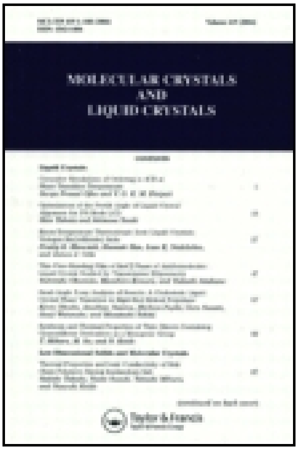

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Electrically Conducting Amorphous Molecular Material: Iodine Doped m-MTDATA as a Hole Injection Buffer Layer in Organic Electroluminescent Devices

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An electrically conducting amorphous molecular material was prepared by iodine doping of 4,4′,4″-tris[3-methylphenyl(phenyl)amino]triphenylamine (m-MTDATA). The use of iodine-doped m-MTDATA, which was identified as m-MTDATA radical cation species with counter anions, as a hole-injection buffer layer in tris(8-quinolinolato)aluminum (Alq_3)-based organic electroluminescent devices led to the reduction of drive voltage and the enhancement of external quantum efficiency as compared with the corresponding device using undoped m-MTDATA. It is indicated that the use of iodine-doped m-MTDATA facilitates not only hole injection from the ITO electrode but also electron injection from the cathode into Alq_3.

Keywords: amorphous molecular material; charge injection; electrical conductivity; iodine doping; m-MTDATA; organic electroluminescent device

INTRODUCTION

Amorphous glasses of small organic molecules have been receiving growing attention in recent years. Since the late 1980's, we have

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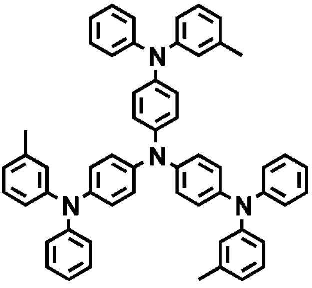
performed a series of studies of the creation of small organic molecules that readily form stable amorphous glasses, amorphous molecular materials [1,2]. In addition, we have proposed several novel concepts for photo- and electroactive organic materials, which include electrically conducting amorphous molecular materials [3,4], photochromic amorphous molecular materials [5], amorphous molecular resists [6], and materials for electronic and photonic devices [1,2]. Amorphous molecular materials have found successful application as materials for use in organic electroluminescent (EL) devices.

Electrically conducting amorphous molecular materials, which constitute a new class of organic conductors, are expected to serve as molecular solders in electronic devices and as charge-injection materials that facilitate charge injection from electrodes in organic EL devices. We report here the preparation of an electrically conducting amorphous molecular material by iodine doping of 4,4′,4″-tris[3-methylphenyl(phenyl)amino]triphenylamine (m-MTDATA), characterization of the doped material, and its application as a hole-injection buffer layer in organic EL devices [7,8].



m-MTDATA

Charge injection from electrodes in organic EL devices, which is one of the key factors that determine the luminous and external quantum efficiencies, is greatly affected by the relative energy levels of the electrode work function and the HOMO/LUMO energy levels of the adjacent organic layer. Several methods for realizing efficient charge injection from electrodes have been reported. The insertion of a thin LiF layer between the Al electrode and an adjacent organic layer enhances electron injection from the cathode [9,10]. The adsorption of polar molecules, e.g., phosphoric and phosphonic acid derivatives, on the surface of the ITO electrode enhances hole injection from the ITO electrode into the hole-transporting layer [11,12]. The use of amorphous molecular materials of the tris(diphenylamino)triphenylamine (TDATA) family, e.g., m-MTDATA [13] and 4,4′,4″-tris(1- or 2-naphthylphenylamino)triphenylamine [14], which are characterized by very low solid-state ionization potentials of ca. 5.1 eV and good quality of their amorphous films, as a hole-injection buffer layer facilitates hole injection from the ITO electrode in organic EL devices [14–16]. The present study shows that the use of iodine-doped m-MTDATA as a hole-injection layer in a tris(8-quinolinolato)aluminum (Alq_3)-based organic EL device enhances the external quantum efficiency as well as reducing the drive voltage.

