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Electroluminescent (EL) emission has been investigated in a system which consisted of molecular dispersion of 1,4-bis(N,N-diphenylaminophenyl-1,3,4-oxadiazolyl)benzene (OXD) in a liquid crystal, 4-octyloxy-4'-cyanobiphenyl (8OCB). EL emission was observed above the temperature where the OXD/8OCB mixture exhibited a liquid-crystalline phase. In addition, we fabricated and evaluated emission of an EL device which consisted of interdigital electrodes coated onto a glass plate.

Keywords: Electroluminescence; Liquid crystal; Oxadiazole; Interdigital electrode; Guest-host

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INTRODUCTION

Electroluminescent (EL) devices based on organic thin layers have attracted much interest because of their possible application as large-area light-emitting displays [1-4]. Electroluminescence in such systems is generated by recombination of holes and electrons in the emitting layer which produces excited states in the emitter material. These EL devices, which consist of a doubled layer structure with an organic hole transport layer and a luminescent electron transport layer, show emission with an operating voltage of a few volts. However, one of the problems associated with such devices is short lifetime of the devices. The device structure with two organic layers contains an interface between the two layers where only a weak van der Waals force exists; therefore, one-layer-type device may achieve an improvement of structural stability because of the absence of these interfaces [5,6].

Recently, the one-layer-type organic EL devices using molecularly-doped polymers (MDPs) have been investigated by many researchers [7]. MDPs are binary solid solutions of charge transport molecules molecularly dispersed in inert and inactive polymeric matrices, and have been used as photoconductors [8-11]. Compared with intrinsically conductive polymers, MDPs are much more flexible in material design. For example, by selecting a proper dopant molecule and a concentration, it is possible to control carrier transport properties. In addition, mechanical properties of the MDPs can be adjusted by selecting the host binder. Thus, this class of materials is ideally suited for the fabrication of EL devices [7].

Liquid crystals (LCs) are promising materials in terms of a unique self-organizing nature and fluidity. Some low-molecular-weight LCs containing either hole (benzothiazole) or electron (oxadiazole) conducting groups as mesogens have been synthesized [12,13] and

some have been investigated as charge transport and, in some cases, EL emission materials. These LCs show high electron and/or hole drift mobilities based on aligned and stacked structures in a smectic (Sm) phase. It was presented that EL devices using these LCs exhibited polarized EL emissions [12]. However, one-layer-type EL devices consisting of single LCs suffer not only from smaller freedom in molecular design but also from restriction in design of devices.

There may be an interesting alternative to active devices: fluorescence switching of a fluorescent "guest" dissolved in an LC "host" matrix by an external voltage was considered for LC display applications as early as in 1973 by Larrbee [14] and was revisited more recently by Sariciftci *et al.* [15], who reported a switchable photoluminescence (PL) contrast of approximately 10 between homogeneous and homeotropic states. Such a system is called as a polarizing excitonic energy transfer (EET) [16]. Recent introduction of polarizing EET into a guest/host system has made it an attractive alternative to active device concepts. Their devices were, however, excited with polarized light and belonged to the PL devices.

In the present study, we investigated EL devices using molecularly-doped host LCs and evaluated in detail emission behavior of the EL devices. In this system, emission colors, electronic properties and electro-optical properties are expected to be tuned by using various dyes, hole transport and electron transport materials.

EXPERIMENTAL SECTION

Materials and LC behavior

The system used in this study was molecular dispersion of 1,4-

bis(N,N-diphenylaminophenyl-1,3,4-oxadiazolyl)benzene (OXD) [17] in a low-molecular-weight liquid crystal: 4-octyloxy-4'-cyanobiphenyl (8OCB). OXD is a luminescent material possessing hole and electron transport properties and has been used as a luminescent layer in EL devices. Structures of materials used in this study are shown in Figure 1. OXD was synthesized by the reference to the previous paper [17]. 8OCB as a host is a widely used LC for many applications which is electrochemically inert and shows an SmA phase and nematic (N) phase (SmA: 55 ~ 67 °C; N: 67 ~ 80 °C). It was purchased from Merck Japan, Ltd., and used after recrystallization.

