

Preparation and Characterization of Organic Electroluminescent Devices Using Fluorescent Polyimides as a Light-Emitting Layer

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The electroluminescence (EL) properties of the organic electroluminescent devices (OELDs) using three kinds of fluorescent polyimides, ODPA/DCHM (HFPI-1), 10FEDA/DCHM (HFPI-2), and P2FDA/DCHM (HFPI-3), for light emitting layers were investigated. The HOMO energy levels of HFPI-1 and HFPI-2 were determined as 6.7 and 6.9 eV, respectively, using cyclic voltammetry. Single-layer EL devices having the ITO/HFPI/Al structure were fabricated using HFPI-1 and HFPI-2, but these devices did not exhibit any current and EL properties. This is due to the quite large energy gaps between ITO (work function: 4.7 eV) and the HOMO levels of polyimides (> 2.0 eV). Further, multilayer devices were fabricated using carrier transport materials. For these devices, the carrier injection properties from both electrodes were expected to be improved. However, no current and EL properties were observed for all devices. These experimental facts indicate that fluorescent polyimides have little carrier transportability. The EL properties of the devices using TPD-dispersed fluorescent polyimides as hole transport layers were also investigated. In case of using HFPI-3 whose excitation spectrum is overlapped with the emission of Alq3, the device emits a distinct EL at 520 nm under the operation at 15 V. Further, the emission was displaced to 560 nm under the operation at 30 V, which can be explained by the energy transfer to HFPI-3 or the displacement of the recombination zone of electrons and holes from Alq3 to HFPI-3+TPD layer. This device mechanism might be promising as a novel wavelength-tunable OELD.

Keywords: Polyimide, Organic electroluminescent device (OELD), Wavelength-tunable

1. Introduction

Organic electroluminescent (EL) devices (OELDs) have attracted much interest because of their possible applications such as flat panel displays. Tang and VanSlyke [1] have first demonstrated that a multilayered OELD shows much improved efficiency. Since then, various multilayer devices, fluorescent dyes, and electrode materials have been investigated to improve the efficiency and stability of devices. In addition, since the initial discovery of conjugated polymers, such as poly(phenylene vinylene) (PPV), for emitting layers (EMLs) of OELDs [2], considerable efforts have been focused on polymer OELDs. One of the biggest challenges in producing conformable displays is the development of a low-cost manu-

facturing process. The use of polymer layers allows a low-cost approach, such as ink-jet technology or gravure printing, to the large-area coating of substrates.

Thermal stability is one of the most important requirements for OELD materials because the joule-heat generated during driving may severely relax and damage organic materials with inherently lower thermal stability than inorganic materials or metals. Thermal stability is directly related to the device properties such as current density-voltage-EL intensity (I - V - L) characteristics, EL spectra, and lifetime.

During the past decade, considerable interests have been devoted to aromatic polyimides in response to the increasing technological applications in a vari-

ety of fields, such as the aerospace, automotive industries, interlayer dielectric insulators, alignment layers for liquid crystal displays, and the microelectronics industry, because of their excellent thermal and chemical stabilities, mechanical strength, and good film formability [3].

Fully aromatic polyimides are also known to show fluorescence in the visible region [4,5]. Since the fluorescence generally originates from the charge transfer (CT) excitation and emission mechanisms [6], the quantum yields of the fluorescence observed for conventional polyimides are relatively low due to their strong CT nature. Hence, a limited number of studies are reported for applications of fully aromatic polyimides to EMLs, in which dye-moieties are incorporated in the main chains or dye compounds are doped [7,8]. On the other hand, the present authors and other groups have reported that polyimides can be used as hole transport layers (HTLs) [9-13] or flexible substrates for OLED [14,15].

We have recently predicted that the use of alicyclic diamines efficiently suppresses the CT interaction of polyimides based on density functional theory (DFT) calculations and successfully achieved to synthesize 'highly fluorescent polyimide' [16]. One of them exhibits a fluorescence quantum yield of 0.3 ± 0.05 . These polyimides also have high thermal ($T_g > 200^\circ\text{C}$) and environmental stability. In this study, we made an attempt to apply these polyimides to EMLs in organic EL devices.

