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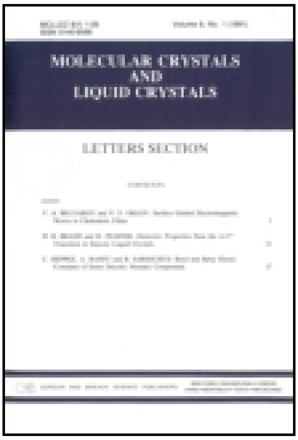

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Synthesis of New Conjugated Polymers as Hole Injection Layer and Performance of OLED Devices

Tae Wook Yoo [a] , Chul Park [b] , Nguyen Thi Mai [b] , Dong Uk Kim [c] & Lee Soon Park [a c d]

[a] Department of Sensor & Display Engineering , KyungPook National University , Daegu , 702-701 , Korea

[b] Department of Polymer Science , Kyungpook National University , Daegu , 701-702 , Korea

[c] Department of Science Education , Daegu National University of Education , Daegu , 705-715 , Korea

[d] Mobile Display Research Center , Kyungpook National University , Daegu , 701-702 , Korea

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Synthesis of New Conjugated Polymers as Hole Injection Layer and Performance of OLED Devices

TAE WOOK YOO,[1] CHUL PARK,[2] NGUYEN THI MAI,[2]
DONG UK KIM,[3] AND LEE SOON PARK[1,3,4,*]

[1]Department of Sensor & Display Engineering, KyungPook National University,
Daegu 702-701, Korea
[2]Department of Polymer Science, Kyungpook National University,
Daegu 701-702, Korea
[3]Department of Science Education, Daegu National University of Education,
Daegu 705-715, Korea
[4]Mobile Display Research Center, Kyungpook National University,
Daegu 701-702, Korea

*The fluorene-based poly(dioctylfluorene-*alt*-biphenylamine)s with styrylpyridyl group were synthesized by using Pd-catalyzed polycondensation reaction. These hole injection/transport polymers showed very good solvent resistance after photo-crosslinking which could facilitate the subsequent spin coating of the emitting layer polymer solution. Moreover these polymers could be patterned by using distyrylpyridyl alkyl monomer (DSM) as crosslinking agents. The OLED devices with configuration of ITO/HIL/Alq$_3$:NPD/LiF/Al in which synthesized polymer was used as hole injection layer (HIL) were fabricated and their performance was compared with the commercially available PEDOT:PSS as HIL layer.*

Keywords: Organic Light Emtting Diode; OLED; Synthesis; Conjugated polymers

Introduction

Conjugated polymers have drawn much attention due to their potential applications to polymer light-emitting devices (PLED) [1,2]. To date many types of conjugated polymers e.g poly(acetylene)s, poly(thiophene)s, poly(fluorene)s, and poly(phenylene)s have been synthesized [3–6]. Among these polymers, poly(fluorene)s are well-known in the polymer OLEDs due to their easy processability, long term stability and high fluorescence quantum efficiency [7]. The common method to get thin film using polymer is solution casting such as spin coating and inkjet printing. However this method is difficult to apply in OLED because the first layer formed by solution coating can be partly dissolved by the solvent used in the following spin coating process. Thus a challenge of the solution process OLED is to control the solubility of OLED materials. One of the approaches is to develop novel polymers containing crosslinkable moieties which not only become insoluble in common organic solvents but also can simultaneously be patterned like a negative photoresist using standard photolithographic techniques. In this work, we synthesized a series of crosslinkable