LC behavior and phase-transition behavior of the OXD/LC mixture were examined on an Olympus Model BH-SP polarizing microscope equipped with a Mettler hot stage EP-82 and a DSC (Seiko I&E SSC 5000) at a heating rate of 2 °C/min.

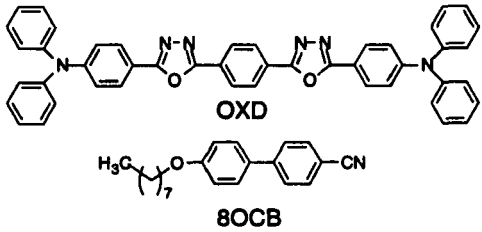

FIGURE 1. The structures of materials used in this study.

Measurements of electroluminescent behavior

The EL devices prepared in this study are shown in Figure 2. We fabricated the cell with two glass plates, on which indium tin oxide (ITO) was evaporated, whose surfaces were overcoated with polyimide (PI; 50 nm thickness). In order to establish homogeneously aligned OXD in the OXD(30 wt%)/LC mixtures, the PI was used on both of the

ITO electrodes which were mechanically rubbed prior to cell fabrication. The cell was filled with the mixture by capillary action. Measurements of the EL behavior was carried out with a luminance meter (Minolta L-100) on the thermostated block equipped with a heater and a temperature probe.

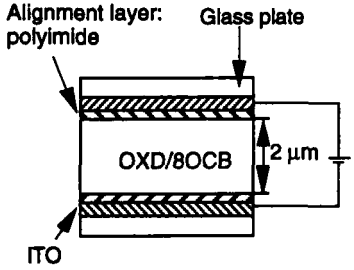

FIGURE 2. Configuration of the cell for measurements of EL emission.

RESULTS AND DISCUSSION

LC behavior of OXD/8OCB

Generally, a guest/host mixture shows different phase transition temperature from those of the host LCs. In this system, with increasing the fraction of OXD, the temperature range where the mixture showed the N phase became narrower. The OXD/8OCB mixture showed a stable LC phase even at the fraction of OXD of 30 wt%. At 30 wt%, however, the mixture did not exhibit an N phase but an SmA phase alone (60 ~ 75 °C on heating; 77 ~ 28 °C on cooling).

EL behavior of OXD(30 wt%)/8OCB

Emission of blue green region was observed from the EL cell when

operated in a continuous dc mode. Taking literature data into account, OXD shows PL with a peak at 489 nm and strong blue green emission due to extended π-conjugation [17]. Thus, it appears that the EL emission from the cell is originated from OXD and 8OCB does not affect the EL emission.

Figure 3 shows the EL emission behavior as a function of temperature. When operated at 135 V, no EL emission was observed in the crystalline phase of the mixture from 40 to 55 °C on heating. This may be due to capturing of carriers by traps at grain boundaries in a polycrystalline state of the mixture. However, on heating, luminescence started to be observed at 60 °C (SmA phase) presumably owing to disappearance of the grain boundaries due to fluidity of LCs. Above 65 °C, the luminance of the mixture did not increase remarkably with temperature. It was found that the luminance in an isotropic phase (I phase) was as high as that in the SmA phase. On cooling down to 60 °C, the EL emission in the SmA phase showed the same luminance as

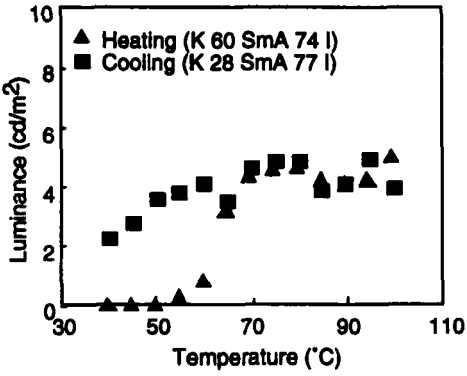

FIGURE 3. EL behavior as a function of temperature operated at 135 V: (closed triangle), on heating; (closed square), on cooling.

that in the I phase. On the other hand, from 60 °C the luminance decreased gradually with temperature. The emissions from the EL cell both in the SmA and I phases were not polarized even though homogeneous alignment of the mixture was performed before application of voltage.