EXPERIMENTALS

Iodine Doping of m-MTDATA

m-MTDATA was prepared according to the method described in our previous paper [13]. Iodine doping of m-MTDATA was performed either by exposure of the vacuum-deposited amorphous film of m-MTDATA to iodine vapor in a closed vessel at room-temperature for 46 h, followed by the removal of the excess iodine at 10^{-1} Pa for 5 h or by dissolving m-MTDATA and iodine with a molar ratio of 2:1 in dichloromethane, followed by spin coating. The compositions of the resulting doped materials were determined by elemental analysis.

Measurements

Electrochemical oxidation of m-MTDATA was carried out for dichloromethane solution containing tetra-n-butylammonium perchlorate (0.1 mol dm^{-3}) at 0.2 V vs. Ag/Ag^+ reference electrode using a thin-layer spectroelectrochemical cell (ca. 0.2 mm thick) with an ITO-coated glass as the optical transparent electrode and a platinum wire as the counter electrode. Electrical conductivity was measured by a two-probe d.c. method for the pressed pellets (thickness: 260–270 μm) of iodine-doped m-MTDATA powders. Gold was vacuum-deposited onto the pellets to make electrodes. The activation energy for electrical conduction was determined in a temperature range from 200 to 300 K.

Fabrication of Organic EL Devices

The spin-coated films (thickness: 420 nm) of undoped and iodine-doped m-MTDATA were prepared on a cleaned ITO-coated glass substrate at a spinning rate of 3,000 rpm at room temperature using dichloromethane solution of undoped or iodine-doped m-MTDATA, followed by immediate drying at 10^{-5} Pa for 1 h to evaporate any residual solvent. Then, the thin films of N,N′-diphenyl-N,N′-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD) and Alq_3 were successively vacuum deposited onto the undoped or iodine-doped m-MTDATA film at a deposition rate of $2 \sim 3\,Å\,s^{-1}$ at 10^{-5} Pa, followed by vacuum deposition of an alloy of magnesium and silver (atomic ratio 10:1) by simultaneous evaporation from two separated sources. Likewise, hole-only and electron-only devices were fabricated.

RESULTS AND DISCUSSION

Characterization of Iodine-doped m-MTDATA

Iodine-doped m-MTDATA was characterized by X-ray diffraction (XRD), electronic and FT-IR absorption, ESR, and Raman spectroscopy. The XRD patterns of iodine-doped m-MTDATA powders exhibited only broad halos as observed for undoped m-MTDATA, indicating that iodine-doped m-MTDATA also retains the amorphous state. Figure 1 shows the electronic absorption spectra of undoped and iodine-doped m-MTDATA films and electrochemically oxidized m-MTDATA in solution. The iodine-doped m-MTDATA film showed new absorption bands peaking at 440 and 1180 nm, which are attributed

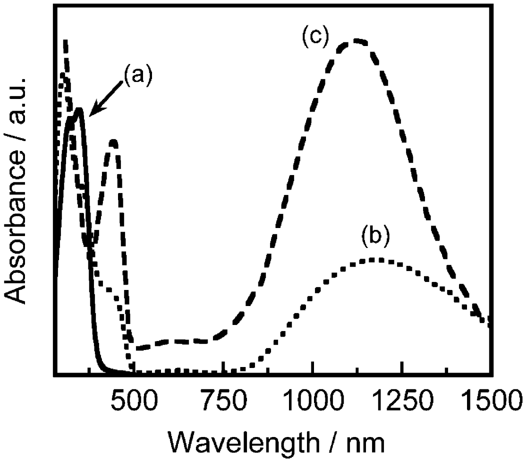


FIGURE 1 Electronic absorption spectra of m-MTDATA. (a) Amorphous glass sample obtained by vacuum vapor deposition. (b) Iodine-doped amorphous glass sample obtained by exposure to iodine vapor. (c) Electrochemically-oxidized m-MTDATA in CH_2Cl_2 at 200 mV vs. Ag/Ag^+ (0.01 mol dm^{-3}).

