

Suppression of Initial Degradation via an Interfacial Charge-Induced Overshooting Effect in Solution-Processed Organic Light-Emitting Diodes

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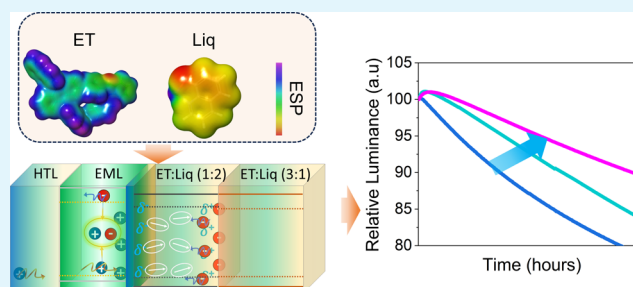
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ABSTRACT: As the chemical stability of organic materials in organic light-emitting diodes (OLEDs) greatly impacts devices' lifetime, a thoughtful and advanced design of materials and device structures is necessary. In our work, we have achieved lifetime enhancement at its initial stage for solution-processed OLEDs. This improvement was realized through the implementation of a double electron transporting layer (dETL) composed of 2-[4-(9,10-dinaphthalen-2-yl-anthracen-2-yl)-phenyl]-1-phenyl-1H-benzimidazole (ET) and hydroxyquinolinolato-lithium (Liq). A giant surface potential was generated at the surface of a constituent electron transport layer (ETL) that contained a higher concentration of Liq with high polarity. This giant surface potential simultaneously promoted the injection of trapped/accumulated electrons through the interface within dETL and the injection of holes from the anode, generating more exciton recombination events and ultimately enhancing efficiency by 133.0% and lifetime LT95 (luminance dropped by 5%) by 300% with an overshooting effect. Additionally, the degradation at the emitting layer was mitigated by shifting the degradation zone to the dETL, which was evidenced by laser desorption/ionization–time-of-flight (LDI–TOF) mass spectroscopy.

KEYWORDS: overshooting, giant surface potential, solution-processed OLEDs, lifetime, double ETL, LDI–TOF



1. INTRODUCTION

The instability of organic materials negatively impacts the lifetime of OLEDs, especially for solution-processed OLEDs (s-OLEDs), significantly hampering their widespread commercialization.^{1,2} In OLED displays, burn-in typically occurs at LT95, which dramatically reduces the image quality of the display, causing inadequate user satisfaction. Therefore, suppressing the initial degradation is practical and crucial to advancing the dominance of OLED displays in display technology. The initial degradation observed may result from the intrinsic degradation of unstable organic molecules, which has been proposed to be from the chemical dissociation of emissive molecules through bimolecular annihilation reactions,³ electrochemical instability of radical cations and anions contributing to OLED degradation at a long time scale,⁴ and the bond dissociation reactions and deep traps from long-lived stabilized free radicals caused by chemical reactions.⁵ In addition, an unstable excited state causes the degradation of OLEDs.^{6–8} To mitigate material degradation, minimizing stress on materials within the emitting layer (EML) or at the interface with the EML is necessary. Reducing the charge and exciton concentration could mitigate the stress and lower the possibility of exciton quenching. However, this could also

reduce device efficiency due to less photon emission. Therefore, to obtain both a long lifetime and high performance, the recombination efficiency should be maximized by controlling the charge flowing into the EML to meticulously optimize the charge balance and spatial distribution of excitons. The occurrence of charge accumulation at the interface with the EML, typically causing undesirable phenomena in OLEDs such as interface degradation due to exciton–polaron quenching,⁹ prompted further investigation.

8-Hydroxyquinolinolato-lithium (Liq) has been reported to be used as an ultrathin interlayer,¹⁰ a bilayer, or a single ETL (sETL) after being mixed with various electron transport layer (ETL) materials to improve the operational lifetime.^{11–17} However, not many works have reported combining a bilayer and a mixed layer using Liq to suppress the initial degradation. In addition, spontaneous orientation polarization (SOP),

