensity ($<1\,cd/m^2$), indicating that there was an insufficient supply of electrons from the Au electrode due to the high workfunction of the electrode.

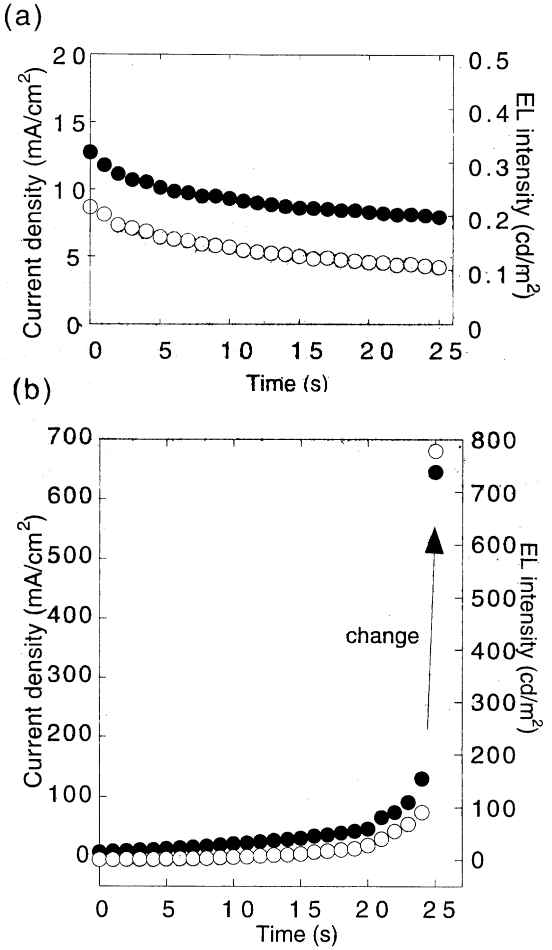

FIGURE 2 Current density (solid circles) and electroluminescence (open circles) for (a) ITO/PVCz:BND: coumarin 6 (100:17:3 mol)/Au undoped device and (b) ITO/PVCz:BND:coumarin 6:Bu_4NBF_4 (100:17:3:1 in mol)/Au salt-doped device, at applied voltage of 17 V.

The same measurements for the salt-doped device are shown in Figure 2b. Although the only difference between the devices is the addition of a small amount of ammonium salt, the doped device exhibits markedly different and unique behavior. The EL intensity of the doped device begins at the same low levels as the undoped device. However, as the current in the device is gradually increased, the EL intensity also increases (over 24 s). This behavior can be explained by the mechanism of electrochemical doping of PVCz with ammonium salts. Under the external field, PVCz is gradually doped with ammonium salts and carrier injection barriers are gradually weakened within it.

In the short interval at 24–25 s, current density and EL intensity increase rapidly. The EL intensity changes from 90 cd/m^2 to 778 cd/m^2, reflecting the transition mentioned before. A unique change in the emission state was observed in this transition. A bright yellow-green point of light appeared at the center of the cathode area, and then spread quickly. For the experiment in Figure 2b, the bias voltage was turned off as soon as the EL had spread over the entire cathode area. If the bias voltage is not turned off at this time, the current and EL intensity initially decrease, thereafter becoming steady. Below, we describe the characteristics of the devices altered by this transition.

Figure 3 shows the current density–voltage and EL intensity–voltage characteristics of the altered device shown in Figure 2b, under both forward and backward bias. Despite the fact that the workfunction of Au (5.0 eV) is higher than that of ITO (4.9 eV), EL emission and clear carrier injection were observed only when the Au electrode was negative. The altered emission color did not revert to its original state under opposite bias. These results indicate that this phenomenon is irreversible. This unique transition was observed in all salt-doped devices using cathodes of other metals. However, this transition was not observed when ITO was used as the negative electrode. The reason for this is unclear. A likely reason is the difference between the cathartic activity of the metals and ITO for certain electrochemical reactions related to this transition.

The change in the EL spectra corresponding to the abrupt transition is shown in Figure 4. Before the transition, the EL spectrum of the device is similar to that of the undoped device, and is identified as the emission of coumarin 6. The EL spectrum of the device after the transition is also similar to that of coumarin 6, suggesting that coumarin 6 is also the primary emission site in the altered device. However, a shoulder emerges at around 550 nm, implying that another emission source is created in the transition.

