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Effects of Hole Transport Layers on the Characteristics of Organic Light Emitting Diodes

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Abstract

In this paper, we examine the properties of two series of hole transport materials. One is FTPD, having triphenylamine and fluorene structure. The FTPDs have high glass transition temperatures above 80°C because of their rigid fluorene moiety. The ionization potentials (Ips) of the FTPDs were correlated with the Hammett constants of the substituents of the FTPDs. The driving voltages of the double layer organic light emitting diodes (LEDs) fabricated with FTPDs and tris(8-quinolinolato) aluminum complex (Alq₃) were affected by the Ips of the FTPDs. The other is OTPAC, which has a triphenylamine oligomeric structure that improves thermal stability further. The glass transition temperatures of the OTPACs are higher than those of the FTPDs. The driving voltages of the double layer LEDs fabricated with OTPACs and Alq₃ were lower than those of the devices with FTPDs, and they have no relationship to the Ips of the OTPACs. It is likely that the morphological character of the hole transport layers mainly affects the performance of the LEDs in the case of the OTPACs.

Key-words: *Organic light emitting diodes, Hole transport materials, Triphenylamine derivatives, Glass transition temperatures, Ionization potentials*

1. Introduction

Research on organic light emitting diodes (LEDs) has attracted considerable attention since Tang and VanSlyke first reported an organic LED with high luminance (1000 cd/m²) and low driving voltage (under 10 V)^{1,2)}. They fabricated a double layer device which is composed of a hole transport layer used for the

transport of holes and an emitting layer used for both the transport of electrons and the emission of light.

It has been reported that triphenylamine derivatives are very useful as hole transport materials for organic LEDs³⁻⁷⁾. *N,N'*-diphenyl-*N,N'*-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) is one of the best compounds in the class of triphenylamine derivatives. However, TPD readily crystallizes during operation because of Joule's heat generated by electric resistance^{8,9)}. It is well known that the morphological change of an amorphous film begins occurring at around glass transition

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temperature (T_g). Therefore, a material which has high T_g is necessary for the thermal stability of the organic LED. In addition, the material should possess a suitable ionization potential (I_p) and electron affinity in order to match the energy levels at the interfaces between the electrode and the organic material in the charge carriers injection process.

In the present study, we investigated the properties of two series of hole transport materials, FTPDs and OTPACs. FTPDs are expected to have high glass transition temperatures because of the rigid fluorene moiety¹⁰. FTPDs with various I_p s can be designed by changing the substituents on the phenyl rings, according to Hammett's law¹¹. The OTPACs are the oligomers of triphenylamines connected through cyclohexanes or methylcyclohexanes. These structures are presumed to have high glass transition temperatures and to be morphologically stable. The physical properties and the characteristics of the double layer organic LEDs based on FTPDs and OTPACs were evaluated in detail.

2. Experimental

All organic materials were synthesized and purified in our laboratory. The FTPDs (**Fig. 1**) were synthesized by the Ullmann reaction of 9,9-bis(4-aminophenyl)fluorene with iodobenzene derivatives, and recrystallized from acetic acid or acetonitrile / methanol solution. OTPACs were synthesized by reaction of triphenylamine derivatives with cyclohexanone or methylcyclohexanone in the presence of methanesulfonic acid at 100°C for 20 hours in glacial acetic acid under a nitrogen atmosphere. Tris(8-quinolinolato) aluminum complex (Alq_3) was synthesized by the conventional method¹². FTPDs and Alq_3 were purified using a train-sublimation technique. Molecular weights of OTPACs were measured by FD-MS using a HITACHI M2000.

Thermal properties were determined with

differential scanning calorimetry (DSC) using a TA Instruments DSC2910 thermal analyzer. The ionization potentials were measured using a Riken Keiki AC-1 photoelectron emission spectrometer in dry air at room temperature. The energy gap was estimated from the lower energy threshold of the electronic absorption spectrum. Electronic absorption spectra were measured using a Hitachi U-3500 spectrophotometer. Oxidation potentials were measured with conventional cyclic voltammetry in a mixture of CH_3Cl : CH_3CN ($v/v=1:4$) containing 0.1 mol/dm³ tetrabutylammonium perchlorate.

The organic light emitting diode devices were fabricated using a vacuum deposition technique. The O1 device fabrication using a dip coating method was also tried with a 1 wt% chloroform solution and a 100 mm/min drawing rate. The device structure was: anode / hole transport layer (HTL) / Alq_3 (emitting layer) / cathode, where FTPDs and OTPACs were used as an HTL. The organic materials were coated onto an ITO coated glass substrate, and an Mg: Ag alloy (10: 1, atomic ratio) layer was deposited on an Alq_3 layer by simultaneous evaporation to form the

FTPDs

FTPDs	R_1
F1	4-OCH ₃
F2	4- <i>iso</i> -C ₃ H ₇
F3	4-CH ₃
F4	3-OCH ₃
F5	3-CH ₃
F6	H
F7	2-CH ₃

OTPACs ($n=1\sim4$)

OTPACs	R_2	R_3
O1	4-CH ₃	H
O2	4-CH ₃	CH ₃
O3	3-CH ₃	H
O4	3-CH ₃	CH ₃
O5	4-OCH ₃	H

Fig. 1 Molecular structures of hole transport materials.

cathode. The emitting area of the device was 4 mm². The thickness of the organic layers was fixed at 50 nm. Luminance was measured with a Minolta LS-110 luminance meter.

