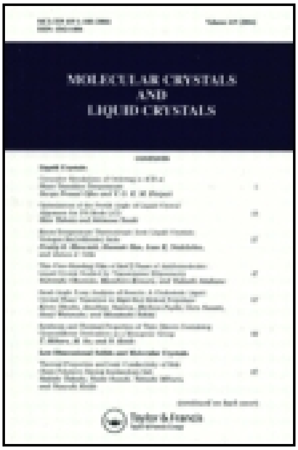

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Organic Electroluminescent Devices Using Novel Starburst Molecules, 1,3,5-Tris[4-(3-Methylphenyl-Phenylamino)Phenyl]Benzene And 4,4′,4″-Tris(3-Methyl-Phenylphenylamino)Triphenylamine, as Hole-Transport Materials

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ORGANIC ELECTROLUMINESCENT DEVICES USING NOVEL STARBURST MOLECULES, 1,3,5-TRIS[4-(3-METHYLPHENYLPHENYLAMINO)PHENYL]BENZENE AND 4,4',4"-TRIS(3-METHYLPHENYLPHENYLAMINO)TRIPHENYLAMINE, AS HOLE-TRANSPORT MATERIALS

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Abstract Organic electroluminescent devices using novel starburst molecules, 1,3,5-tris[4-(3-methylphenylphenylamino)phenyl]benzene (*m*-MTDAPB) and 4,4',4"-tris(3-methylphenylphenylamino)triphenylamine (*m*-MTDATA), as hole-transport materials and tris(8-quinolinolate)aluminium (Alq_3) as an emitting material were fabricated and their performance characteristics examined. The starburst molecules were found to function as excellent hole-transport materials. The ITO/*m*-MTDATA(300 Å)/*m*-MTDAPB(200 Å)/Alq_3(500 Å)/MgAl device exhibited a luminance of *ca.* 17,000 cd m^{-2} at a driving voltage of 16 V and a luminous efficiency of 1.9 lm W^{-1} at a luminance of 300 cd m^{-2}.

INTRODUCTION

Since it was reported that a double-layered organic electroluminescent (EL) device consisting of a hole-transport layer and an emitting layer exhibited a luminance over 1,000 cd m^{-2} at a driving voltage of less than 10 V, organic EL devices have received attention in view of potential application to full-color flat-panel display. Organic EL devices are attractive because of low driving voltage, capability of multicolor emission by the selection of emitting materials, and easy fabrication of large-area thin-film devices. There have been extensive studies on organic EL devices using both low-molecular-weight organic materials[1-10] and polymers[11-16] with the aim of achieving high brightness and multicolor emission. However, improvement in the luminous efficiency and in particular durability of devices remains to be solved.

Poor durability of organic EL devices has been attributed partly to the degradation of electrode materials with low work function and partly to morphological, thermal and

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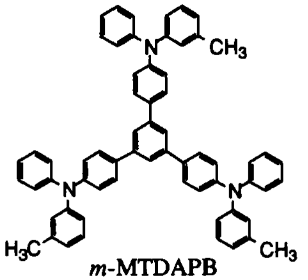
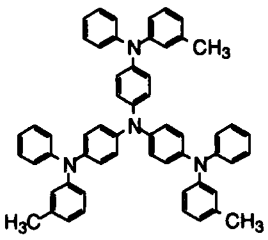
chemical instability of organic materials.[4,17,18] Crystallization or melting of organic amorphous materials and a short-circuit current caused by pinholes generated in organic thin films are thought to be the causes for the damage of devices using molecular materials. It is, therefore, necessary to develop both morphologically and thermally stable amorphous organic materials that permit the formation of uniform films without pinholes.