Figure 5 shows a comparison of the EL intensity–voltage characteristics of altered devices with undoped devices for a variety of cathode metals. The sweep rate of 0.5 V/s was sufficiently fast to avoid inducing the permanent transition in unaltered devices and did not affect the state of the altered devices. The performance of undoped devices can be seen to be significantly dependent on the workfunction of the cathode metals. The EL intensity of the device with an Au cathode was lower by three orders of magnitude than that of the device having a MgAg cathode at the same voltage. By contrast, all altered devices required lower driving voltage and exhibited higher

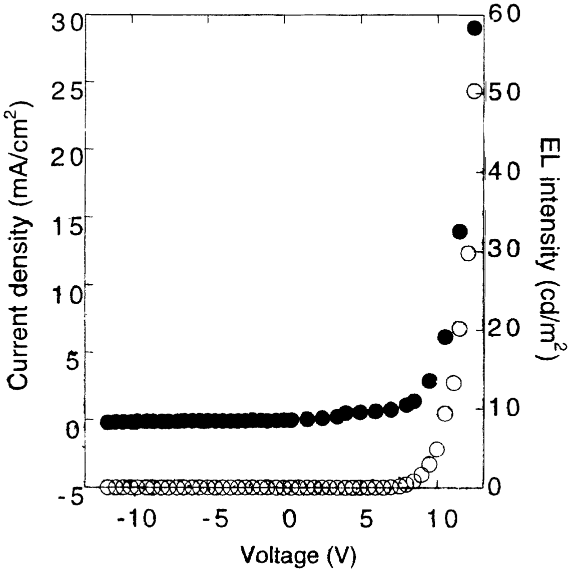

FIGURE 3 Current density–voltage characteristics (solid circles) and EL intensity–current density characteristics (open circles) of ITO/PVCz:BND:coumarin 6:Bu_4NBF_4 (100:17:3:1 mol)/Au altered device.

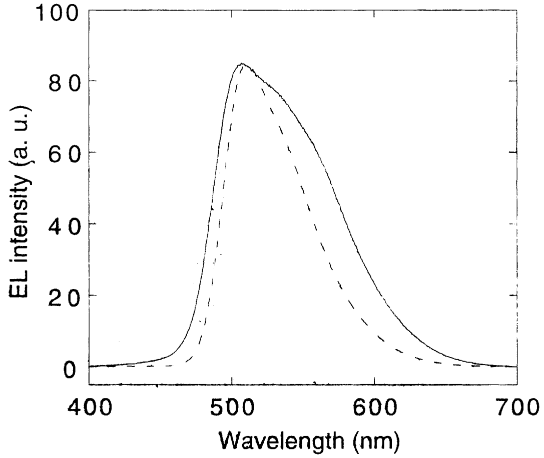

FIGURE 4 EL spectra of ITO/PVCz:BND:Coumarin 6:Bu_4NBF_4 (100:17:3 mol)/Au device before transition (dashed line) and after transition (solid line).

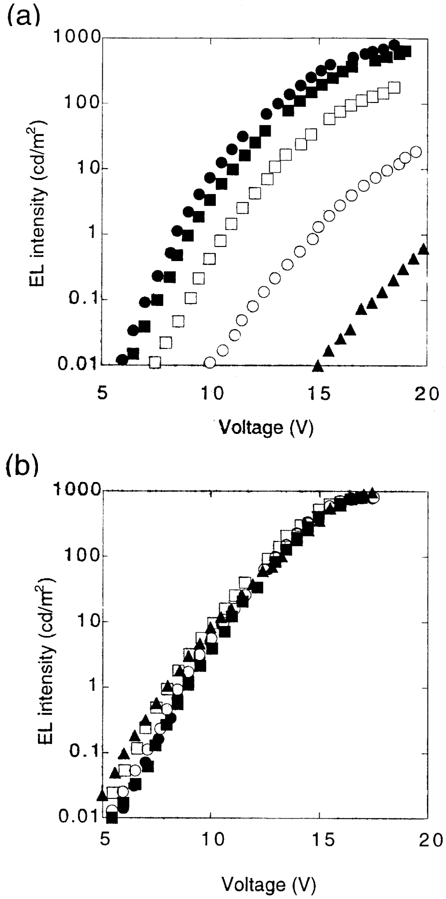

FIGURE 5 EL intensity–voltage characteristics of (a) ITO/PVCz:BND:coumarin 6 (100:17:3 mol)/cathode undoped devices and (b) ITO/PVCz:BND:coumarin 6:Bu_4NBF_4 (100:17:3:1 mol)/cathode altered devices. Cathodes are MgAg (solid circles), Al (open circles), Ag (solid squares), Cu (open squares), and Au (solid triangles).

maximum EL intensity than the undoped devices for the same cathode. Furthermore, all altered devices exhibited almost the same EL intensity–voltage curve, indicating that the electron injection barrier of all cathodes was reduced to almost the same level.