8OCB used as a host matrix possesses positive dielectric anisotropy. Operated at dc voltage, the OXD/8OCB mixture was aligned parallel to the electric field. Homeotropic alignment of the mixture was confirmed by examination with a polarizing microscope under an applied field at 135 V. Therefore, much of emission from the EL cell seemed to be "in-plane".

We fabricated the EL cell using interdigital electrodes (ID cell), which was made of transparent ITO, to align 8OCB parallel to the substrate under the applied field (Figure 4). The interdigital electrodes have proven to be useful in investigation of acoustic surface waves [18],

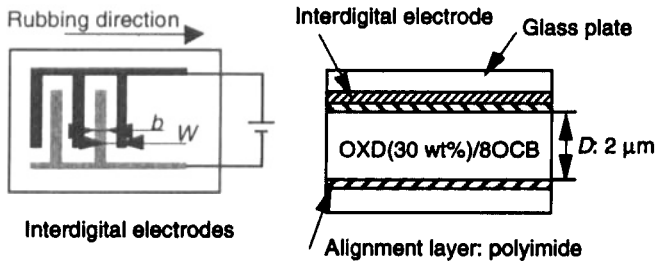

FIGURE 4. Interdigital electrodes on a glass plate and configuration of the EL cell with the interdigital electrodes. The electrodes were interleaved sets of parallel strip-shaped fingers located on a plane. Adjacent fingers were connected alternately to the positive and negative side of dc.

integrated optics [19] and electro-optics [20]. In the ID cell in this study, the upper substrate consisted of a glass plate coated with interdigital electrodes whose surface was overcoated with PI. The PI surface was mechanically rubbed prior to cell fabrication. The lower substrate which was composed of rubbed PI on a glass plate was completely insulated. The fingers of interdigital electrodes had a width b and were separated uniformly by a distance W (50 μm). The gap between substrates was D (2 μm); $D<<W$ in this case. It is then not necessary to have conductors on the lower substrate because the electric field lines emanating from the upper substrate fringe outward and have a strong influence on the molecular alignment at the lower substrate [21].

Polarized EL emission was evaluated with an apparatus schematically illustrated in Figure 5. A polarizer was placed between the ID cell and a luminance meter, and set either parallel or perpendicular to the electric field. Dichroic ratio (R) of the EL emission was analyzed by $R = I_{//} / I_{\perp}$: $I_{//}$ and $I_{\perp}$ are the EL intensity polarized parallel and perpendicular to the electric field, respectively.

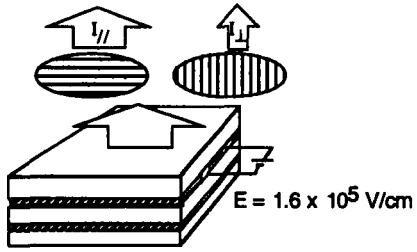

FIGURE 5. Schematic representation of the apparatus used for polarized EL emissions.

When luminance was 0.5 cd/m^2 at an applied electric field of 1.6 x 10^5 V/cm, the *R* value in the SmA phase was 2.91 and significantly larger than that in the I phase (1.44). The *S* value in the SmA phase was 0.40 and four times as large as that in the I phase (0.10), where the *S* can be determined in a similar manner as absorption. These results clearly demonstrate that polarized EL emission was obtained by orientation of OXD due to aligned host 8OCB under the applied field. Even in the I phase where molecular alignment is considered to disappear, the *S* value of 0.1 was observed. It seemed that OXD was oriented by the alignment of host 8OCB owing to the high electric field. Each LC molecule still tends to create an ordered structure in the microscopic region even in the I phase [22]. Accordingly, these seem to prove that the external electric field gives the orientation of dopants due to aligned LC molecules even under thermal fluctuation. In addition, the LCs and the guest/host LC mixtures in the I phase usually show lower viscosity and a shorter response time to external fields. The observation of polarized EL emission in the I phase is of important interest for new functional devices.

CONCLUSION

In this study, we confirmed the emission from one-layer-type EL devices consisting of OXD/8OCB mixtures above the temperature where the mixture showed an LC phase. Furthermore, we fabricated the ID cell and observed polarized EL emission of the cell. These results mean that refinement of the device structure gives various EL emissions. Our demonstration of polarized EL emission from the ID cell is expected to lead to the fascinating possibility of combining the electrically pumped emission mode with an electro-optical switching mode in LCs.

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