Effect of Hole-Transporting Film Thickness on the Performance of Electroluminescent Devices Using Polymer Langmuir−Blodgett Films Containing Carbazole

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ABSTRACT: Electroluminescence (EL) of a film of poly(*N*-dodecylacrylamide-*co*-2-(9-carbazolyl)ethylacrylate) (DDA/CzEA copolymer) as a hole-transporting layer was investigated as a function of the mole fraction of CzEA and the film thickness. The EL devices have double-layer structures consisting of vacuum-deposited tris(8-quinolinolato)aluminum(III) complex (Alq3) as an electron-transporting and emitting layer, and the DDA/CzEA copolymer Langmuir−Blodgett (LB) films on anodic indium−tin-oxide (ITO) electrodes. The EL performance of the double-layer devices was compared with that of the single-layer device of Alq3. The DDA/CzEA copolymers with less than 0.31 mole fraction of CzEA formed stable LB films which acted as a good electron-blocking layer. The current density decreased with increasing film thickness of the DDA/CzEA copolymer LB films. The light conversion efficiency was improved and became almost constant with more than 11 layers because the excitons generated by the recombination of holes and electrons around the interface between the DDA/CzEA copolymer LB film layer and the Alq3 layer was not being quenched by the ITO anodes.

Introduction

Organic electroluminescent (EL) devices have been intensively investigated since the first efficient device was demonstrated,[1] because they can be color tuned from blue to red and the applications to flat panel displays. In particular, polymer EL devices using π-conjugated polymers,[2] matrix polymers doped with light-emitting materials,[3] hole-electron-transporting polymers, and fluorescent polymers[4] have recently received much attention because of easy processing of film formation and mechanical flexibility. Their polymer films are fabricated by spin-coating, inkjet printing,[5] layer-by-layer deposition,[6] and Langmuir−Blodgett (LB) techniques,[7−13] instead of vacuum thermal vapor deposition. In film formation, the LB technique is attractive because it offers the fabrication of an organized assembly with a controlled thickness at molecular dimensions and with well-defined molecular orientation and the preparation of hetero-structures by successive deposition of different kinds of monolayers.[7] Several organic EL devices using LB films of amphiphilic complexes as emitting layers[8−11] and the polymer LB films of poly(*p*-phenylene vinylene)[12] and poly(3-alkylthiophene)[13] have been reported to realize low voltage-driven devices and molecular electronic devices. To achieve low voltage-driven devices, it is necessary to decrease the hole- and electron-injection barriers at the interfaces of anode and cathode, respectively, and to reduce the device thickness. The former has been achieved by the selection of low-work-function metals such as calcium as a cathode and by the insertion of an insulating layer such as LiF between the cathode and the electron transporting layer. The latter has been easily achieved by the LB technique. However, reduction of the device thickness leads to another problem, that is, excitons generated by recombination of holes and electrons are quenched by metal electrodes through an energy transfer process, thus reducing the light emitting efficiency.[14] Here, we describe the influence of exciton quenching by electrodes as a function of the film thickness using the LB technique.

For this purpose, poly(*N*-dodecylacrylamide-*co*-2-(9-carbazolyl)ethylacrylate) (DDA/CzEA copolymer) LB films were used as a hole-transporting layer (Figure 1). Carbazole is well-known as hole-transporting materials and widely used as hole-transporting materials for EL devices.[15] In a previous study, the photoinduced electron-transfer quenching process of the DDA/CzEA copolymer LB films was investigated in detail.[16] In this study, we describe the dependence of EL performance in the polymer LB film devices upon the mole fraction of CzEA and the film thickness in DDA/CzEA in the LB films. The EL devices in this study have a double-layer structure consisting of vacuum-deposited tris(8-quinolinolato)aluminum(III) complex (Alq3) as an electron-transporting and emitting layer, and the DDA/CzEA copolymer LB films with various numbers of layers on anodic indium-tin-oxide (ITO) electrodes.

Experimental Section

DDA/CzEA copolymers were prepared by free-radical polymerization in toluene at 60 °C with 2,2′-azobis(isobutyronitrile). The polymers were purified twice by reprecipitation in a large excess of acetonitrile from a chloroform solution and dried under vacuum at room temperature. The mole fractions of CzEA in the copolymers were determined to be 0.15, 0.21, 0.31, and 0.37 by NMR and UV absorption spectroscopies.