2. Experimental

2.1. Materials

The fluorescent polyimides were synthesized from an alicyclic diamine, 4,4'-diaminocyclohexylmethane (DCHM), and three kinds of dianhydrides, 4,4'-oxydiphthalic dianhydride (ODPA), 1,4-bis-(3,4-dicarboxytrifluorophenoxy)tetrafluorobenzene dianhydride (10FEDA), and difluoropyromellitic dianhydride (P2FDA) by the *in situ* silylation method [17] (Fig. 1). ODPA, 10FEDA, and P2FDA were supplied by Nippon Telegraph and Telephone Co., Ltd. (NTT). DCHM was purchased from Tokyo Kasei Kogyo Co., Ltd. The stoichiometric amounts of the dianhydride and diamine were dissolved in anhydrous *N,N*-dimethylacetamide (DMAc) and stirred at room temperature for 48 h for obtaining the respective poly(amic acid) silyl ester (PASE) solutions. The solid contents of the solutions were 15-18 wt%.

A fully aromatic polyimide (PI-4) synthesized from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) (Fig. 1) was used as a binder for *N,N'*-diphenyl-*N,N'*-di(*m*-tolyl)ben-

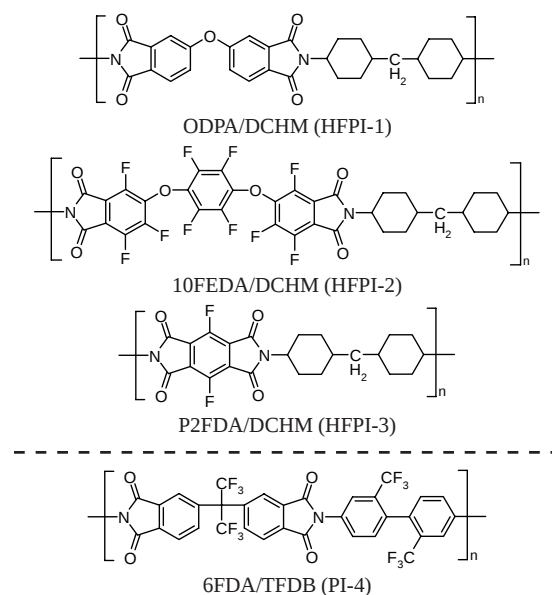


Fig. 1 The chemical structures of the polyimides used in this study.

zidine (TPD), the most popular hole transport material. The synthesis of poly(amic acid) (PAA) solution (15 wt% in DMAc) of 6FDA/TFDB was reported elsewhere [18].

2.2. Device Fabrication

PASE solutions were diluted to 3.5-5.0 wt% in DMAc and spin-coated onto ITO-coated glass substrates at spinning rates of 5000-7000 rpm for 1 min. These samples were dried at 70°C for 1 h, followed by thermal imidization at 300°C for 1 h under nitrogen. The heating rate was $2^\circ\text{C}/\text{min}$. TPD-dispersed PI-4 was used as a thermally stable HTL. Addition of TPD into PASE solution was in a weight ratio of TPD:PASE (repeating unit) = 30:70. The solutions were stirred for 24 h at room temperature before spin-coating. The thicknesses of cured films of EML and HTL were 50-90 nm.

Low molecular-weight compounds and/or metal (aluminum and gold) electrodes were sequentially deposited by thermal evaporation at 2×10^{-5} Torr using a vacuum evaporator (VPC-260, ULVAC KIKO Inc.). TPD and tris(8-hydroxyquinolino)aluminum (Alq3) were used as a HTL and an electron transport layer (ETL), respectively. The thicknesses of the deposited films were 40-50 nm.

2.3. Measurements

The current density-voltage-EL intensity (*I-V-L*) characteristics of the OLEDs were measured using a photomultiplier-tube (Hamamatsu Photonics Co.) and an electrometer (Keithley 6517). UV-Vis absorption spectra were measured with U-3500 spectrophotometer (Hitachi Co., Ltd.). Fluorescence

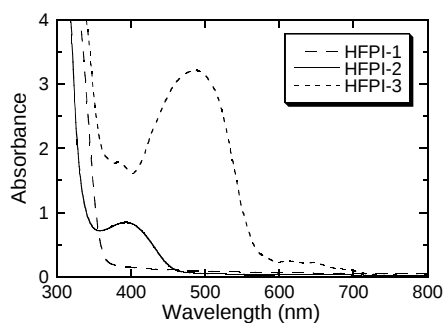


Fig. 2 Absorbance spectra of the highly fluorescent polyimides.

