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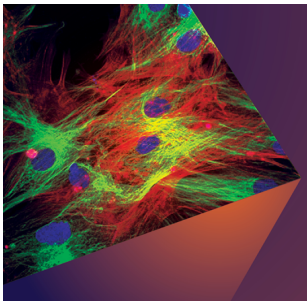
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Organic electroluminescent devices based on molecularly doped polymers

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Electroluminescent devices were fabricated using poly(methyl methacrylate) (PMMA) molecularly doped with triphenyldiamine derivative and tris(8-quinolinolato)aluminum(III) complex (Alq). A cell structure of glass substrate/indium–tin–oxide/doped PMMA/Mg:Ag was employed. Carrier injection from the electrodes to the doped PMMA layer through the dopants and concomitant electroluminescence from Alq were observed. Green emission with luminance of 920 cd/m^2 was achieved at a drive voltage of 17 V.

Electroluminescent (EL) devices based on organic thin layers have attracted much interest because of their possible application as large-area light-emitting displays.[1–10] Electroluminescence in such systems is generated by recombination of holes and electrons in the emitting layer, which excites the emitter material. Tang and VanSlyke[1] were the first to demonstrate that the use of a hole transport layer for hole injection from the electrode into the emitting layer significantly lowers the drive voltage to a value of a few volts. Their devices consisted of a doubled layer structure with an organic hole transport layer and a luminescent electron transport layer. In this case, the hole transport layer plays an important role in transporting holes and blocking electrons, thus preventing electrons from moving into the opposite electrode without recombining with holes.

One of the problems associated with such devices is the lifetime of the cell. Although a lifetime of 100 h has been reported,[1] a much longer lifetime is required for practical use. The degradation of the cell is partly caused by crystallization of organic layers. In this case, the contact between each layer may be destroyed by the crystallization of each layer.[3]

Such problems could be solved by the use of less crystalline polymetric materials, and the utility of poly(methylphenysiline)[7] and poly(vinylcarbazole)[8] as the hole transport layer has been demonstrated. However, the cell structure with two organic layers contains an interface between the two organic layers where only the weak van der Waals force exists between the layers. Such interface may not be physically strong enough for the long term use of the devices; therefore, one-layer-type device rather than two-layer-type device may achieve an improvement of structural stability. Recently, one-layer-type EL devices with intrinsically conductive polymers have been reported.[9,10]

In this letter, we report the one-layer-type organic EL device using molecularly doped polymers (MDPs). MDPs are binary solid solution of a charge transporting molecules molecularly dispersed in an inert, inactive polymetric binders, and have been used as photoconductors in xerography.[11] Compared with intrinsically conductive polymers, MDPs are much more flexible in material design. For example, by selecting a proper dopant molecule and the concentration, it is possible to optimize carrier transport properties. In addition, the mechanical properties of the MDPs can be chosen by selecting the host polymer binder. Thus, this class of materials is ideally suited for the fabrication of EL cells.

The MDPs used in this study is the molecular dispersion of *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD) and tris(8-quinolinolato)-aluminum(III) (Alq) complex in poly(methyl methacrylate) (PMMA). TPD has a high hole drift mobility of 10^{-3} cm^2/V s,[12] and its hole transport properties in polymer matrix was reported.[12] Alq is a luminescent metal complex possessing electron transport properties and has been used as a luminescent layer in EL cells.[1,2,7,8] PMMA is optically and electronically inert, and has good film forming properties with a high glass transition temperature of 105 °C.[13]

Figure 1 shows the cell configuration and the molecular structures of the materials used in this study. The EL cell was a one-layer structure with doped PMMA sandwiched between electrodes. The doping concentration was kept constant at 50 wt %, and the molar ratio of TPD to Alq (TPD/Alq) was varied from 0.43 to 1. PMMA with a number average molecular weight of 100 000 was employed. A dichloroethane solution containing proper amounts of TPD, Alq, and PMMA was dip coated onto an ITO (indium–tin–oxide)-coated glass substrate with a sheet resistance of 10 Ω/□ (Furuuchi Chemistry Co. Ltd.). The thickness of the doped PMMA layer was 1000 Å. Then, 2000 Å of magnesium and silver (10:1) were codeposited on the PMMA layer surface as the top electrode at 3×10^{-5} Torr. The substrate was kept at room temperature during the deposition and the deposition rate for Mg:Ag was 11 Å/s. The emitting area was 0.5×0.5