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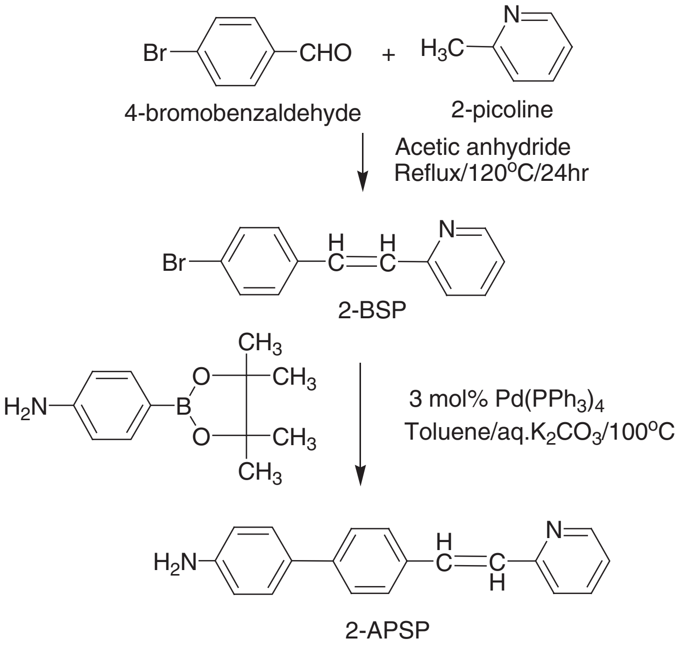
[*]Corresponding author. E-mail: lspark@knu.ac.kr

conjugated copolymers based on alternating fluorene and phenylamine units by using Buchwald-Hartwig reaction in order to investigate their potential as hole injection (HIL) or transporting (HTL) materials in the OLED devices. The synthesized polymers could be patterned by using distyrylpyridyl alkyl monomer (DSM) as crosslinking agents.

Experimental

(1) Synthesis of Conjugated Polymers

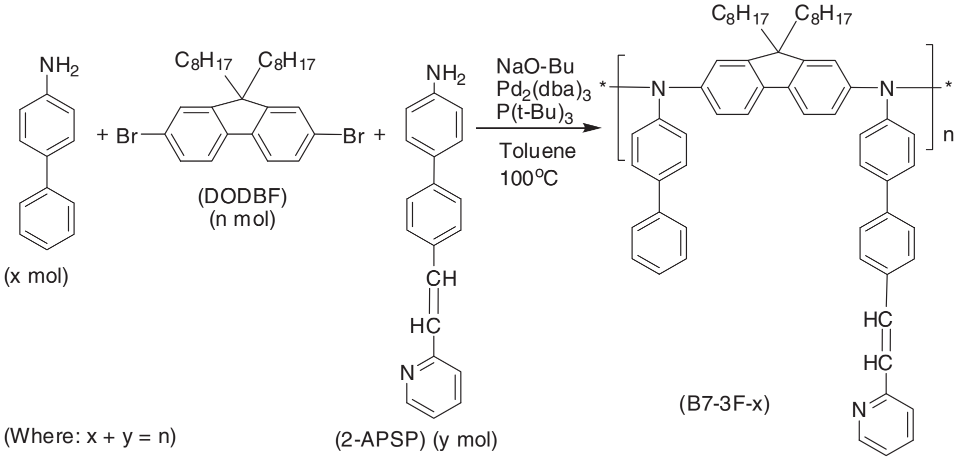
The synthetic scheme of intermediate (2-BSP) and monomer (2-APSP) for the conjugated copolymers are shown in Scheme 1 [8–10].



Scheme 1. Synthesis of monomer.

The synthesis of crosslinkable HIL copolymer was carried out by Buchwald-Hartwig reaction as shown in Scheme 2.

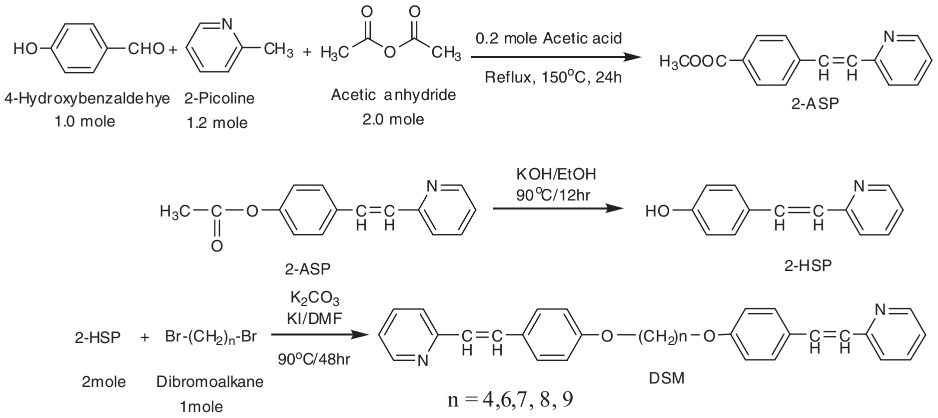
First, 9,9-dioctyl-2,7-dibromofluorene (DODBF) (1.82 mmol), 4-aminobiphenyl (1.64 mmol), 2-(4-aminophenyl-styryl)pyridine (2-APSP) (0.18 mmol), sodium-tert-butoxide (NaO-Bu) (5.47 mmol), and tris(dibenzylideneacetone) dipalladium ($Pd_2(dba)_3$) (0.05 mmol) were dissolved in anhydrous toluene (50 ml) at room temperature. The catalyst tris-tert-butylphosphine ($P(t\text{-}Bu)_3$) (0.27 mmol) was added to the reaction mixture by using syringe. The polymerization was carried out at 100∞C for 72h to get yellow solution. After cooling to room temperature, the product solution was extracted with ammonium water and dichloromethane, washed with water and dried with $MgSO_4$. The residue was concentrated by rotary evaporator and the organic fraction was precipitated in methanol to give the yellow product in 92% yield [11].



