Macromol. Symp. ***125**, 171–180 (1997)*

THERMALLY STABLE ORGANIC ELECTROLUMINESCENT DEVICE USING NOVEL AMORPHOUS MOLECULAR CHARGE-TRANSPORT MATERIALS, 4,4',4"-TRIS[BIS(4'-*tert*-BUTYLBIPHENYL-4-YL)AMINO]TRIPHENYLAMINE AND 4,4',4"-TRI(*N*-CARBAZOLYL)TRIPHENYLAMINE

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Abstract: For the purpose of developing an amorphous molecular material with a high glass-transition temperature (Tg) and a low ionization potential for use as a charge-transport layer in organic electroluminescent (EL) devices, a novel starburst molecule, 4,4',4"-tris[bis(4'-*tert*-butylbiphenyl-4-yl)amino]triphenylamine (*t*-Bu-TBATA), was designed and synthesized. *t*-Bu-TBATA was found to form readily a stable glass with a Tg of 203 °C. A multilayer EL device consisting of double hole-transport layers of *t*-Bu-TBATA and 4,4',4"-tri(*N*-carbazolyl)triphenylamine and an emitting layer of tris(8-quinolinolato)aluminum was fabricated and its performances were examined. The device was found to exhibit good performances and to be thermally stable, operating even at 170 °C.

INTRODUCTION

Organic electroluminescent (EL) devices, which are attractive because of their capability of multicolor emission, ease of fabrication, and operation at a low driving voltage, have been attracting a great deal of attention due to their

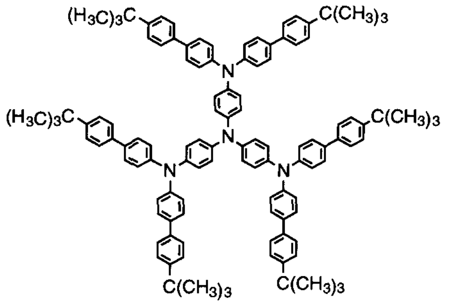
CCC 1022-1360/97/$ 04.00

potential application as full-color flat-panel displays. Since it was reported in 1987 that a bilayer organic EL device consisting of a diamine hole-transport layer and a tris(8-quinolinolato)aluminum (Alq_3) emitting layer exhibits high performances (Ref. 1), extensive studies have been made of organic EL devices toward achieving high brightness, high luminous efficiency, multicolor emission, and in particular improving their durability (Refs. 2-10). Both low molecular-weight organic materials and polymers are used for the fabrication of organic EL devices. As compared with single-layer devices using an emitting material alone, layered devices consisting of charge-transport and emitting layers generally exhibit higher performances, because a suitable combination of a charge-transport material and an emitting material in layered devices reduces the energy barrier for the injection of charge carriers from the electrodes, leading to better balance in the number of injected holes and electrons. Therefore, it is necessary to develop not only emitting materials but also charge-transport materials.

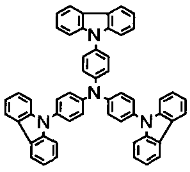
For the practical use of organic EL devices, they are required to be thermally stable because crystallization or melting of organic amorphous materials caused by Joule heat is thought to be a cause for the device damage. A number of emitting and charge-transport materials have been studied. With regard to low molecular-weight organic materials, Alq_3 and *N,N'*-bis(3-methylphenyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (TPD) have been most widely used as excellent green emitting and hole-transport materials, respectively, in organic EL devices (Refs. 1-10). However, the TPD amorphous film undergoes crystallization during the storage in ambient atmosphere and during the operation of the EL device (Refs. 11, 12) and lacks thermal stability because of its relatively low glass-transition temperature (Tg) of ~60 °C. There are a limited number of amorphous molecular materials with Tg's above 100 °C. Developing both morphologically and thermally stable amorphous organic materials that permit the formation of uniform films without pinholes is a subject of importance.

