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THERMAL STABILITY OF ORGANIC ELECTROLUMINESCENT DEVICES FABRICATED USING NOVEL CHARGE TRANSPORTING MATERIALS

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Abstract: Novel hole and electron transporting materials have been synthesized to improve the thermal stability of organic electroluminescent (EL) devices. Molecular structures of such hole and electron transporting materials were designed based on triphenylamine (TPA) and oxadiazole (OXD) moieties, respectively. It has been found that the resulting materials have high glass transition temperatures (Tg) over 100℃ and the vacuum-deposited thin films are significantly thermally stable. For the two-layer EL devices using the novel hole transporting materials and the typical emitting material, tris(8-quinolinolato) aluminum, the thermal stability has been clearly seen to depend on the Tg of the hole transporting material ; excellent thermal stability was achieved. For the three-layer EL device using the novel electron transporting material, good emission efficiency and good stability were achieved. The electron transporting materials have been also applied to the polymeric system with polyvinylcarbazole matrix.

INTRODUCTION

Electroluminescent (EL) devices based on organic materials are much attractive for full-color flat display applications (Ref. 1-11). For such applications, the durability of the EL device is the most important subject. Generally, the organic layers are preferred to be amorphous because of an excellent film-forming ability. It is known that the morphological change of the amorphous organic layers caused by crystallization is related to the degradation of the device characteristics (Ref. 7, 12,13). In such amorphous films the high glass transition temperature (Tg) is a significantly important factor, because the crystallization is due to local molecular motion at near the Tg. Therefore, the development of novel materials having a high Tg is required to realize the high durability, especially at high temperature and at high current driving. In this paper, we present novel hole and electron transporting materials for the EL device. The basic structures of those hole transporting materials are a linear linkage and

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branched linkage of triphenylamine moiety. On the other hand, the electron transporting materials are based on oxadiazole moiety and have branched and twisted structures. The EL characteristics of the EL devices using these materials will be demonstrated.

EXPERIMENTAL

The hole transporting materials we synthesized are shown in Fig. 1. Although the number and position of the methyl unit are not identical, these materials belong to the class of triphenylamine oligomer. These materials were synthesized through an Ullmann coupling reaction (Ref. 14). We use the abbreviations as follows: TPTR, trimer; TPTE, tetramer; TPPE, pentamer; TPTE(s), starburst tetramer. On the other hand, four electron transporting materials (OXD1-4, Fig. 2) were synthesized by the cyclization of corresponding bis(acyl)hydrazines in thionyl chloride and pyridine (Ref. 15). More recently, similar materials have been independently reported (Ref. 16). The Tgs of these materials were measured by differential scanning calorimetry (DSC).

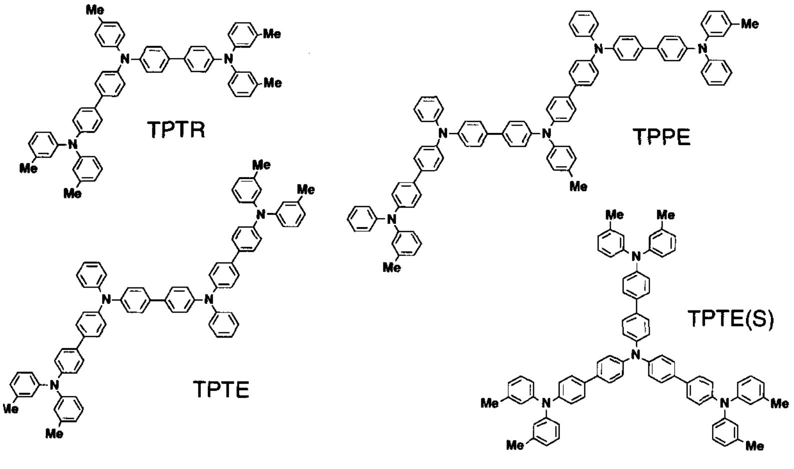

Fig. 1 Molecular structures of novel hole transporting materials.