Scheme 2. Synthesis of HIL polymer.

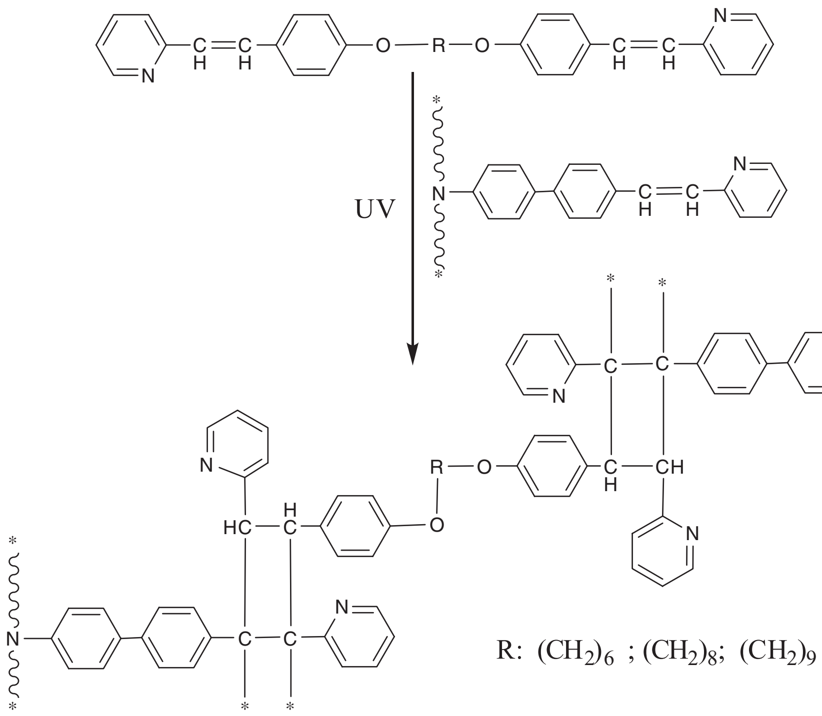
(2) Synthesis of Crosslinking Agents

Crosslinking agents were synthesized as shown in Scheme 3 with the example of typical crosslinking agent (DSM-6).



Scheme 3. Synthesis of crosslinking agent.

Potassium carbonate (2.312 g, 15.20 mmol) and potassium iodide (0.253 g, 1.5 mmol) were added to a solution of 2-HSP (3.00 g, 15 mmol) in DMF (40 ml) with magnetic stir bar. 1,6-Dibromohexane was then added to the mixture. The reaction mixture was heated at 90°C for 48 hours. After cooling to room temperature, the reaction mixture was washed with 20% Na_2CO_3 and with distilled water (50 mL × 2). The separated organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated by a rotary evaporator. The solid was dissolved in CH_2Cl_2 (15 mL) and precipitated in n-hexane to get solid product (70% yield) [12–16].



Scheme 4. Crosslinking reation of fluorene-base conjugated polymer.

(3) HIL Patterning with Crosslinking Agent DSM

A photoresist system (DSM_n-B7-3F) containing the synthesized copolymers B7-3F-3 and DSM crosslinking agent was used to fabricate crosslinked HIL layer. The crosslinking reaction between copolymer B7-3F-3 and DSM are shown in Scheme 4.