Measurements of surface pressure (π)-area (A) isotherms and the deposition of monolayers were carried out with a computer-controlled Langmuir−Blodgett trough (FSD-11, USI) at 15 °C. Distilled and deionized water (Millipore Milli-Q) was used for the subphase. Chloroform was used as a solvent for spreading monolayer on a water surface. The monolayers of DDA/CzEA copolymers were transferred onto ITO electrodes (Geomatic Co., 10 Ω/square) at a dipping speed of 10 mm/min under a surface pressure of 30 or 25 mN/m at 15 °C. Alq3 and

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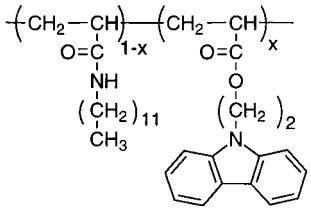

Figure 1. Chemical structures of poly(*N*-dodecylacrylamide-*co*-2-(9-carbazolyl)ethylacrylate)s.

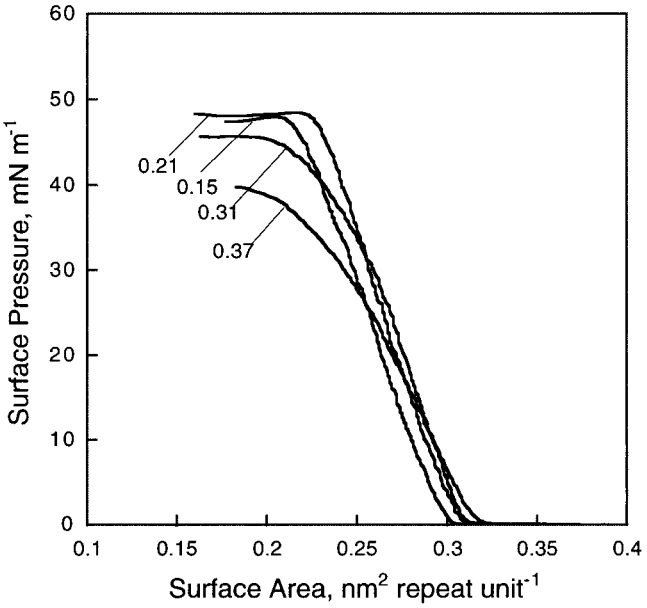

Figure 2. π-A isotherms of DDA/CzEA copolymers with different mole fraction of CzEA at 15 °C.

Al were successively deposited onto the DDA/CzEA LB films on a ITO electrode by vacuum deposition at 1×10^{-5} Torr. The LB film-deposited substrates were kept at 15 °C under the vacuum deposition to avoid thermal influence on the DDA/CzEA copolymer LB films. The deposition rates of Alq3 and Al were less than 0.3 and 1.1 nm/sec, respectively. The film thicknesses of Alq3 and Al were determined to be 50 and 150 nm, respectively by a Sloan DEKTAK ST Surface Profiler.

Bias voltages were applied at EL devices and current was measured with a source measure unit (Keithley Model236). The emitting area was 0.3×0.3 cm^2 and luminance was measured with a Minolta luminance meter LS-100 at room temperature under an ambient atmosphere.

Results and Discussion

Monolayer Behaviors of DDA/CzEA Copolymers at the Air/ Water Interface. DDA/CzEA copolymers with different mole fractions of CzEA were spread on a water surface from a chloroform solution to investigate the monolayer behavior of DDA/CzEA copolymers on the air/water interface. The π−A isotherms for the copolymers at 15 °C were shown in Figure 2. The isotherms show a steep rise in surface pressure and high collapse pressure, indicating the formation of a stable monolayer on the water surface. The collapse pressure decreased with an increasing mole fraction of CzEA in the copolymers. The limiting molecular occupied surface area per monomer unit, which is obtained by extrapolation of the linear part of π−A curves to zero surface pressure, increases with the mole fraction of CzEA in the copolymers. Since the limiting surface area of *N*-dodecylacrylamide homopolymer was reported to be 0.28 nm^2 repeat unit-^{1},[17] the limiting surface area of CzEA was estimated to be 0.40 nm^2. We assume that the monolayer conformation of DDA/CzEA copolymers on the water surface has the hydrophilic amide and ester moieties in the DDA/CzEA copolymers placed on the water surface with the alkyl side chains of *N*-dodecylacrylamide unit standing up from the water surface to the air phase. The CzEA exists in the hydrophobic alkyl side chain region.

