New Hole-Transporting Amorphous Molecular Materials with High Glass-Transition Temperatures for Organic Light-Emitting Diodes

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New hole-transporting amorphous molecular materials with high glass-transition temperatures (Tgs), 4,4',4''-tris[9,9-dimethyl-2-fluorenyl(phenyl)amino]triphenylamine (TFATA) and *N,N,N',N'*-tetrakis(9,9-dimethyl-2-fluorenyl)-[1,1'-biphenyl]-4,4'-diamine (FFD), have been developed. TFATA and FFD exhibit hole drift mobilities of 1.7×10^{-5} and 4.1×10^{-3} $cm^2V^{-1}s^{-1}$, respectively, at 293 K at an electric-field of 1.0×10^5 Vcm^{-1} in their amorphous glasses. These materials permit the fabrication of thermally stable, high-performance organic light emitting diodes.

The thermal stability and the operational durability of organic light-emitting diodes (OLEDs) are the crucial issues for their practical use in flat panel displays, in particular for loading in cars. Both charge-transporting and emitting materials with high performance and high glass-transition temperatures (Tgs) should be developed to solve this problem.

With regard to low molecular-weight organic materials, tris(8-quinolinolato)aluminum (Alq_3)[1] and *N,N'*-bis(3-methylphenyl)-*N,N'*-diphenyl-[1,1'-biphenyl]-4,4'-diamine (TPD)[2,3] have been most widely used as green emitting and hole-transporting materials, respectively. TPD, however, lacks both thermal and morphological stability, and hence, the double-layer device consisting of an Alq_3 emitting layer and a TPD hole-transport layer lacks operational durability.

We have created a novel hole-transporting amorphous molecular material, 4,4',4''-tris[3-methylphenyl(phenyl)amino]-triphenylamine (*m*-MTDATA),[4] and shown that the multilayer OLEDs consisting of an Alq_3 emitting layer and double hole-transporting layers, with *m*-MTDATA used as hole-transport layer 1 (HTL1) in contact with the ITO electrode and TPD or other materials as HTL2 (Figure 1), exhibit higher luminous efficiency and significantly enhanced operational durability than the double-layer device consisting of the Alq_3 emitting layer and the hole-transport layer of TPD or other materials.[5] *m*-MTDATA, which is characterized by a very low solid-state ionization potential of 5.0–5.1 eV and good amorphous film quality, plays the role of facilitating hole injection from the ITO electrode. The multilayer device such as shown in Figure 1 has since been widely used.

Although TPD (Tg = 62 °C) and *m*-MTDATA (Tg = 75 °C) are excellent hole-transporting materials for use in HTL2 and HTL1, respectively, enhancement of thermal stability remains to be solved in order to fabricate thermally more stable OLEDs. The thermal stability of a recently developed TPD derivative, *N,N'*-bis(1-naphthyl)-*N,N'*-diphenyl-[1,1'-biphenyl]-4,4'-diamine (α-NPD)[6] (Tg = 95 °C), is not satisfactory, either.

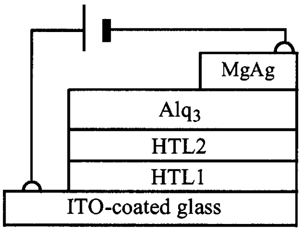
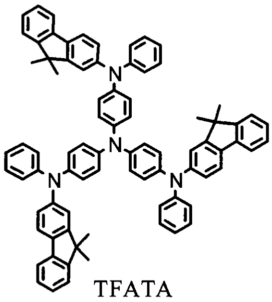


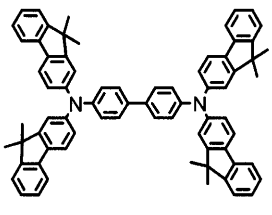
Figure 1. Side view of a multilayer OLED.

We report here new hole-transporting amorphous molecular materials with high Tgs for HTL1 and HTL2, 4,4',4''-tris[9,9-dimethyl-2-fluorenyl(phenyl)amino]triphenylamine (TFATA) and *N,N,N',N'*-tetrakis(9,9-dimethyl-2-fluorenyl)-[1,1'-biphenyl]-4,4'-diamine (FFD). We expected that the incorporation of a rigid fluorene moiety increases Tg without significantly affecting the oxidation potentials of the parent compounds, *m*-MTDATA and TPD.

TFATA was synthesized by the Ullmann reaction of *N*-phenyl-9,9-dimethyl-2-fluorenylamine with tris(4-iodophenyl)-amine in mesitylene in the presence of copper powder and potassium hydroxide (Yield: 22%). FFD was synthesized by the Suzuki coupling reaction of *N,N*-bis(9,9-dimethyl-2-fluorenyl)-4-bromoaniline with 4-[*N,N*-bis(9,9-dimethyl-2-fluorenyl)amino]phenylboronic acid in tetrahydrofuran in the presence of tetrakis(triphenylphosphine)palladium(0) (Yield: 46%). Both compounds were purified by silica-gel column chromatography, followed by recrystallization from toluene/hexane, and identified by various spectroscopic methods, mass spectrometry, and elemental analysis.[7]



TFATA



FFD

TFATA and FFD were found to readily form stable amorphous glasses with Tgs of 131 °C and 165 °C, respectively, as determined by differential scanning calorimetry. They also form uniform amorphous films by vacuum deposition.