We have presented a new concept, "starburst molecule", for the molecular design of amorphous molecular materials for organic EL devices, showing that a few novel families of π-electron starburst molecules function as excellent hole-transport materials for organic EL devices (Refs. 5-9). They include 4,4',4"-tris(3-methylphenylphenylamino)triphenylamine (*m*-MTDATA, Tg 75 °C) (Refs. 5-8, 13), 4,4',4"-tris(1-naphthylphenylamino)triphenylamine (1-TNATA, Tg 113 °C) (Ref. 8), 4,4',4"-tris(2-naphthylphenylamino)-triphenylamine (2-TNATA, Tg 110 °C) (Ref. 8), 4,4',4"-tri(*N*-carbazolyl)triphenylamine (TCTA, Tg 151 °C) (Refs. 6, 8), 1,3,5-tris[4-(3-methylphenylphenylamino)phenyl]benzene (*m*-MTDAPB, Tg 105 °C) (Ref. 7, 14), and 1,3,5-tris[*N*-(4-diphenylaminophenyl)phenylamino]benzene (*p*-DPA-TDAB, Tg 108 °C) (Refs. 9, 15), which function as hole-transport materials and 1,3,5-tris(4-*tert*-butylphenyl-1,3,4-oxadiazolyl)benzene (TPOB) (Ref. 8), which functions as an electron-transport material. We have reported that the multilayer device consisting of double hole-transport layers of novel starburst molecules, *m*-MTDATA and TCTA, and an emitting layer of Alq_3 exhibits significant thermal stability, operating at a temperature even over 100 °C (Ref. 6).

m-MTDATA has been found to function as an excellent material for use as a hole-transport layer in contact with the ITO electrode in the multilayer organic EL device (Refs. 5-8, 16). It is expected that the development of another new material with a higher Tg than that of *m*-MTDATA enables the fabrication of thermally more stable EL devices. For the purpose of developing a new amorphous charge-transport material with almost the same ionization potential as that of *m*-MTDATA but a higher Tg than that of *m*-MTDATA, we have designed and synthesized a novel π-electron starburst molecule, 4,4',4"-tris[bis(4'-*tert*-butylbiphenyl-4-yl)amino]triphenylamine (*t*-Bu-TBATA) (Ref. 17). This paper describes the synthesis and properties of *t*-Bu-TBATA, and the fabrication and performances of a multilayer EL device consisting of double hole-transport layers of *t*-Bu-TBATA and TCTA and an emitting layer of Alq_3.



t-Bu-TBATA



TCTA

EXPERIMENTAL PART

Materials

TCTA was prepared according to our previous paper (Ref. 6). *t*-Bu-TBATA was synthesized by the reaction of 4,4',4"-triaminotriphenylamine with 4-*tert*-butyl-4'-iodobiphenyl in the presence of copper and potassium hydroxide at *ca.* 160 °C in mesitylene for 24 h under nitrogen. It was purified by alumina column chromatography with benzene as an eluent, followed by recrystallization from benzene/hexane to give pale yellow needles. *t*-Bu-TBATA was identified by various spectroscopies, mass spectrometry, and elementary analysis. Anal. Calcd. for $C_{114}H_{114}N_4$: C, 88.90; H, 7.46; N, 3.64 %. Found: C, 88.87; H, 7.46; N 3.73 %.

Fabrication of EL device

The multilayer EL device was fabricated by successive vacuum deposition of the organic materials onto an ITO-coated glass substrate at a deposition rate of 2-3 Å s^{-1} at 10^{-5} Torr. Then an alloy of magnesium and silver (ca.10:1 in volume ratio) was deposited onto the organic layer by simultaneous evaporation from two separate sources. The emitting area was ~4 mm^2.

Measurement of thermal stability of EL device

The EL device placed in a cryostat at 10^{-3} Torr was heated to a given temperature and kept at that temperature for 15 min, and then a constant current density of 5 mA cm^{-2} was applied to the device to measure the luminance. The luminance at 22 °C was 120 cd m^{-2}.

Apparatus

Current-voltage-luminance characteristics of the EL device were measured with an electrometer (ADVANTEST TR6143) and a luminance meter (MINOLTA LS-100). The EL and PL spectra were measured with a fluorescence spectrophotometer (HITACHI model 4500).