Schematic structure of the vacuum-deposited organic EL device and chemical structures of the emitting materials are shown in Fig. 3. The tris (8-quinolinolato) aluminum (Alq) is a well-known emitting material which is one of the most stable molecules in the class of metal chelates. The Alq was purified by a train sublimation method. The organic EL devices have been fabricated by a conventional vacuum deposition technique. The glass substrates coated

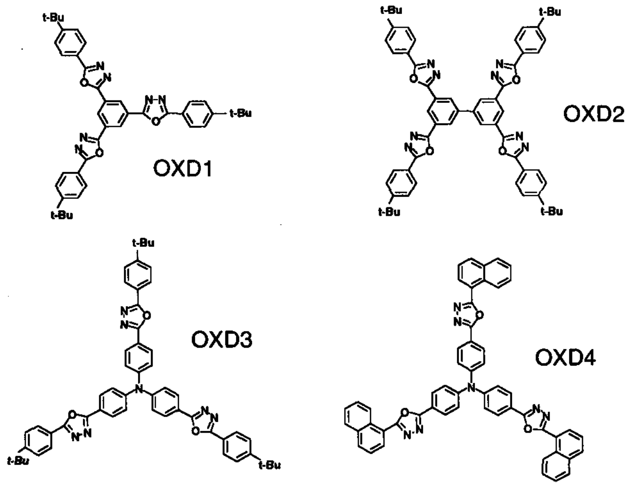

Fig. 2 Molecular structures of novel electron transporting materials

with ITO (sheet resistance 15Ω/□) were cleaned ultrasonically in methanol and isopropyl alcohol, and dried in an oven kept at 90 °C. Prior to use the substrates those were treated with a UV ozone chamber. At first, the hole transporting layer (typically 700 Å thick) was deposited on the ITO electrode from a graphite crucible in a vacuum chamber with a pressure of 5 x 10^{-8} Torr. Then, the emitting layer (typically 700 Å thick) was deposited on the hole-transporting layer. The deposition rates were typically 0.6 Å/s for the transporting and emitting layers. Finally, the cathode electrode of Mg:Ag (9:1) mixed film (1800 Å) was deposited from two metal sources under a vacuum of 5 x10^{-7} Torr in another vacuum deposition chamber. An emitting area of the EL devices was typically 0.09 cm^2.

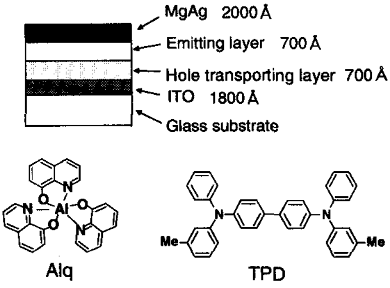

Fig. 3 Schematic structure of EL device and typical emitting and hole transporting materials.

The electron transporting materials were used in polymeric system (Ref. 6, 17) with polyvinylcarbazole (PVK) as a hole transporting matrix and coumarin 6 (1wt%) as an emitting molecule. In this case, the organic layers were prepared on the ITO-coated glass substrates by dipping from chloroform solutions.

The luminance-current and current-voltage characteristics were measured with a programmable voltage/current source (TAKEDA RIKEN TR-6150) and a Minolta photometer (nt- 1°P). In the high temperature experiments, the EL device was set in a small stainless steel chamber filled with nitrogen to prevent oxidation of the MgAg electrodes. The measurement chamber was heated from room temperature to 160 °C by heating tapes connected to a programmable temperature controller. Light output was measured through a glass viewport (ANELVA ø70) of the chamber.

RESULTS AND DISCUSSION

1. Hole transporting materials

It is known that, a well-known hole transporting material, the triphenylamine dimer (TPD) has a low Tg (60 °C). The Tgs of the novel hole transporting materials are found from DSC data of Fig. 4 ; 95 °C for TPTR, 130 °C for TPTE, 145 °C for TPPE, 106 °C for TPTE(S) (Ref. 14, 19). The linear linkage of triphenylamine causes extremely a rise in the Tg. This result indicates that, as we expected, the linear linkage of triphenylamine is the promising way to realize the high Tg hole transporting materials.