Table 1. Characterization of fluorine-based conjugated polymers

Conjugated Polymer	Monomer (mole%) x	Monomer (mole%) y	Mw	PDI	Yield (%)
B7-3F-1	90	10	29,000	2.38	92
B7-3F-3	70	30	27,000	1.71	94
B7-3F-7	30	70	20,000	1.92	87
B7-3F-9	10	90	19,000	2.07	84

x : biphenyl amine.
y : 2-APSP comonomer.

Result and discussion

Characterization of Copolymers

The yields of copolymers by the Buchwald-Hartwig reaction were relatively high in the range of 84 to 94% and the molecular weights of copolymers were in the range of 29,000–19,000 g/mol as shown in Table 1.

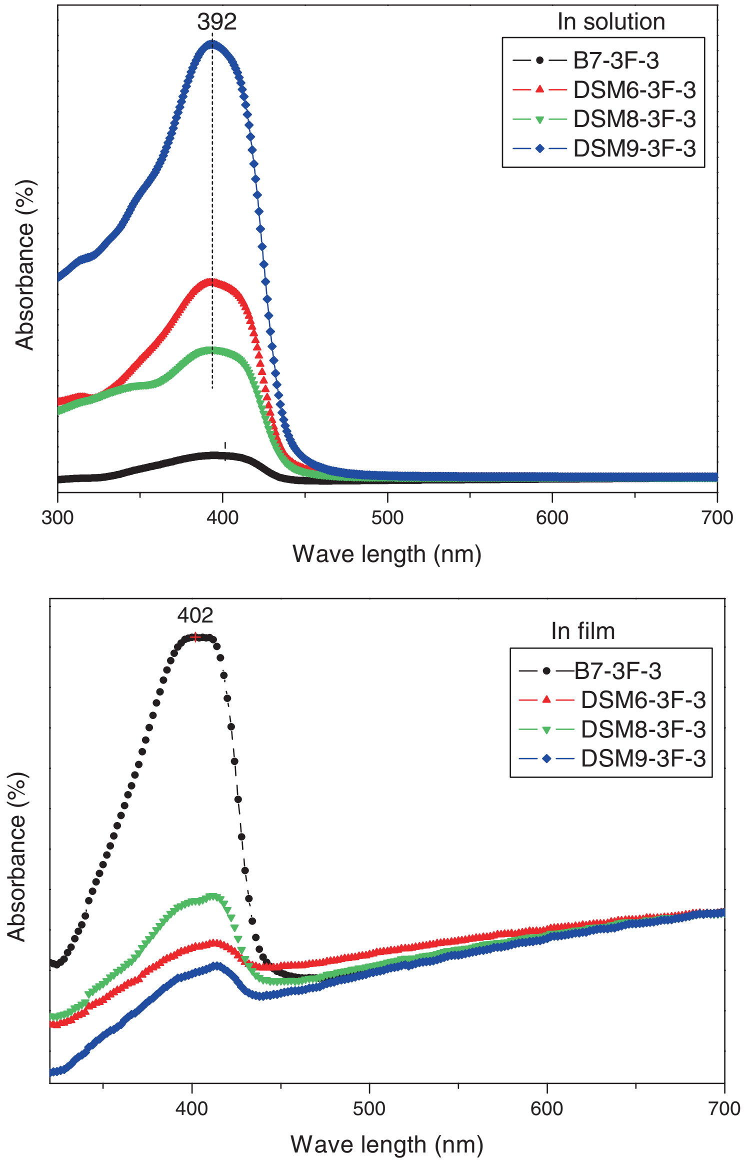


Figure 1. UV-Vis absorbance spectra of DSMn-B7-3F-3.

Table 2. Structure of OLED devices

OLEDs	HIL	EML	EIL	Cathode
No. 1	PEDOT:PSS	Alq3	LiF	Al
No. 2	B7-3F-3	Alq3	LiF	Al
No. 3	DSM6-B7-3F-3	Alq3:NPB (3:1)	LiF	Al
No. 4	DSM8-B7-3F-3	Alq3	LiF	Al
No. 5	DSM9-B7-3F-3	Alq3:NPB (3:1)	LiF	Al

Photoreactivities of Copolymers

The photoreactivities of crosslinkable conjugated polymers as well as photoresist system DSM_n-B7-3F were analyzed by UV—visible and PL spectrophotometer. In the presence of DSM as crosslinking agent, the photoresist system DSM_n-B7-3F can form a crosslinked net work as shown in Scheme 4.