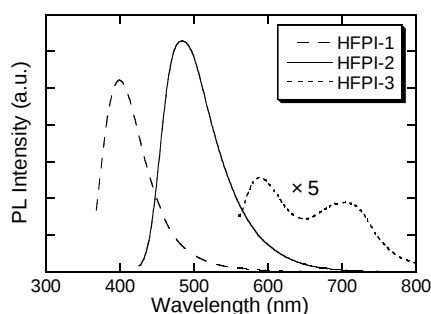


Fig. 3 Fluorescence (PL) spectra of the highly fluorescent polyimides.

(photoluminescence; PL) and EL spectra were obtained with a F-4500 fluorescence photometer (Hitachi Co., Ltd.). Thicknesses of spin-coated and cured thin films were measured using a DekTak-3 surface profiler (Sloan Co., Ltd.). Thicknesses of deposited films were controlled by a quartz crystal deposition controller. The cyclic voltammetry (CV) was carried out using a Pt counter electrode and an Ag/Ag⁺ reference. The electrolyte was 0.1M of tetrabutylammoniumtetrafluoroborate in acetonitrile.

3. Results and Discussion

3.1. Optical and Electrochemical Properties of Fluorescent Polyimide

Fig. 2 shows the UV-Vis absorption spectra of three kinds of fluorescent polyimides (thickness: 10 μm). Characteristic absorption peaks are observed at 390 nm (HFPI-2) and 490 nm (HFPI-3). Their PL spectra are shown in Fig. 3. PL peaks were observed at 400 nm (HFPI-1), 485 nm (HFPI-2), and 580 and 700 nm (HFPI-3). The intensities of the PL peaks of HFPI-1 and HFPI-2 are appreciably strong, whereas that of HFPI-3 is relatively weak though this peak intensity is stronger than that of conventional fully aromatic polyimides (5 times as strong as BPDA/PDA polyimide).

Fig. 4 shows the cyclic voltammograms (oxidation) of HFPI-1 and HFPI-2. In this experiment, PASE solution of each polyimide was measured because

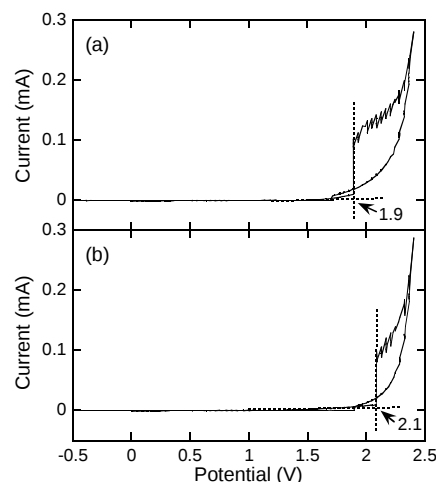


Fig. 4 Cyclic voltammograms (oxidation curves) of (a) HFPI-1 and (b) HFPI-2.

Table 1 Energy levels and band gap energies of the polyimides.

	HFPI-1	HFPI-2
HOMO	6.7 eV	6.9 eV
LUMO	3.3 eV	4.2 eV
Band gap	3.4 eV	2.7 eV

both polyimides are insoluble in any solvents. For HFPI-1 and HFPI-2, the onset of oxidation (E_{ox}) occurred at 1.9 V and 2.1 V, respectively. The energy levels of the polyimides can be estimated from the following equations [8]:

$$\begin{aligned} \text{HOMO} &= 4.8 + E_{\text{ox}} \text{ (eV)} \\ \text{LUMO} &= \text{HOMO} - \text{Band gap (eV)}, \end{aligned}$$

where HOMO and LUMO are the highest occupied and the lowest unoccupied molecular orbitals, respectively. The constant 4.8 is the HOMO energy level of ferrocene relative to the vacuum level [19]. The band gap energies were estimated from the edges of the absorption spectra. The HOMO and LUMO levels for the two polyimides are summarized in Table 1.