We have been studying the syntheses of novel organic π-electron systems for making photo- and electro-active amorphous molecular materials, and their morphology, crystal structures, molecular and solid-state properties, and applications.[19-31] We have reported that novel organic π-electron systems, which we refer to as "starburst" molecules in view of their molecular structures, 4,4',4"-tris(3-methylphenylphenylamino)triphenylamine (*m*-MTDATA) and 4,4',4"-tri(*N*-carbazolyl)triphenylamine (TCTA), function as excellent hole-transport materials for use in organic EL devices.[30,31] We have shown that a novel multilayered organic EL device consisting of double hole-transport layers of *m*-MTDATA and 4,4'-bis(3-methylphenylphenylamino)biphenyl (a derivative of N,N,N',N'-tetraphenylbiphenyl-4,4'-diamine, TPD) and an emitting layer of tris(8-quinolinolate)aluminium (Alq_3) exhibits a high luminous efficiency and significant durability.[30] A multilayered organic EL device consisting of double hole-transport layers of *m*-MTDATA and TCTA and an emitting layer of Alq_3 is thermally stable above 100°C.[31]

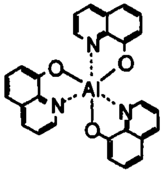
We report here the fabrication and performances of organic EL devices using 1,3,5-tris[4-(3-methylphenylphenylamino)phenyl]benzene (*m*-MTDAPB) and *m*-MTDATA as hole-transport materials and Alq_3 as an emitting material.



m-MTDAPB



m-MTDATA



Alq_3

EXPERIMENTAL

1,3,5-Tris[4-(3-methylphenylphenylamino)phenyl]benzene (*m*-MTDAPB) was synthesized by the reaction of 1,3,5-tris(4-iodophenyl)benzene with 3-methylphenylphenylamine in the presence of copper and potassium hydroxide at 170°C in decalin for 9h under nitrogen.[25] The crude product was chromatographed over silica gel with benzene/hexane as an eluent, followed by recrystallization from benzene/hexane. It was identified by IR, electronic absorption, and ^1H and ^{13}C NMR spectroscopies, mass spectrometry and elemental analysis. Found: C, 89.03; H, 5.98; N, 4.97. Calcd. for $C_{63}H_{51}N_3$: C, 89.01; H, 6.05; N, 4.94. *m*-MTDATA and TPD were prepared according to the methods described in ref. 19 and 32, respectively.

EL devices were fabricated by successive vacuum deposition of organic materials onto an indium-tin-oxide (ITO) coated glass substrate, followed by vacuum deposition of an alloy of magnesium and silver or aluminium with an atomic ratio of 10:1 by simultaneous evaporation from two separate sources. The evaporation rate of organic materials was 1-5 Å s^{-1} at 10^{-5} Torr. The emission area was 4 mm^2. Current-voltage-luminance characteristics of the EL devices were measured with a current/voltage unit, Kithley model 236 and a luminance meter, TOPCON BN-8. The solid-state ionization potentials of *m*-MTDAPB, *m*-MTDATA and Alq_3 were determined with a Rikenkeiki AC-1.

RESULTS AND DISCUSSION

The starburst molecules, *m*-MTDATA and *m*-MTDAPB, readily form transparent glasses with glass-transition temperatures of 75 and 105°C when the melt samples are cooled on standing in air, as evidenced from differential scanning calorimetry and X-ray diffraction.[19,25] The *m*-MTDATA and *m*-MTDAPB glasses are very stable; no crystallization has been noticed for years at room temperature. Vacuum deposition of *m*-MTDATA and *m*-MTDAPB also provides uniform, smooth amorphous films. The solid-state ionization potentials of *m*-MTDATA, *m*-MTDAPB and Alq_3 are 5.1, 5.7 and 5.8 eV, respectively, as determined with a surface analyzer.

An EL device consisting of a single hole-transport layer of *m*-MTDAPB and an emitting layer of Alq_3, ITO/*m*-MTDAPB(450Å)/Alq_3(500Å)/MgAg (Type A), and a device consisting of double hole-transport layers of *m*-MTDATA and *m*-MTDAPB, ITO/*m*-MTDATA(300 Å)/*m*-MTDAPB(200 Å)/Alq_3(500 Å)/MgAl (Type B), were fabricated. Figure 1 shows the structures of the EL devices fabricated. The type B

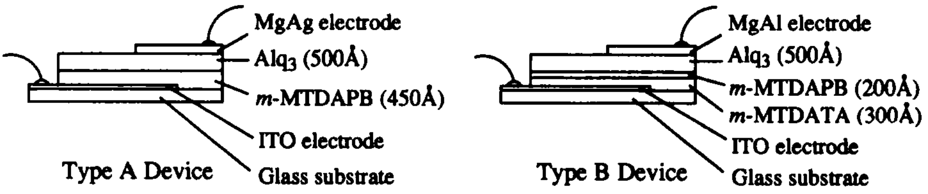


FIGURE 1 The structures of EL devices.

device was fabricated in view of diminishing energy barrier for hole injection from the ITO electrode directly into the *m*-MTDAPB layer.