The UV absorbance spectra of conjugated polymer (B7-3F-3) and photoresist system (DSMn-3F-3 series) showed maximum UV absorbance at 392 and 402 nm in solution and solid film, respectively, as shown in Figure 1. The shape decrease of the UV maximum peaks indicated that the $(2\pi+2\pi)$ photo-cycloaddition had occurred. The PL spectra of the photoresist system exhibited maxima at 434 and 542 nm in solution and solid film, respectively as shown in Figure 2. It was noted that the PL intensity increased with the spacer number (n in DSMn) in the photoresist system.

OLED Performance

A series of OLED devices with different structures were made to investigate HIL properties of the synthesized fluorine-based conjugated polymers as shown in Table 2. In these devices, the HIL polymer (B7-3F-3) andphotoresist system (DSMn-B7-3F) were used as hole injection layers with ~60 nm thickness. Tris(8-hydroxyquinoline)aluminum and bis[N-(1-naphthyl)-N-phenyl]benzidine (Alq3:NPB) (wt/wt 3:1) were used as emitting layer.

As shown in Table 3 the OLED devices indicated that the B7-3F-3 uncrosslinked copolymer (Device No. 2) exhibited higher luminance than commercially available HIL

Table 3. Performance of OLED devices with new HIL layer

		Sample				
Property	Step	No. 1	No. 2	No. 3	No. 4	No. 5
Spin coating speed (rpm)	1st (30s)	3000	3000	4500	4500	4500
	2nd (10s)	4500	4000	7000	7000	7000
Thickness (nm)		66	34	45	72	68
Luminance (cd/m^2)		1581	1852	2241	484	1280
Drive voltage (V)		5	5	4	5	4
Current efficiency (cd/A)		0.17	0.18	0.008	0.002	0.005
Color coordinate	x	0.29	0.29	0.29	0.29	0.29
	y	0.52	0.52	0.52	0.52	0.52