3. Results and Discussion

3.1 Material properties and device characteristics of the FTPDs

3.1.1 Material properties

Every FTPD showed higher T_g compared to TPD (63°C) (Table 1), which is expected from the rigidity of the fluorene moiety. Since Alq₃ has high T_g (about 170°C), the thermal stability of the two layer LED with Alq₃ depends on the T_g of the hole transport material⁷⁾. Therefore, the LEDs fabricated with FTPDs are presumed to be thermally stable.

It is known that the I_p values of hole transport materials are related to the Hammett constants of the substituents¹¹⁾. We designed seven FTPDs with various I_ps, using Hammett's law, to investigate the influence of the hole injection barrier height on the performance of the organic LEDs. Table 1 shows the properties of FTPDs, e.g., oxidation potentials, ionization potentials, etc., compared with the Hammett constants (σ^+) of the substituents of the FTPDs. The data in Table 1 indicate good correlation among the oxidation potentials, I_ps, and the Hammett constants. We obtained FTPDs having I_ps from 5.42 eV to 5.

80 eV by changing the substituents.

3.1.2 Device characteristics

Double layer organic LEDs with FTPDs as the hole transport layer and Alq₃ as the emitting layer were fabricated. Each device was confirmed to emit green luminescence, and the emission maximum wavelength was 510 nm. The luminescence originates from the excited singlet state of Alq₃, the state which is generated through the recombination of holes and electrons. Table 2 shows the characteristics of the LEDs with FTPDs. A maximum luminance over 10,000 cd/m² was obtained for each device, except for F6 and F7. This indicates that the FTPD layer, like TPD, can transport holes which are injected from the ITO to the Alq₃ layer and block the electrons injected from the Alq₃ layer.

The applied voltage necessary to generate 1 cd/m² increased and the luminance at 8 V decreased with increasing I_ps of the HTLs except for F6 (Fig.2). High driving voltage and low maximum luminance of the device with F6 might be due to the polycrystallization of the thin film. In the case of FTPDs, the energy barrier between the inorganic electrode (ITO, whose work function is 4.95 eV) and the organic layer (HTL) is larger than that between HTL and Alq₃ (5.87 eV), since the FTPDs have I_ps in the range of 5.42 - 5.80 eV. Therefore, the influence of the energy barrier

Table 1 Glass transition temperatures, Hammett constants of the substituents, oxidation potentials, ionization potentials and energy gaps of the FTPDs

FTPDs	T _g (°C)	Hammett constant (σ^+)	Oxidation potential (V)	Ionization potential (eV)	Energy gap (eV)
F1	102.8	-0.778	+0.72	5.42	3.49
F2	117.9	-0.280	+0.86	5.52	3.51
F3	85.4	-0.311	+0.89	5.63	3.52
F4	80.2	0.047	+0.92	5.67	3.56
F5	102.7	-0.066	+0.97	5.66	3.54
F6	111.1	0	+0.99	5.73	3.56
F7	112.5	a)	+1.03	5.80	3.68

a) The value is not available for 2-substituent.

Table 2 The characteristics of the double layer organic LEDs with FTPDs

FTPDs	Voltage for 1cd/m ² (V)	Luminance at 8V (cd/m ²)	Maximum luminance (cd/m ² (V))	Luminous efficiency (cd/A)
F1	3.93	340	9700(12)	1.99
F2	5.24	84	11100(12)	1.97
F3	4.98	60	10100(14)	2.06
F4	5.81	22	12600(13)	2.10
F5	6.01	29	14800(12)	2.17
F6	9.29	1.28	6400(13)	1.85
F7	6.53	12	6900(12)	2.18

Fig. 2 The dependence of the voltage for 1cd/m² (■) and the luminance at 8V (○) on the ionization potential for the double layer organic LEDs with FTPDs.

between ITO and HTL is important and the driving voltages of the devices depends on the Ips of the FTPDs.

3.2 Material properties and device characteristics of the OTPACs

3.2.1 Material properties

OTPACs are oligomeric triphenylamines connected through cyclohexanes or methylcyclohexanes. Every OTPAC is a mixture of trimer to hexamer and has a molecular weight distribution. The molecular weights of OTPACs were confirmed by the FD-MS spectra.