RESULTS AND DISCUSSION

A novel starburst molecule, 4,4',4''-tris[bis(4'-*tert*-butylbiphenyl-4-yl)amino]triphenylamine (*t*-Bu-TBATA), was found to form readily a stable glass with a high Tg of 203 °C when the melt sample was cooled on standing in air (Ref. 17). Figure 1 shows a DSC curve for a *t*-Bu-TBATA glass sample. When the glass sample was heated at a heating rate of 10 °C min^{-1}, a glass-transition phenomenon was observed at *ca.* 203 °C and on further heating crystallization took place, leading finally to the crystal having the highest melting point of 365 °C *via* phase transitions. When the melt sample was cooled on standing in air, the transparent glass was formed *via* a supercooled liquid. The same DSC curve was reproduced on heating of the glass. The glassy state of *t*-Bu-TBATA is very stable and no crystallization has been noticed at room temperature for three years up to this time. The formation of the glass was evidenced by X-ray diffraction and polarizing microscopy. *t*-Bu-TBATA forms an amorphous film by vacuum evaporation.

The half-wave potential for the oxidation ($E_{1/2}^{ox}$) of *t*-Bu-TBATA is 0.09 V vs. Ag/Ag^+ (0.01 mol dm^{-3}), as determined by cyclic voltammetry in dichloromethane, which is similar to that of *m*-MTDATA ($E_{1/2}^{ox}$ = 0.06 V vs. Ag/Ag^+).

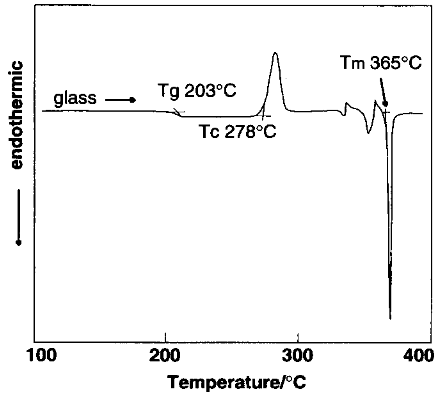


Fig. 1. DSC curve of a *t*-Bu-TBATA glass obtained by cooling the melt. Heating rate: 10°C min^{-1}.

t-Bu-TBATA, which is suggested to possess a solid-state ionization potential comparable to that of *m*-MTDATA, is expected to function as a hole-transport material in place of *m*-MTDATA for thermally stable organic EL devices. In the present study, a multilayer EL device consisting of double hole-transport layers of *t*-Bu-TBATA and TCTA and an emitting layer of Alq_3 was fabricated and its performances were examined. The structure of the fabricated EL device is shown in Fig. 2. The ITO/*t*-Bu-TBATA(450Å)/ TCTA(150Å)/Alq_3(600Å)/MgAg EL device emitted bright green light when a positive voltage was applied to the ITO electrode. Figure 3 shows the photoluminescence spectrum of Alq_3 and the electroluminescence spectrum for the EL device. The electroluminescence spectrum is in accordance with the photoluminescence spectrum of Alq_3; this indicates that the electroluminescence originates from the electronically excited singlet state of Alq_3, which is generated by the recombination of holes and electrons injected.

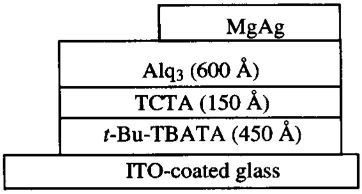


Fig. 2. Side view of the EL device.

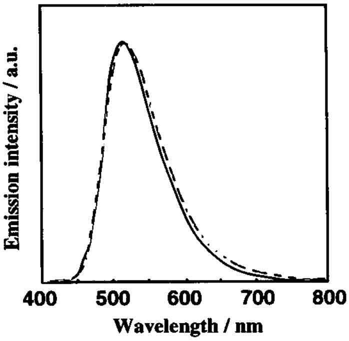


Fig. 3. Photoluminescence spectrum of an evaporated Alq_3 film (solid line) and electroluminescence spectrum for the EL device (dashed line).