3.2. EL Properties

Firstly, single-layer devices having a structure of ITO/HFPI/Al using HFPI-1 and HFPI-2 were fabricated. The dependence of current density and EL intensity on the applied voltage (I - V - L) observed for the OLEDs are shown in Fig. 5. The currents hardly increase as the increase in applied voltage for both polyimides. When the applied voltage was increased to higher than thresholds ((a) 30 V, (b) 40 V), spark due to dielectric breakdown of polyimides was observed. Fig. 6 shows the energy diagrams of these OLEDs. For both polyimides, the hole injection barriers from the anode, which corresponds to the dif-

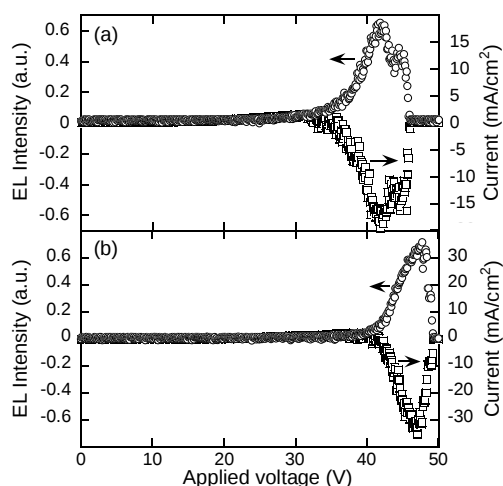


Fig. 5 Current density-voltage-EL intensity (*I-V-L*) characteristics of the single-layer OLEDs using (a) HFPI-1 and (b) HFPI-2.

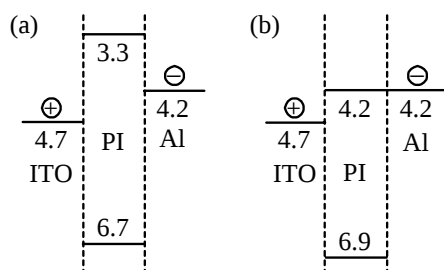


Fig. 6 Energy diagrams of the single layer OLEDs using (a) HFPI-1 and (b) HFPI-2.

ference between the HOMO level and the work function of anode, are larger than 2.0 eV. This clearly indicates that the large barriers make hole injection difficult in the devices having ITO/HFPI/Al structure.

The use of conductors having high work functions as anode is expected to reduce the hole injection barriers. Thus, single-layer devices using Au (work function: 5.1 eV), *i.e.* Au(anode)/HFPI-2/ITO(cathode), were fabricated. In this case, the hole injection barrier was decreased to 1.8 eV, however, spark was also observed when the applied voltage was increased to higher than 25 V (figure is not shown). From the above results, the standard single-layer devices using fluorescent polyimides are unlikely to emit EL.

In most cases, single-layer devices are fabricated for polymer OLED systems [2]. However, multilayer structures using HTLs and/or ETLs were recently adapted to polymer OLED to improve the efficiency of carrier transport and injection [20,21]. TPD (*N,N'*-diphenyl-*N,N'*-di(*m*-tolyl)benzidine) is one of the most popular materials for hole transportation, but the glass transition temperature of TPD deposited in vacuum is 65°C [22], which is much lower than the final curing temperature of polyimide

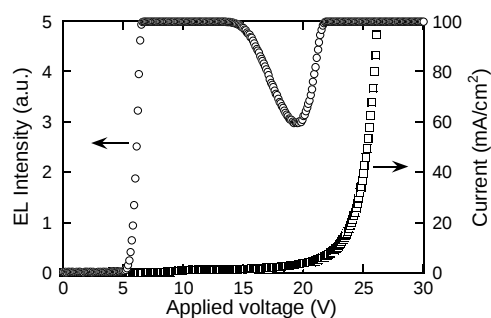


Fig. 7 Current density-voltage-EL intensity (*I-V-L*) characteristics of the device using TPD dispersed PI-4 layer.

Table 2 The structures of multilayer devices.

Device	Anode	HTL	EML	ETL	Cathode
I	ITO	PI-4+TPD	HFPI-1		Al
II	ITO	PI-4+TPD	HFPI-2		Al
III	Au	TPD	HFPI-2		ITO
IV	ITO	PI-4+TPD	HFPI-2	Alq3	Al
V	Au	TPD	Alq3	HFPI-2	ITO

*HOMO and LUMO levels of TPD and Alq3 are 5.7 and 3.2 eV, respectively.