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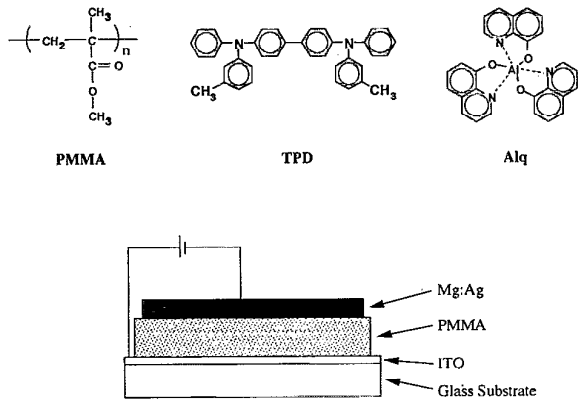

FIG. 1. Configuration of EL cell and molecular structures of materials used.

cm^2. Luminance was measured with a Minolta luminance meter LS-100 at room temperature under nitrogen atmosphere.

Green emission was observed from the EL cell when operated in a continuous dc mode for a forward bias ITO at positive polarity. The EL spectrum is shown in Fig. 2 together with the photoluminescence (PL) spectra of Alq and TPD molecularly dispersed in PMMA. The El spectrum is identical to the PL spectrum of Alq, indicating that the electroluminescence originates from Alq. Luminescence was negligible for the cells without doped TPD. This indicates that TPD plays a role of transporting injected holes from ITO, thus enabling the recombination of the two carriers in the PMMA layer.

Figure 3 shows a typical current–voltage and luminance–voltage curves for an EL cell (TPD/Alq =0.67). Luminance was proportional to the injection current as well as the bias voltage. Luminescence started at a voltage as low as 6 V and the maximum luminescence of 920 cd/m^2 and a current density of 170 mA/cm^2 were

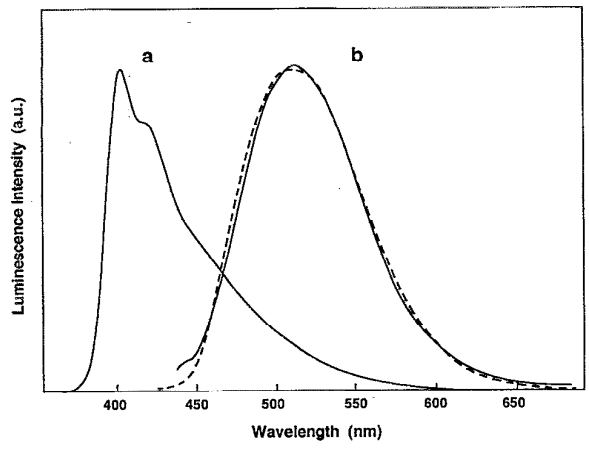

FIG. 2. Photoluminescence and electroluminescence spectra: (solid lines) PL spectra of PMMA film doped with TPD (a) or Alq (b), (broken lines) EL spectrum of ITO/PMMA:TPD:Alq/Alq/Mg:Ag cell (TPD/Alq=1).