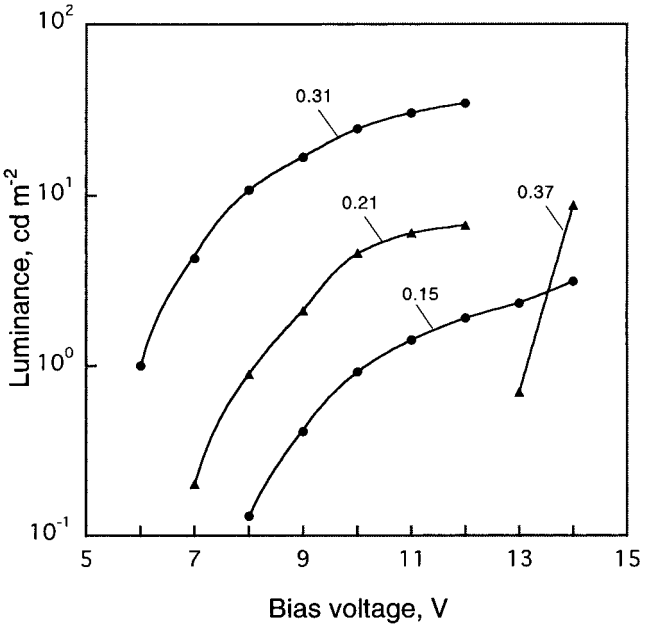

Figure 3. Plots for luminance vs bias voltage observed at the double-layer EL devices using DDA/CzEA copolymer LB films with different mole fractions of CzEA in the copolymers.

The monolayers of the copolymers except DDA/CzEA copolymer with 0.37 mole fraction of CzEA (DDA/CzEA37 copolymer) were transferred onto ITO electrodes as a Y-type LB film with a transfer ratio of unity under a surface pressure of 30 mN/m. The monolayer of DDA/CzEA37 copolymer was transferred onto ITO electrodes under a surface pressure of 25 mN/m with a downward and upward transfer ratio of 0.8 and 0.6, respectively. Since the π−A isotherm of DDA/CzEA37 copolymer behaves as an expanding monolayer, it may be difficult to transfer it uniformly onto ITO substrates.

Electroluminescent Performance of EL Devices Using DDA/CzEA Copolymer LB Films. The double-layer EL devices using the DDA/CzEA copolymer LB films with 11 monolayers were characterized as a function of the mole fraction of CzEA in the copolymers. Plots of luminance vs bias voltage obtained at the devices using the DDA/CzEA copolymer LB films with different mole fractions of CzEA are shown in Figure 3. The turn-on bias voltage decreased and the luminance at the same bias voltage increased with the mole fraction of CzEA in the copolymers. The hole transport in the LB film layer increases with the mole fraction of CzEA, resulting in an increasing hole-electron annihilation. However, when the mole fraction of carbazole is 0.37, a higher bias voltage is necessary for the device to emit light. This seems to be caused by a disorder in the layer structure of the LB film. In fact, the transfer ratio was less than unity at the DDA/CzEA37 copolymer monolayer. Therefore, the luminance of the EL devices using DDA/CzEA copolymer LB films is influenced by two factors, i.e., the mole fraction of CzEA and the ordering of the LB film structure. The optimum mole

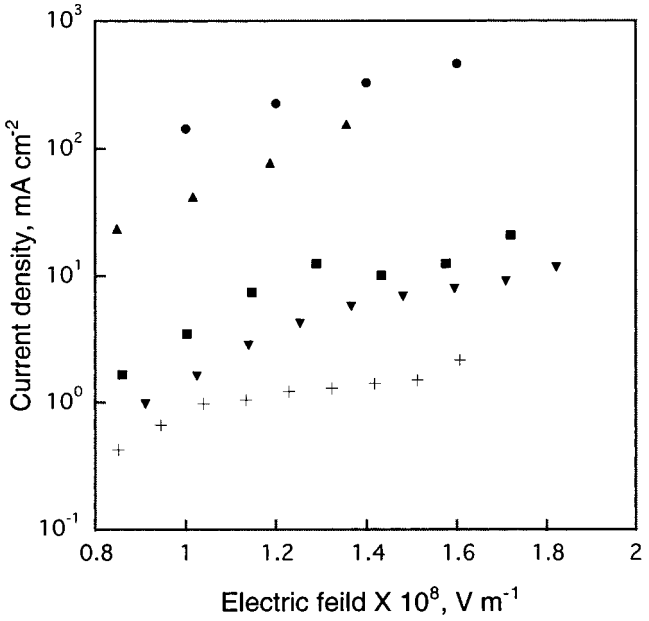

Figure 4. Plots for the current and electric field observed at the EL devices using DDA/CzEA31 copolymer LB films with different number of layers. Single-layer device (circle), double-layer devices using DDA/CzEA31 copolymer LB films with 5 layers (triangle), 11 layers (square), 15 layers (anti-triangle), and 21 layers (plus).

fraction of CzEA in the copolymers was found to be 0.31 for the hole-transporting materials. In the following study, the dependence of electroluminescent property on the number of layers is investigated using the DDA/CzEA copolymer with 0.31 mole fraction of CzEA (DDA/CzEA31 copolymer).