(300°C). Consequently, TPD-dispersed polyimides [10,11,13], whose thermal stability is same as that of the host polyimide, was used as a HTL. Fig. 7 shows the hole transport property of TPD-dispersed PI-4 (PI-4+TPD) whose device structure is ITO/PI-4+TPD/Alq3/Al. The EL from Alq3 was clearly observed, and the turn-on voltage, that is the voltage for the initiation of charge injection, was 5 V. A desirable hole transport property was confirmed. Accordingly, several multilayer devices were fabricated combining PI-4+TPD, TPD, and Alq3 using Al and Au electrodes. The structures of the multilayer devices were summarized in Table 2. For all devices, in particular for Device III, the carrier injection barriers were decreased by the dispersion of TPD, and the hole / electron injection barriers of 0.6 / 0.5 eV were attained. These values are considerably low and well balanced. Fig. 8(a) shows the *I-V-L* curves of Device III. The shape of charge injection is similar to the typical diode characteristics, indicating the injection of holes and electrons occurred from anode and cathode, respectively. However, the EL spectrum shows no EL peak but spark due to the breakdown (Fig. 8(b)). Spark was also observed for the other devices. In addition, another device using HFPI-2 as an ETL was fabricated (Device V) since the LUMO energy level of HFPI-2 is more desirable for EML, but this device showed spark without EL. From these experimental results, we concluded that carriers almost never transfer in the fluorescent polyimides.

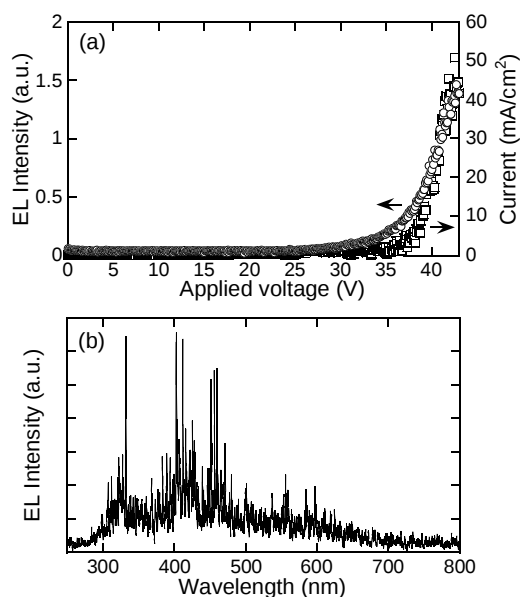


Fig. 8 EL properties of Device III. (a) Current density-voltage-EL intensity (*I-V-L*) characteristics and (b) EL spectrum.

3.3. Doping of Low Molecular-Weight Compound

For the next step, we tried to use fluorescent polyimides as host materials for TPD-dispersion, and their hole transport and emitting properties were analyzed.

Fig. 9 shows the *I-V-L* curves of a device using TPD-dispersed HFPI-2 (HFPI-2+TPD) having a structure of ITO/HFPI-2+TPD/Alq3/Al. An EL from Alq3 was clearly observed with a turn-on voltage of 7 V. Thus, TPD-dispersed fluorescent polyimides (semi-aromatic polyimides) exhibit desirable hole transport properties.

These results provide a novel concept shown in Fig. 10. The excitation spectrum of HFPI-3 is overlapped with the emission peak of Alq3 as shown in Fig. 10(a), indicating that the EL of Alq3 induces the PL of HFPI-3. Hence, when the double-layered device is fabricated using TPD-dispersed HFPI-3 (HFPI-3+TPD) as shown in Fig. 10(b), a novel emission mechanism is expected: Firstly, simultaneous hole transfer in the HFPI-3+TPD layer and electron transfer in Alq3 layer causes EL emission of Alq3 (520 nm) by the recombination of holes and electrons. Secondly, HFPI-3 absorbs the EL radiation of Alq3 and emits PL at longer wavelengths (580 and 700 nm).

Fig. 11(a) shows the *I-V-L* curves of the device having a structure of ITO/HFPI-3+TPD/Alq3/Al. The shape of the charge injection shows typical diode characteristics with a turn-on voltage of 8 V. Fig. 11(b) shows the EL spectra of the device. When the device was operated at 15 V, the maximum EL peak is observed at the same wavelength of ca.520 nm,

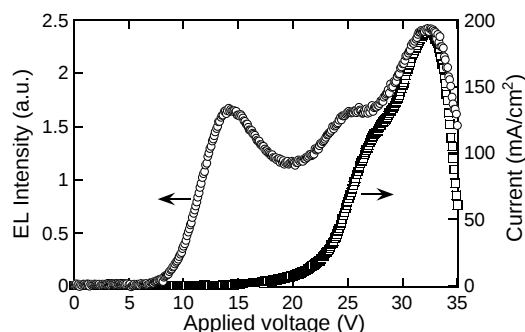


Fig. 9 Current density-voltage-EL intensity (*I-V-L*) characteristics of the device using TPD dispersed HFPI-2 layer.