Figures 4 and 5 show the luminance versus applied voltage characteristics together with the injected current density versus applied voltage characteristics and the luminance versus injected current density characteristics for the present ITO/*t*-Bu-TBATA(450Å)/TCTA(150Å)/Alq_3(600Å)/MgAg EL device. The emission with a luminance over 1 cd m^{-2} started at a driving voltage of 4 V, and a luminance of 12300 cd m^{-2} was obtained at a driving voltage of 19 V. Table 1 lists the performance characteristics for the present EL device in air, which are comparable to those of the ITO/*m*-MTDATA(650Å)/TCTA(150Å)/Alq_3(650Å)/MgAg EL device (Ref. 8).

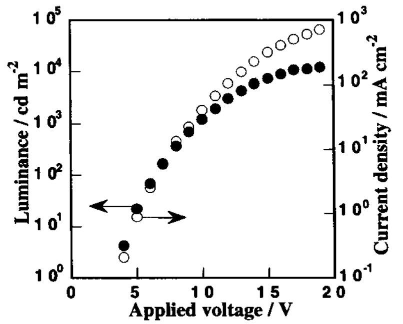


Fig. 4. Luminance and current density versus applied voltage characteristics for the ITO/*t*-Bu-TBATA/TCTA/Alq_3/MgAg EL device.

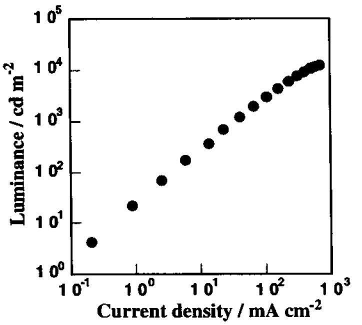


Fig. 5. Luminance versus current density characteristics for the ITO/*t*-Bu-TBATA/TCTA/Alq_3/MgAg EL device.

Table 1 .

Performance characteristics for the ITO/*t*-Bu-TBATA/TCTA/Alq3/MgAg device.[a]

Driving voltage (V)	Current density (mA cm^{-2})	Luminous efficiency (lm W^{-1})	Maximum luminance[b] (cd m^{-2})
7.7	11	1.1	12300

[a] at a luminance of 300 cd m^{-2}. [b] at a driving voltage of 19 V.

It is expected that the present EL device using *t*-Bu-TBATA and TCTA as hole-transport materials and Alq_3 as an emitting material is thermally stable. Thermal stability of the EL device was examined in a cryostat at 10^{-3} Torr. Figure 6 shows the temperature dependence of the luminance for the EL device, together with the temperature dependence of the intensity of the photoluminescence of Alq_3 film. The present EL device consisting of double hole-transport layers of *t*-Bu-TBATA and TCTA worked even at 170 °C, although the luminance decreased with increasing temperature. The present results show that the decrease in the luminance with temperature may be attributed partly to the drop in the fluorescence quantum efficiency of Alq_3 with an increase of temperature but partly to other factors associated with the charge-transport materials and the electrodes. When the device was again cooled to room temperature, it worked in the same way as before.

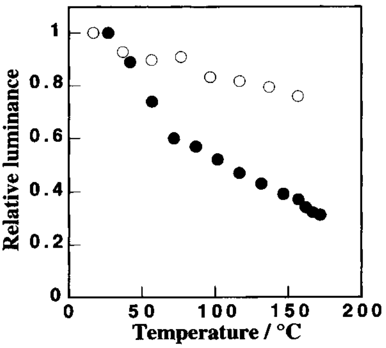


Fig. 6. Temperature dependencies of the intensity of the photoluminescence of the Alq_3 film (○) and electroluminescence for the ITO/*t*-Bu-TBATA/TCTA/Alq_3/MgAg EL device (●).

SUMMARY

A novel starburst molecule, *t*-Bu-TBATA, was designed and synthesized for making an amorphous molecular material with a high Tg for use as a hole-transport material in organic EL devices. *t*-Bu-TBATA was found to form readily an amorphous glass with a very high Tg of 203 °C. To the best of our knowledge, this material seems to possess the highest Tg among the low molecular-weight organic charge-transport materials for use in organic EL devices hitherto reported. The multilayer organic EL device using *t*-Bu-TBATA and TCTA as hole-transport materials and Alq_3 as an emitting material was found to be thermally stable even at 170 °C.

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