Figure 6 shows the current density–voltage and EL intensity–current characteristics of altered devices for a range of salt concentrations and an undoped device. The molar ratio of PVCz:BND:C6:Bu_4NBF_4 was 100:17:3:x (x = 0, 0.5, 1, 2, 3). For x = 0 to 1, the carrier injection

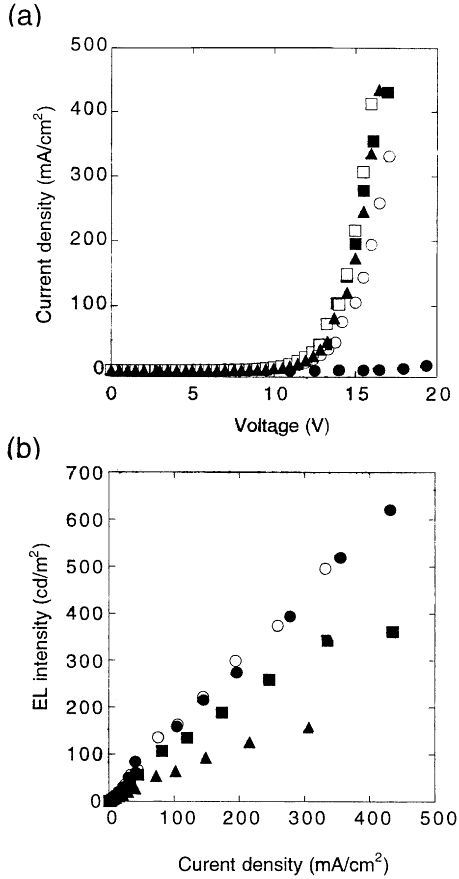

FIGURE 6 (a) Current density–voltage characteristics and (b) EL intensity–current density characteristics of ITO/PVCz:BND:coumarin 6/cathode undoped device (solid circles) and ITO/PVCz:BND:coumarin 6:Bu_4NBF_4 cathode altered devices. The molar ratios of PVCz:BND:coumarin 6:Bu_4NBF_4 in these organic layers is 100:17:3:x. Here, x is 0.5 (open circles), 1 (solid squares), 2 (open circles), and 3 (solid triangles).

characteristics of the devices improved with salt concentration. At $x > 1$, the devices exhibited almost the same current–voltage characteristics. The EL intensity decreased with increasing salt concentration for a given current density, implying an increase in the concentration of quenching sites with salt concentration.

As shown in Figure 1, doped devices also have improved carrier injection characteristics before the transition. In a previous study, we explained the mechanism of the improvement in this state in terms of the electrochemical doping of PVCz [12]. When bias voltage is applied between the electrodes, the anode side of the PVCz is electrochemically doped to p-type [13] with ammonium salts, and the anode contact becomes ohmic. As a result, almost all bias voltage is applied to the anode side and the tunneling barrier of the cathode weakens.

The mechanism of the improvement of carrier injection characteristics in devices after the transition is not clear at this time. We consider that there are two possibilities. One possible mechanism is that the number of doped PVCz groups suddenly increases due to joule heat at high voltage, and the conductivity of the film increases accordingly (24–25 s in Figure 2b). In this state, the tunneling barrier of the cathode is much narrower. From Figure 5b, the carrier injection barrier of the altered devices for a range of cathode metals appears to be the same. Therefore, if this mechanism is responsible, the contact between the cathode electrode and organic layer should be ohmic. The saturation of the improvement in carrier injection with salt concentration and the quenching behavior shown in Figure 6 support this assumption.

However, there are points that can not be fully explained by the mechanism of electrochemical doping. For example, this transition phenomenon takes place only when the metal electrode is negative. Furthermore, this transition phenomenon is irreversible, as shown in Figure 3. These facts differ from that of doped devices reported earlier [3–6]. The other possible mechanism is that an irreversible electrochemical reaction takes place, creating new materials at the electrode interfaces. We will investigate the chemical structures of the materials in organic layer in detail in future studies, in order to clarify the mechanism of this phenomenon.

CONCLUSIONS

EL devices based on PVCz were found to exhibit a transition phenomenon at high bias voltage, with a simultaneous and remarkable improvement in carrier injection as a result of ammonium salt doping of the organic layer. The altered devices require significantly lower driving voltage and exhibit higher EL intensity compared to undoped devices and have characteristics that are independent of the workfunction of the cathodes.

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