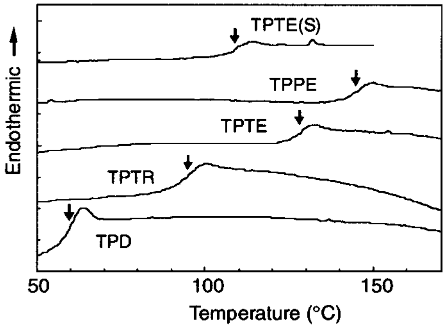

Fig. 4 DSC data (measured at a rate of 10 °C/min) of novel hole transporting materials.

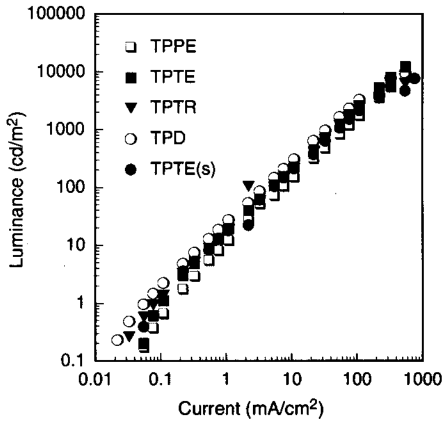

Fig. 5 Luminance-current characteristics of EL devices using various hole transporting materials.

Fig. 5 shows the luminance-current (L-I) characteristics, at room temperature, in the two-layer EL devices using various hole transporting materials and the Alq. Each EL device exhibited a high brightness of about 10000 cd/m^2 at a driving current less than 1 A/cm^2. The "turn-on-voltages" for light emission were around 3V which were almost identical in all devices. The devices with TPTR, TPTE and TPTE(S) exhibited high luminous efficiencies of about 1.0 lm/W (at 100 cd/m^2) which is comparable to that of the representative device, TPD/Alq, (Tab. 1). However, the efficiency of the device with TPPE is little low compared with other devices. The reason for the low efficiency is not clearly understood. It may be attributed to a small amount of contamination caused from a decomposition of TPPE during evaporation for the deposition.

Tab. 1. Turn-on-voltage, emission efficiency and quantum efficiency.

HTL	Turn-on-voltage (V)	Emission efficiency (lm/W)	Quantum efficiency (%)
TPD	3.0	1.05	1.0
TPTR	3.5	0.94	0.87
TPTE	3.1	1.0	0.87
TPTE(s)	3.0	1.0	0.87
TPPE	3.2	0.68	0.59

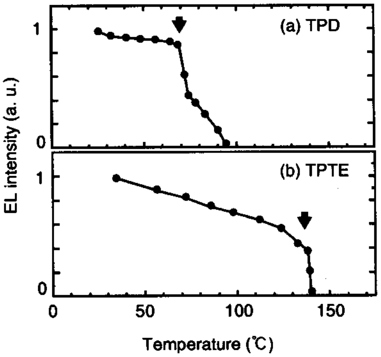

Fig. 6 Temperature dependence of EL intensity in EL devices using TPD and TPTE.

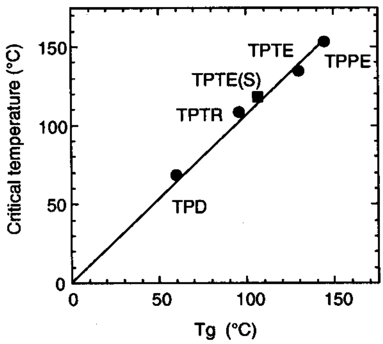

Fig. 7 Relationship between Tg and critical temperature.

The thermal stability of the EL devices was examined from the temperature dependence of EL intensity measured under a constant-current-drive condition. For all the EL devices, the EL outputs gradually decreased with increasing the temperature, which can be explained by the temperature dependence of photoluminescence of Alq (Ref. 10). The TPD/Alq device exhibits a drastic drop of the EL output at 70 °C, which is well corresponding to the Tg (60 °C) as shown in Fig. 6 (a). On the other hand, the output drop of the TPTE/Alq device occurs at around 135 °C (Ref. 18). Similar phenomena were observed in all the devices. The temperatures of such output drop (critical temperature) for other EL devices were 110 °C for TPTR, 155°C for TPPE and 125 °C for TPTE(S) (Ref. 19). The highest thermal stability was achieved in the EL device using TPPE. From this systematic experiments, we have found a linear relationship between the Tg and the critical temperature as shown in Fig. 7. This undoubtedly indicates that the thermal stability of EL device with Alq emitting layer is still dominated by that of the hole transporting layer. The intensity drop at temperature above the Tg is attributable to the morphological change of the hole transporting layer.