Both devices emitted bright green light when a positive voltage was applied to the ITO electrode. The electroluminescence spectrum was in agreement with the photoluminescence spectrum of Alq_3. It is indicated that the recombination of holes injected from the ITO electrode through the hole-transport layer and electrons injected from the MgAg or MgAl electrode takes place in the Alq_3 layer to generate a singlet exciton of Alq_3, which emits fluorescence.

Figure 2 shows the voltage - injected current density characteristics of the EL devices fabricated. The injected current density - luminance characteristics of the devices are shown in Figure 3. The emission started at a voltage of *ca.* 6V. Maximum luminances of 16,600 and 16,900 cd m^{-2} were obtained at driving voltages of 17 and 16V for the type A and type B devices, respectively. The driving voltage for obtaining a luminance of 300 cd m^{-2} was 9.2 and 7.3V for the type A and type B devices, respectively. The luminous efficiencies of the type A and Type B devices were 1.3 and 1.9 lm W^{-1} at a luminance of 300 cd m^{-2}, respectively.

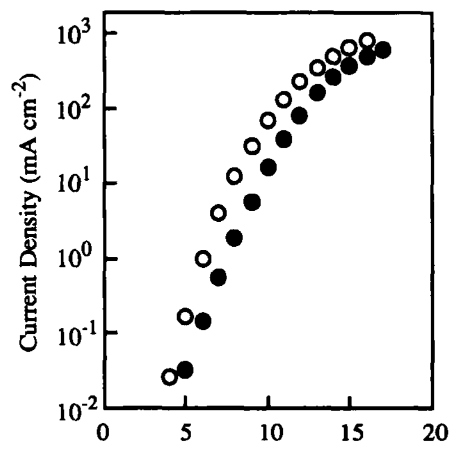


FIGURE 2 Voltage - injected current density characteristics of the EL devices.
●: Type A device
○: Type B device

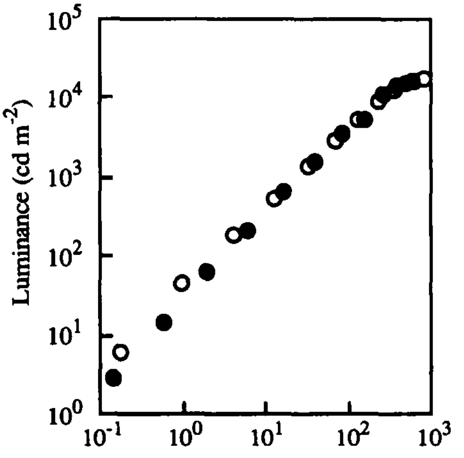


FIGURE 3 Injected current density - luminance characteristics of the EL devices.
●: Type A device
○: Type B device

The performances of the present devices using the starburst molecules, *m*-MTDAPB and *m*-MTDATA, as hole-transport materials are more or less similar to those of the device using TPD, which has been reported to be an excellent hole-transport material, as a single hole-transport layer and Alq_3 as an emitting layer.[30] However, the device consisting of a single hole-transport layer of TPD and Alq_3 as an emitting layer often stops emission during the continuous operation at constant current and undergoes deterioration when the temperature rises to *ca.* 60 °C.[31] The morphological and thermal instability of TPD may be responsible for this.[18] The present starburst molecules, *m*-MTDAPB and *m*-MTDATA, are thermally and morphologically more stable than TPD. It is expected that starburst molecules based on π-electron systems may be promising candidates for materials for use in organic EL devices.

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