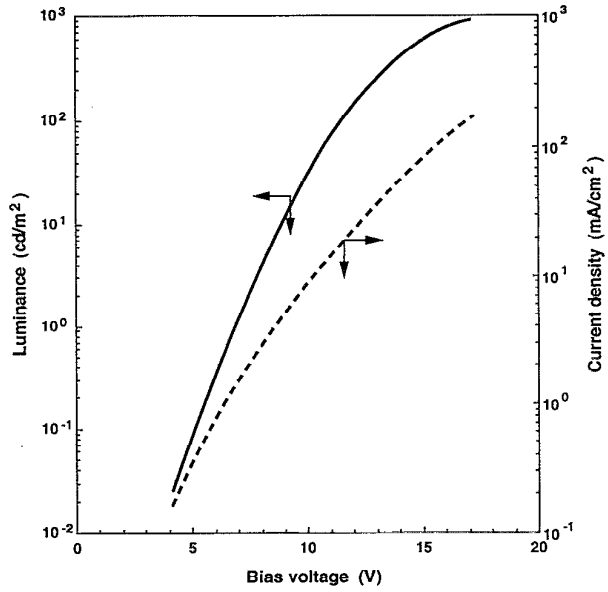

FIG. 3. Luminance–voltage (solid line) and current–voltage (broken line) characteristics of a typical ITO/PMMA:TPD:Alq/Mg:Ag cell (TPD/Alq=0.67).

reached at 17 V. This is clearly visible in a lighted room: The luminance is much higher than that of a common CRT, which is less than 100 cd/m^2.

The EL intensity is dependent on the ratio of the dopants in the PMMA layer. Cells with the molar ratio TPD/Alq of 1 and 0.43 exhibited lower EL intensity compared to the cell with 0.67 at the same drive voltages. For example, at 17 V, luminance of 430 cd/m^2 at 90 mA/cm^2 was observed for the cell with TPD/Alq=1, and that of 180 cd/m^2 at 60 mA/cm^2 for the cell with TPD/Alq=0.43. The lower luminance in those cells is not only due to the lower current densities but also due to lower EL efficiencies which may be caused by the failure in recombination between electrons and holes. In other words, carriers pass through the polymer layer without encountering the carrier with opposite polarity.

Although the mechanism involved in the excitation of Alq is uncertain at present, the carrier transport mechanism in MDPs is believed to be due to hopping between the dopant molecules of the same kind, which can be assumed to be an oxidation–reduction process. Thus, electrons and holes are transported in the polymer layer through Alq and TPD, as shown below:

$$Alq^{\cdot -} + Alq \rightarrow Alq + Alq^{\cdot -} ,$$

$$TPD^{+} + TPD \rightarrow TPD + TPD^{+} .$$

Therefore, the following two mechanisms for the excitation of Alq are possible. One is the direct excitation of Alq by the reaction between a radical anion of Alq and a radical cation of TPD:

$$Alq^{\cdot -} + TPD^{+} \rightarrow Alq^{*} + TPD.$$

The other mechanism involves the excitation of TPD by the reaction of the two charge carriers. It is followed that

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the excited energy is transferred to an adjacent Alq molecule via Förster type energy transfer:

$$Alq^{-} + TPD^{+} \rightarrow Alq + TPD^{*},$$

$$Alq + TPD^{*} \rightarrow Alq^{*} + TPD.$$

In the photoluminescence of PMMA film containing both Alq and TPD, since luminescence from Alq was observed by the excitation of TPD, the latter mechanism of energy transfer from TPD to Alq cannot be excluded.

In systems containing electron-donor molecules and electron-acceptor molecules, complexes such as charge transfer complex and exciplex could be formed. It has been reported that poly(vinylcarbazole) forms strong charge transfer complex with trinitrofluorenone[11] and TPD forms exciplex with some organic luminescent dyes,[3] which causes the spectral shift of the luminescent molecules to the longer wavelength. In case of TPD and Alq, since the EL spectrum exactly matches the PL spectrum of Alq, there is no such complexes formed between the two molecules, thus maintaining the green color of Alq. This may be due to the structural feature of the Alq molecule which has an octahedral configuration.[14]

In conclusion, the use of MDPs enables easy fabrication of EL devices in which carriers are injected through the dopants to the polymer layer resulting in electroluminescence. We are currently optimizing the cell configuration, and investigating the durability of the cells and the effect of polymer binder by using other polymer systems. We are also attempting to obtain different luminescent colors by doping the system with other luminescent materials.

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