The double-layer devices using the DDA/CzEA31 copolymer LB films with different number of layers were fabricated to investigate the elctroluminescent property and the quenching effect on the film thickness of the hole-transporting layer. The plots of current vs applied electric field observed at the double-layer devices with various numbers of layers and at the single-layer device with Alq3 are shown in Figure 4. The current density was plotted against the electric field (Vm^{-1}) instead of the bias voltage (V) in order to avoid the influence of the film thickness of the LB films with different number of layers. We simply assume that the electric field profile is linear in the DDA/CzEA31 copolymer LB film and Alq3 layers of the double-layer devices. The current density is exponentially proportional to the electric field in all the devices, indicating semiconductor behavior. The current density observed at the Alq3 single-layer device was larger than those of the double-layer devices using DDA/CzEA31 copolymer LB films. Thus, we suggest that the electron injection efficiency at the Al cathode into the Alq3 layer and the electron-transporting rate through the Alq3 layer are relatively higher than the hole injection efficiency at the ITO anode into the DDA/CzEA31 copolymer LB film layer and the hole-transporting rate through the DDA/CzEA31 copolymer LB film layer. Therefore, the current density observed in the double-layer device is controlled by the hole injection efficiency and the hole-transporting rate. In the double-layer devices with the different number of layers, the current density decreases with increasing number of layers. According to the space-charge-limited current as reported previously,[18] the current density is proportional to V^2L^{-3}.

$$I = (9/8)\epsilon_r\epsilon_0\mu V^2 L^{-3}$$

Where I is the current density, $\epsilon_r\epsilon_0$ is the permittivity of the material, μ is the carrier mobility, V is the bias voltage and L is the film thickness. Hence, the current density decreases with the film thickness at a constant electric field.

On the other hand, dependence of the luminance on the electric field is different from the current density's dependence. Dependence of the luminance on the electric field observed at the double-layer devices using the DDA/CzEA31 copolymer LB films with the different number of layers is shown in Figure 5. The luminance observed at the double-layer devices based on DDA/CzEA31 copolymer LB films with 5 and 11 layers is larger than that observed at the Alq3 single-layer device. The improvement of the luminance at the double-layer devices with 5 and 11 layers is due to the introduction of the hole-transporting layer. The introduction of the DDA/CzEA31 copolymer LB film results in a decrease in current density and in improvement of the balance of the electron- and hole-injection at the cathode and anode, respectively. The luminance decreases with increasing number of layers because of a decrease in the current density. The current observed at the Alq3 single-layer device mainly consists of the electron transport without the hole transport because Alq3 is the electron transporting materials. Therefore, the electrons that reach the ITO anode are leaked to the ITO anode, resulting in a decrease in the probability of the hole and electron annihilation.

The luminance observed at the double-layer devices using the DDA/CzEA copolymer LB films with the different number of layers was plotted against the current density (Figure 6). The luminance intensity is proportional to the current density in the EL devices irrespective of the number of layers. The conversion efficiency of the current density to the luminance can be determined from the slope obtained in Figure 6. The conversion efficiency of the Alq3 single layer device is lower than those of the double-layer devices because it is more difficult to inject holes from the ITO anode to the Alq3 layer than to the DDA/CzEA copolymer LB film layer. Hence, the magnitude of the current is mainly dominated by the electron mobility of the Alq3 layer in the single-layer device. Since most electrons are transported through Alq3 layer to the ITO anode without recombination with holes, the conversion efficiency is lower at the Alq3 single-layer device. Furthermore, the emission of the excited state of Alq3 should take place near the ITO anode because of the difficulty of the hole transport through the Alq3 layer. Thus, the excited state of Alq3 produced near the ITO anode is quenched by the ITO anode. Therefore, the lower conversion efficiency of the Alq3 single-layer device is caused by the lack of the hole injection ability of Alq3 and the energy transfer quenching of the excited Alq3 to the ITO anode. On the other hand, the conversion efficiency of the double-layer devices based on the DDA/CzEA31 copolymer LB films with 11, 15, and 21 layers is drastically improved in comparison with that of the Alq3 single-layer device because of the presence of the hole-transporting layer. The introduction of DDA/CzEA31 copolymer LB film to the Alq3 single layer device inhibits transporting electrons to the ITO anode, resulting in electron-blocking layers. The conversion efficiency is improved by the balance of the electron injection at