to m-MTDATA radical cation species by comparison with the spectrum of the m-MTDATA radical cation species obtained by the anodic oxidation of m-MTDATA in dichloromethane solution, which showed absorption bands with peaks at 440 and 1120 nm. The ESR spectrum of iodine-doped m-MTDATA measured at room temperature exhibited a signal with a line width of about 6 G and a g-value of 2.004, indicating that the iodine-doped m-MTDATA possesses unpaired electrons originating from the radical cation. The new absorption band at 1163 cm^{-1} in the FT-IR spectrum of iodine-doped m-MTDATA is ascribed to the C-N asymmetric stretching vibration of m-MTDATA radical cation, which is in agreement with the molecular orbital calculations on triphenylamine and its radical cation [17]. The Raman spectrum of iodine-doped m-MTDATA showed two scattering bands at 166 and 111 cm^{-1}, which are ascribed to the I-I symmetric stretching vibration of the I_5^- and I_3^- units, respectively [18,19]. From the results described above, the iodine-doped m-MTDATA was identified as the m-MTDATA radical cation salt with the counter anions of I_3^- and I_5^-.

A sample of iodine-doped m-MTDATA, (m-MTDATA)$I_{0.96}$, obtained from a solution of m-MTDATA and iodine, exhibited a room-temperature conductivity of 7.3×10^{-7} Scm^{-1} with an activation energy of 0.22 eV.

Effect of Iodine Doping on Charge Injection and Device Performance

Organic EL devices using doped hole-transport layers, e.g., TDATA [20] and m-MTDATA [21] doped with tetrafluorotetracyanoquinodimethane and N,N′-dinaphthyl-N,N-diphenylbendizine doped with $FeCl_3$ [22], have recently been reported. The discussion has been focused on the enhancement of hole injection and the reduction of drive voltage. We have studied the effect of iodine-doping of m-MTDATA on charge injection and device performance on the basis of the information obtained from the J-V characteristics of hole-only and electron-only devices [7,8]. In the present study, a thick layer of 420 nm was used for the m-MTDATA hole-injection layer.

As Figure 2 shows, the J-V characteristics of hole-only devices, ITO/undoped or iodine doped m-MTDATA (420 nm)/TPD (30 nm)/Ag, and an electron-only device consisting of a single Alq_3 layer (90 nm) sandwiched between Mg and MgAg electrodes showed that the hole current in the hole-only device using undoped m-MTDATA was approximately four orders of magnitude larger than the electron current in the electron-only device at an applied electric field of 2×10^5 V cm^{-1}, and that the hole current density of the device using

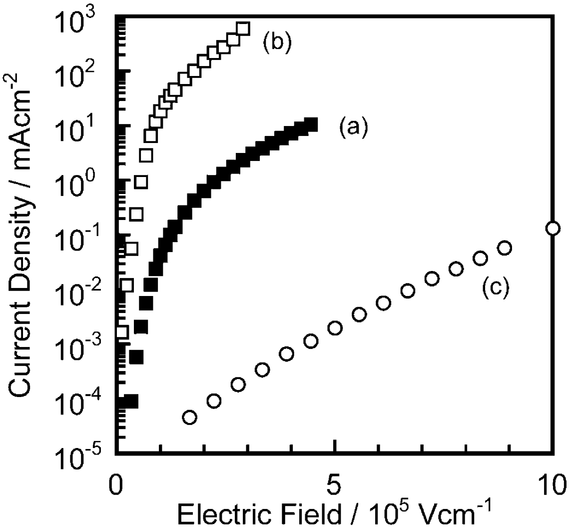


FIGURE 2 Current density – applied electric field characteristics of hole-only device based on m-MTDATA (420 nm)/TPD (30 nm). (a) undoped m-MTDATA, (b) iodine-doped m-MTDATA, and (c) electron-only device using Alq_3(90 nm).

iodine-doped m-MTDATA was approximately two to three orders of magnitude greater than that of the device using undoped m-MTDATA at an applied electric field of 1×10^{5} Vcm^{-1}. These results implied that the major charge carriers injected from the electrodes in organic EL devices consisting of the three layers of m-MTDATA, TPD and Alq_3 are holes, and that the hole current is significantly enhanced by the use of iodine-doped m-MTDATA as the hole-injection buffer layer.