2. Electron transporting materials

Typical electron transporting materials are oxadiazole derivatives such as 2,5-bis(1-naphthyl)-1.3,4-oxadiazole (BND) and 2-(4'-biphenyl)-5-(4"-tert-butylphenyl)-1,3,4-oxadiazole (PBD). However, such materials easily crystallize in a thin film form or in polymer matrix heavily doped with those. The novel electron transporting materials exhibited greatly high Tg; 137 °C for OXD1, 162 °C for OXD2, 154 °C for OXD3 and 121 °C for OXD4. By the vacuum evaporation, these materials were tried to deposited on the glass substrate. However, only the OXD1 could be deposit on a glass substrate without any decomposition. The resulting film showed uniform amorphous state and the morphology was fairly stable even after heating at 100 °C for 1hr. Fig. 8 shows the L-I characteristics of the three-layer EL device using TPTE, Alq and OXD1 comparing with that of the TPTE/Alq device. The turn-on-voltage for light emission was almost the same (at around 3V) and the luminous efficiency was high (about 1.5 lm/W) rather than TPTE/Alq (Ref. 20). This suggests that the OXD1 has high electron transporting and hole-

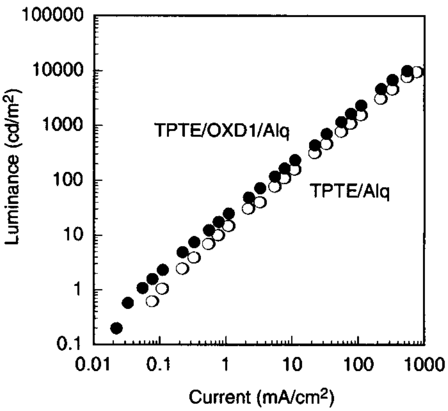

Fig. 8 Luminance-current characteristics of TPTE/Alq/OXD1 and TPTE/Alq devices.

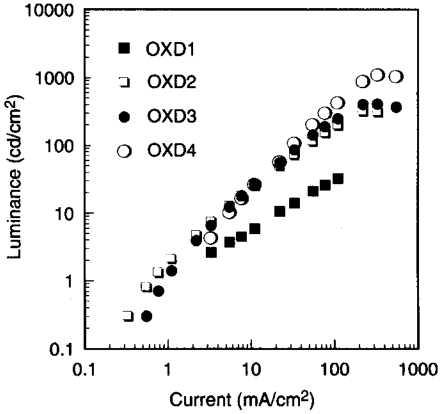

Fig. 9 Luminance-current characteristics of polymer EL devices using novel electron transporting materials.

blocking abilities.

The electron transporting materials were also studied in the polymer EL devices based on PVK film doped with those materials and coumarin 6. The doped PVK films, even highly doped with the OXD derivatives, were found to be morphologically stable; no crystallization of the dispersed derivatives was observed even after 3 months at room temperature and/or heating at 100 °C. The L-I characteristics of the polymer EL devices with 50 wt% OXD derivatives and 1 wt% coumarin 6 are shown in Fig. 9. The OXD4 dispersed device exhibited the lowest turn-on-voltage (at 6 V) and the highest emission efficiency (ca. 0.12 lm/W at 100 cd/m^2) among the EL devices. This result can be explained by lower reduction potential of the OXD4 having nathtyl group.

CONCLUSIONS

The thermal stability of the two-layer EL device using the Alq and hole transporting material is dominated by the stability of the hole transporting layer, that is, the glass transition temperature. The oligomerization of triphenylamine provides the high Tg material and the high EL device performance at high temperature. The novel electron transporting materials based on oxadiazole give good EL characteristics and morphological stability in the vacuum-deposited film and polymeric system. Further study for the EL devices is now in progress by improving the EL device structure and the passivation of the EL devices.

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