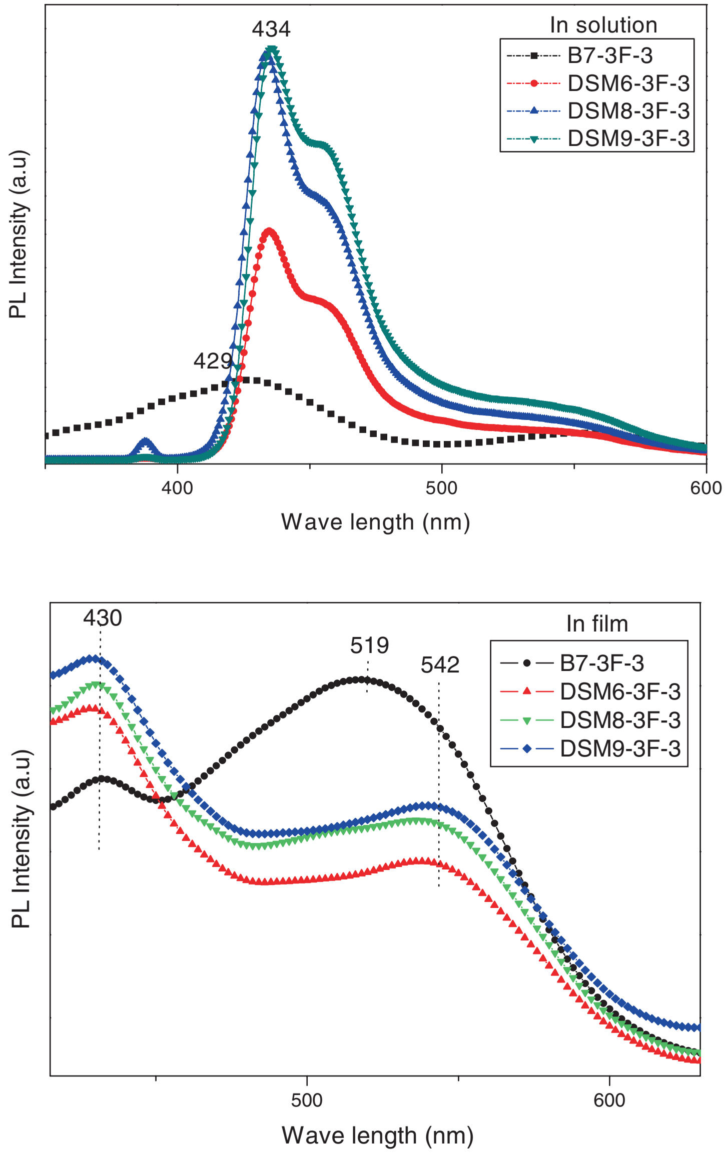


Figure 2. Photoluminescence spectra of DSMn-B7-3F-3.

polymer PEDOT:PSS(Device No.1) with the same configuration. The OLED No.4 with crosslinked copolymer DSM8-B7-3F-3 as HIL layer exhibited lower luminance than commercially available

PEDOT:PSS (Device No.1) with the same device configuration. It was due to the high surface roughness of DSM8-3F-3 HIL layer as examined by SEM images. When small amount of NPB was added as dopant in the Alq3 EML layer, the OLED (No.3) with DSM6-3F-3 as HIL exhibited higher luminance than the B7-3F-3 copolymer as well as PEDOT:PSS as the HIL layers.

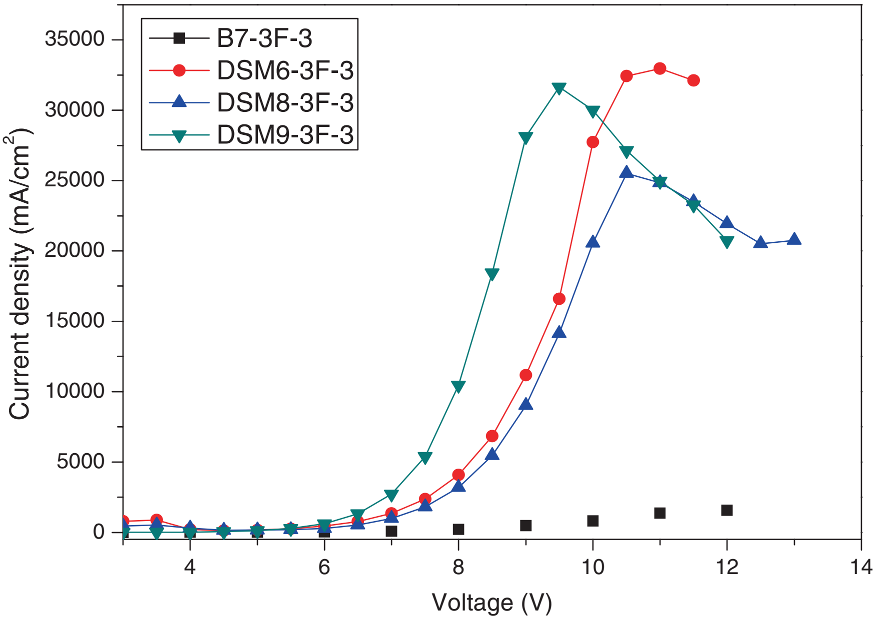


Figure 3. Voltage versus current density profile of OLED devices.

Figure 3 shows the current density versus voltage of the OLED devices. It was noted that the OLED devices with crosslinked DSMn-B7-3F-3 series as HIL layer could withstand higher applied voltage than the OLED device with uncrosslinked B7-3F-3 as HIL layer.

Acknowledgment

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Conclusion

In conclusion we successfully synthesized DSM crosslinking agents and new fluorene-based polymers (B7-3F-X) with photo-crosslinkable styrylpyridyl group. The performance of OLED devices fabricated with crosslinked hole-transport layer (DSM6-B7-3F-3) was better than the one made by commercially available HIL polymer PEDOT:PSS. It was also that the OLED devices with crosslinked DSMn-B7-3F-3 series as HIL layer could withstand higher applied voltage than the OLED device with uncrosslinked B7-3F-3 as HIL layer.

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