The anodic oxidation processes of TFATA and FFD were reversible. The half-wave oxidation potentials of TFATA and FFD were 0.08 and 0.40 V vs Ag/Ag^+ (0.01 mol dm^{-3}), respectively. The oxidation potentials of TFATA and FFD are more or less similar to those of *m*-MTDATA (0.06 V vs Ag/Ag^+) and TPD (0.48 V vs Ag/Ag^+).

The hole drift mobilities of TFATA and FFD in their amorphous glassy states were determined to be 1.7×10^{-5} and $4.1 \times$

10^{-3} $cm^2V^{-1}s^{-1}$, respectively, by the time-of-flight method. FFD exhibits very high hole drift mobility among amorphous organic materials.

A multilayer OLED, ITO/TFATA(300 Å)/FFD(200 Å)/ Alq_3(500 Å)/MgAg, was fabricated by sequential vacuum deposition of TFATA, FFD and Alq_3 onto an ITO-coated glass substrate at a deposition rate of 2–3 Å s^{-1} at 10^{-5} Torr. Subsequently magnesium and silver (ca 10:1 in volume ratio) were co-deposited as an alloy onto the organic layer by simultaneous evaporation from two separated sources. The emitting area was ~4 mm^2. For the measurement of thermal stability of the OLED, the device was placed in a cryostat at 10^{-1} Torr and heated to each given temperature and maintained at that temperature for 10 min, and then the constant current needed to obtain the luminance of 300 cd m^{-2} at 25 °C was applied to the device to measure the luminance at each temperature. The temperature was controlled by a temperature controller (Oxford ITC502).

The fabricated multilayer OLED 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. The emission started at a driving voltage of 3.0 V. The device exhibited a maximum luminance of 12100 cd m^{-2} at 12 V with a luminous efficiency of 0.9 lmW^{-1} at a luminance of 300 cd m^{-2}. The performance is similar to that of the device using *m*-MTDATA and α-NPD as the double hole-transporting layers and Alq_3 as the emitting layer.

Figure 2 shows the temperature dependence of the luminance for the device. Although the luminance decreased slightly with increasing temperature due to the drop in the fluorescent quantum efficiency of Alq_3 with rising temperature, the device was found to operate even at 170 °C, retaining a luminance of 70% of the initial value at 25 °C. When the device was cooled down to room temperature after being heated to 170 °C, it worked as before. This device contrasts with the double-layer device using TPD as a hole-transporting material and Alq_3 as an emitting material, which does not work at temperatures above ca. 65 °C.

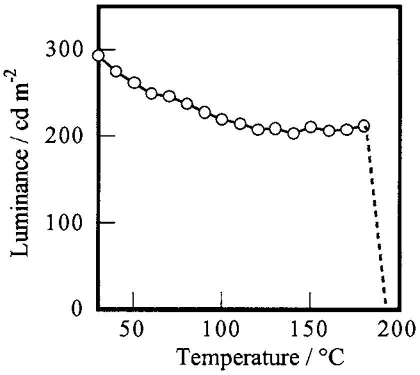


Figure 2. Temperature dependence of the luminance for ITO/TFATA(300A)/FFD(200A)/Alq_3(500A)/MgAg.

Both TFATA and FFD are potential candidates for practical use, serving as materials for HTL1 and HTL2, respectively, in multilayer OLEDs.

In summary, the new hole-transporting amorphous molecular materials with high Tgs for HTL1 and HTL2 in multilayer OLEDs TFATA and FFD were designed and synthesized. It is shown that the introduction of a fluorene moietiy is an effective strategy for achieving high Tg. FFD is characterized by very high hole drift mobility. These materials permitted the fabrication of a thermally stable, high-performance OLED that operates even at 170 °C. The developed materials are expected to be promising candidates for practical use.

References and Notes

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7 TFATA: MS: *m/z* 1094(M^+). Anal.: Found: C, 88.80; H, 6.32; N, 4.90%. Calcd for $C_{81}H_{66}N_4$: C, 88.81; H, 6.07; N, 5.11%. ^1H NMR (THF-d_8): δ (ppm) 7.63 (3H, d), 7.59 (3H, d), 7.37 (3H, d), 7.27–7.16 (15H, m), 7.09 (6H, d), 7.07–6.99 (15H, m), 6.93 (3H, t), 1.38 (18H, s).
FFD: MS: *m/z* 952(M^+). Anal.: Found: C, 90.69; H, 6.49; N, 3.01%. Calcd for $C_{72}H_{60}N_2$: C, 90.72; H, 6.34; N, 2.94%. ^1H NMR (THF-d_8): δ (ppm) 7.66 (4H, d), 7.64 (4H, d), 7.58 (4H, d), 7.40 (4H, d), 7.32 (4H, s), 7.26 (4H, t), 7.23–7.19 (8H, m), 7.09 (4H, d), 1.40 (24H, s).