Table 3 shows the glass transition temperatures, oxidation potentials, ionization potentials, energy gaps, and lowest unoccupied molecular orbital (LUMO) levels of the

OTPACs. OTPACs have higher glass transition temperatures compared to FTPDs. Especially, O1, O2 and O5 which have 4-CH₃ or 4-OCH₃ substituents at R₁ positions show Tg values over 120°C. Accordingly, the devices with OTPACs are presumed to be thermally more stable than those of FTPDs. Every OTPAC has similar oxidation potential and ionization potential except for O5. Introduction of donor substituents such as 4-OCH₃ lowered the oxidation potentials and the ionization potentials in the cases of both FTPDs and OTPACs.

3.2.2 Device characteristics

The double layer LEDs with OTPACs as an HTL and Alq₃ as an emitting layer were fabricated. The characteristics of the LEDs are shown in **Table 4**. It was expected that the driving voltage of the device with O5 would become lower because of its low Ip. On the contrary, the applied voltage necessary to generate 1 cd/m² was lower and the luminance at 8 V higher for the devices with O1 and O2 showing these to have superior performance compared to O5. In addition, the driving voltages of the devices with O3 and O4 were not as low as those of O1 and O2, although O1-O4 have similar Ips. Thus, we conclude that the driving voltages of the devices with OTPACs have no relationship to the Ips.

From the result that the luminous efficiency of O5 was inferior to that of O1-O4, we

assumed that the electron block ability of the HTL might be different for each OTPAC and it affected the performance of the LED. However, the LUMO level of each OTPAC estimated from the energy gap was almost equal (Table 3), and thus the electron block ability on the energy level should be similar.

As another factor, the morphological character of the HTLs was considered. We tried to fabricate the device with O1 using the dip coating method because the morphological character of the film would be different from that obtained from the vacuum deposition technique. The characteristics of the device are shown in Table 4. Although the applied voltage for 1 cd/m² and the luminance at 8 V were inferior to the device fabricated using the vacuum deposition technique, the maximum luminance and the luminous efficiency showed higher values. Since the morphological character of the HTLs changed according to the method used to fabricate the devices, the char-

acteristics of the devices were also different. Although experimental confirmation is needed, there is the possibility that the molecular weight distribution of the film may be different for these two devices and that this difference affects the morphology of the film, because OTPACs are the compounds which are the mixtures of trimer to hexamer. From these results, we conclude that the morphological character of the HTLs may be an important factor affecting the performance of the LEDs in the case of the OTPACs.

4. Conclusion

We studied the properties of two series of hole transport materials, FTPDs and OTPACs. The FTPDs having various I_{ps} could be designed by using Hammett's law. The driving voltages of the double layer LEDs with FTPDs increased with increasing I_p. This effect is attributed to the energy barrier of the hole injection from ITO to HTL. The

Table 3 Glass transition temperatures, oxidation potentials, ionization potentials, energy gaps, and lowest unoccupied molecular orbital (LUMO) levels of the OTPACs

OTPACs	T _g (°C)	Oxidation potential (V)	Ionization potential (eV)	Energy gap (eV)	LUMO level (eV)
O1	129.3	+0.89	5.47	3.54	-1.93
O2	128.2	+0.89	5.45	3.53	-1.92
O3	106.8	+0.93	5.44	3.53	-1.91
O4	119.4	+0.93	5.44	3.54	-1.90
O5	131.7	+0.80	5.36	3.42	-1.94

Table 4 The characteristics of the double layer organic LEDs with OTPACs

OTPACs	Voltage for 1cd/m ² (V)	Luminance at 8V (cd/m ²)	Maximum luminance (cd/m ² (V))	Luminous efficiency (cd/A)
O1	2.83	10600	12100 (9)	2.65
O2	2.92	12400	13200 (9)	2.26
O3	4.42	840	9500(11)	2.12
O4	3.49	2400	10700(10)	2.14
O5	3.18	2400	5100(10)	0.63
O1 ^{b)}	3.39	924	15800(11)	3.40

b) The device was fabricated by a dip coating method.

driving voltages of the LEDs with OTPACs were not correlated with the I_p . The morphological character of the HTL may be different for each OTPAC and it mainly affects the performance of the LEDs.

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有機発光ダイオードの性質に関する正孔輸送層の効果

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要 旨

我々は、トリフェニルアミン誘導体である 2 種類の正孔輸送材料系、FTPD、OTPAC の性質について検討を行った。FTPD は、硬直なフルオレン骨格を有している。FTPD は 80°C 以上のガラス転移温度を持ち、そのイオン化ポテンシャルは、FTPD のフェニル基に置換した置換基のハメット定数と相関があった。FTPD を用いた 2 層型の有機発光ダイオード (LED) の駆動電圧は、FTPD のイオン化ポテンシャルが大きくなるに従って高くなった。OTPAC は、トリフェニルアミンがオリゴマー化した構造を有する。OTPAC のガラス転移温度は、FTPD のそれよりも高かった。有機 LED の駆動電圧は、イオン化ポテンシャルと相関は見られなかったが、FTPD の場合と比べると低くなった。OTPAC については、正孔輸送層のモルフォロジーがデバイスの性能に主として影響を与えていると考えられる。