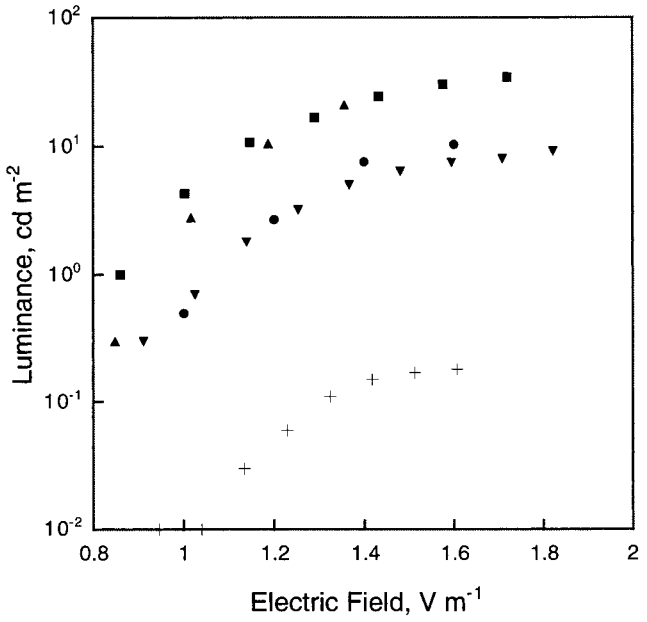

Figure 5. Plots for luminance and electric field observed at the EL devices using DDA/CzEA copolymer LB films with different number of layers. Plot marks are the same as in Figure 4.

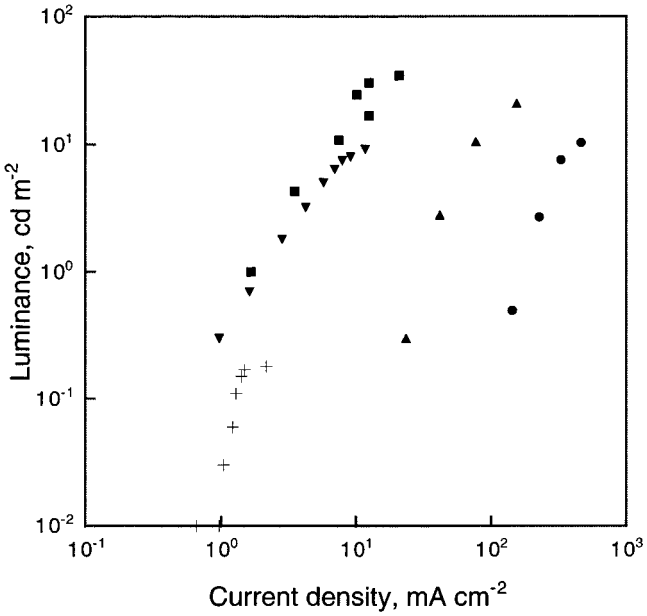

Figure 6. Plots for luminance and current observed at the EL devices using DDA/CzEA copolymer LB films with different number of layers. Plot marks are the same as in Figure 4.

the Al cathodes and the hole injection at the ITO anodes. Moreover, their conversion efficiency values of the double-layer devices based on the DDA/CzEA31 copolymer LB films with 11, 15, and 21 layers are almost the same, so that the probability of the recombination of electrons and holes is constant in this system. Increases in number of layers decreases the hole current, whereas the conversion efficiency remains constant. However, the conversion efficiency of the double-layer device based on the DDA/CzEA31 copolymer LB film with 5 layers is smaller than that with 11, 15, and 21 layers. This is because the excitons produced by the recombination of electrons and holes around the interface between the DDA/CzEA31 copolymer LB film layer and the Alq3 layer are quenched by the ITO anode. The distance from the ITO anode to the interface between the DDA/CzEA copolymer LB film layer and the Alq3 layer is estimated to be ca. 9.0 nm using the monolayer thickness of the DDA/CzEA31 copolymer LB films of 1.8 nm determined by XRD.[17] This distance is sufficient to quench the excitons due to the energy transfer process. Therefore, the optimum configuration of the hole-transporting layer is concluded to be 11 layers in this EL device system. The conversion efficiency is controlled by the hole-transporting process in the DDA/CzEA31 copolymer LB film layer.

In conclusion, we demonstrated that the LB technique enables us to control precisely the film thickness of the electroluminescent devices. There is an optimum number of layers in the electroluminescent characteristics of the double-layer devices. It is important to optimize the thickness of the hole-transporting layer which inhibits the energy transfer quenching of excitons and maintains the hole-transporting ability. High hole-transporting polymer LB films will be required in the next stage.

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