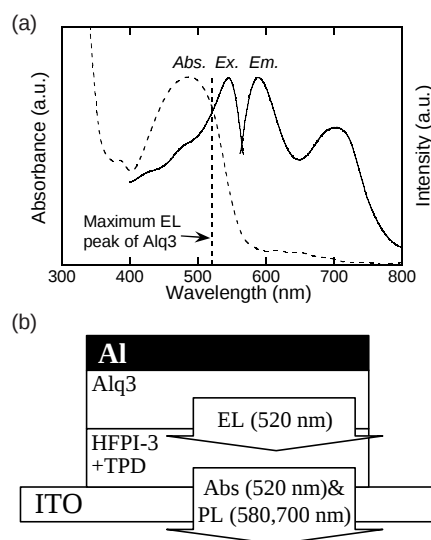


Fig. 10 (a) Absorbance, excitation, and emission spectra of HFPI-3, and (b) a model structure of the novel concept device.

which coincides with those of typical OLEDs using Alq3 as an emitting material. Because of the relatively low quantum yield of HFPI-3 (< 0.02), the energy transfer (wavelength conversion) is unlikely to be very efficient. However, when the device was operated at 30 V, the maximum EL peak was displaced to ca.560 nm. The fact that the maximum PL peaks of HFPI-3 are observed at 580 and 700 nm (for thick films) indicates that the EL properties of the novel device are strongly affected by the emission of HFPI-3. The structure of ITO/HFPI-3+TPD/Alq3/Al might be utilized for a novel wavelength-tunable OLED. Although the mechanism of the wavelength displacement of the EL emission with increasing applied voltage remains unclear, we consider that the efficiency of energy transfer was increased or the recombination zone of electrons and holes was displaced from the Alq3 layer to the HFPI-3+TPD layer.

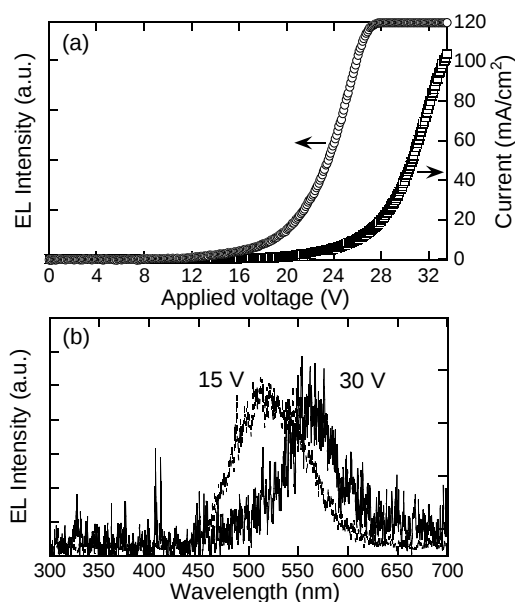


Fig. 11 EL properties of the device using TPD dispersed HFPI-3 layer. (a) Current density-voltage-EL intensity (*I-V-L*) characteristics and (b) EL spectra.

4. Conclusions

The EL properties of the OLED using fluorescent polyimides as a light-emitting layer were widely investigated. The energy levels of HOMO of HFPI-1 and HFPI-2 were determined as 6.7 and 6.9 eV, respectively, from CV measurement. For both polyimides, the hole injection barriers from anode are quite high, and hole injections are fairly difficult. Several kinds of single and multilayer devices were fabricated, but only spark due to dielectric breakdown was observed for all devices. Hence, we concluded that carriers almost never transfer in the fluorescent polyimides.

In contrast, the TPD-dispersed fluorescent polyimides exhibited desirable hole transport properties. In case of using HFPI-3 whose excitation spectrum is overlapped with the emission of Alq₃, the device showed distinct EL at 520 nm under the operation at 15 V. Further, the emission was displaced to 560 nm by the influence of HFPI-3 under the operation at 30 V. These findings indicate that the device structure of ITO/HFPI-3+TPD/Alq₃/Al can be utilized for a novel wavelength-tunable OLEDs.

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