Figure 3 shows the current density – applied voltage – luminance characteristics for organic EL devices, ITO/undoped or iodine-doped m-MTDATA (420 nm)/TPD (30 nm)/Alq_3 (90 nm)/MgAg. The device using iodine-doped m-MTDATA as a hole-injection buffer layer exhibited approximately one order of magnitude larger injected current density and significantly higher luminance than the device using undoped m-MTDATA at an applied voltage of 10 V. The device using iodine-doped m-MTDATA resulted in the reduction of drive voltage relative to the device using undoped m-MTDATA; the turn-on voltages for obtaining a luminance over 1 cd m^{-2} were 7.7 and 4.5 V, and the drive voltages for obtaining a luminance of 300 cd m^{-2} were 20.2 and 8.8 V for the devices using undoped and iodine-doped m-MTDATA, respectively.

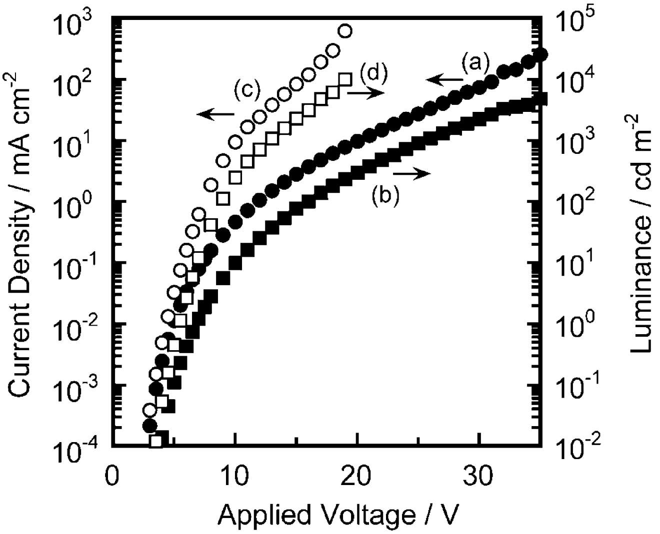


FIGURE 3 Current density – applied voltage and luminance – applied voltage characteristics of ITO/m-MTDATA (420 nm)/TPD (30 nm)/Alq$_3$(90 nm)/MgAg devices. (a) and (b) Undoped m-MTDATA; (c) and (d) Iodine-doped m-MTDATA.

The device using iodine-doped m-MTDATA as the hole-injection buffer layer exhibited an external quantum efficiency of 0.95% at an applied voltage of 10 V, which was approximately twice that of the device using undoped m-MTDATA. The higher luminance and the improved external quantum efficiency at the same applied voltage for the device using iodine-doped m-MTDATA results from the increase in the number of recombined charge carriers and better charge balance relative to the device using undoped m-MTDATA. Since hole carriers are dominant even for the device using undoped m-MTDATA, the results of the enhanced performance strongly suggest that not only hole injection from the ITO electrode but also electron injection from the MgAg cathode into the Alq$_3$ layer is facilitated when iodine-doped m-MTDATA is used. The enhanced electron injection by the use of iodine-doped m-MTDATA is explained as being due to the formation of a steeper electric field in the Alq$_3$ layer. That is, the increased conductivity of the m-MTDATA layer leads to a reduced electric-field strength in the bulk of the m-MTDATA layer but instead to a steeper electric field in the Alq$_3$ layer, and hence, enhanced electron injection from the cathode into the emitting layer takes place. The present results show that increasing the electrical conductivity of the hole-transport layer is one of the effective methods for enhancing not only hole injection from the anode but also electron injection from the cathode, leading to the higher performance of organic EL devices.

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