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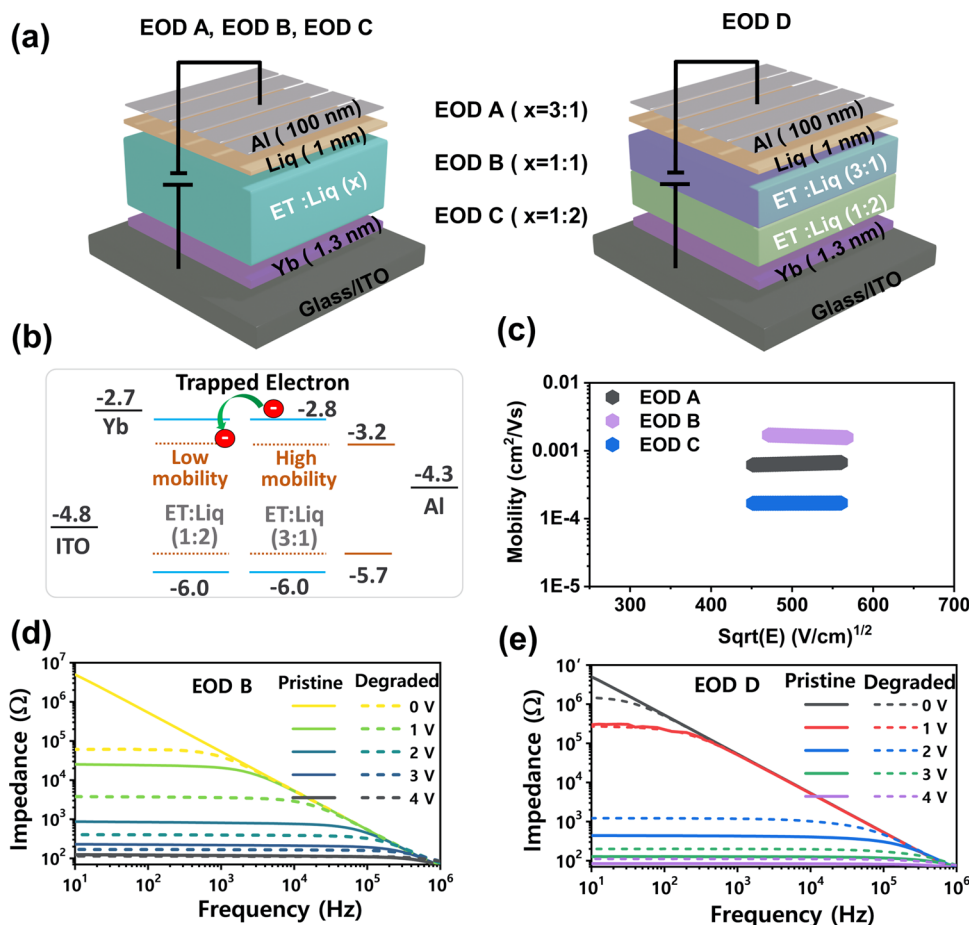


Figure 1. (a) Device structures of EODs with sETL (EOD A, B, and C) and dETL (EOD D). (b) Diagram showing the trapped electron by a deeper lowest unoccupied molecular orbital (LUMO) of Liq at the interface. (c) Electron mobility calculated from the space charge limited current model of EOD A, EOD B, and EOD C. Impedance–frequency measurements were performed in pristine and degraded states of (d) EOD B (sETL) and (e) EOD D (dETL).

which originates from the alignment of the permanent dipole moment (PDM) of the molecules, has been reported to significantly affect the charge transport behavior of the layer.^{18–20} Constant polarization results in a fixed density of polarization charge at the heterointerface, inducing an internal electrical potential slope in the bulk of the film; the film surface then exhibits a giant surface potential (GSP). This GSP can lead to charge accumulation,²¹ increasing the lifetime of storage charges²² or inducing charge injection.²³

In this study, we addressed device degradation by implementing a double electron transport layer (dETL) having two thin ETLs composed of a blend of ET^{24,25} and Liq. The mismatch of charge mobility and energy level creates a charge trap inside the dETL, preventing charge accumulation at the EML interface. Consequently, the initial degradation was effectively mitigated through the phenomenon of overshooting, where luminance surpasses the initial value during the early stages of the lifetime test. The origin of the overshooting effect was studied by analyzing GSP-induced electron injection from the dETL. Simultaneously, improvements in device efficiency were achieved by maximizing the recombination efficiency. It was further confirmed from mass spectrometry that the degradation zone was shifted from the EML interface into the interface inside dETL due to the charge trap there.

2. EXPERIMENTAL AND SIMULATION METHOD

2.1. Materials. PEDOT:PSS (CH8000) was purchased from Heraeus and used as a hole injection layer (HIL). A cross-linkable hole transport material named [4-(9-phenyl-9H-carbazol-4-yl)-phenyl]-bis(4'-vinyl-biphenyl-4-yl)-amine (PbV) was used for preventing interface mixing. A host material, namely, 7,7-dimethyl-5-phenyl-2-(9-phenyl-9H-carbazol-3-yl)-5,7-dihydroindeno[2,1-b]-carbazole (PCIC), and a green dopant (GD), namely, tris[2-(p-tolyl)pyridine]iridium(III) (Ir(mppy)₃), were used for the emitting layer. In addition, an exciton blocking layer (EBL) material, namely, 2,4-diphenyl-6-bis(12-phenylindolo[2,3-a] carbazole-11-yl)-1,3,5-triazine (DIC-TRZ), was used to confine excitons inside the EML. 2-[4-(9,10-Dinaphthalen-2-yl-anthracen-2-yl)-phenyl]-1-phenyl-1H-benzimidazole (ZADN) was used as ET. Lithium quinolate (Liq) was used to mix with ET to form the ETL, and a thin Liq layer was used as an electron injection layer. Finally, Al purchased from Sigma was used as a cathode.

2.2. Device Fabrication. The patterned indium tin oxide (ITO) glasses having an emission area of 9 mm² were cleaned by sonication for 10 min with acetone and then isopropyl alcohol (IPA) followed by UV ozone equipment for 15 min. PEDOT:PSS (CH8000) as a hole injection layer (HIL) was first spin-coated and annealed at 165 °C for 15 min in the atmosphere condition to be used as an HIL. In addition, a solution containing 0.45 wt % x-HTM (cross-linked hole transport material) in toluene was then coated on the HIL (3000 rpm, 30 s) and annealed at 230 °C for 60 min. The EML solution was prepared by mixing PCIC solution (1 wt % in chlorobenzene) and Ir(mppy)₃ (0.5 wt % in toluene) with a weight ratio of 9:1. The solution was spin-coated with the same spin-coating condition as the HTL and

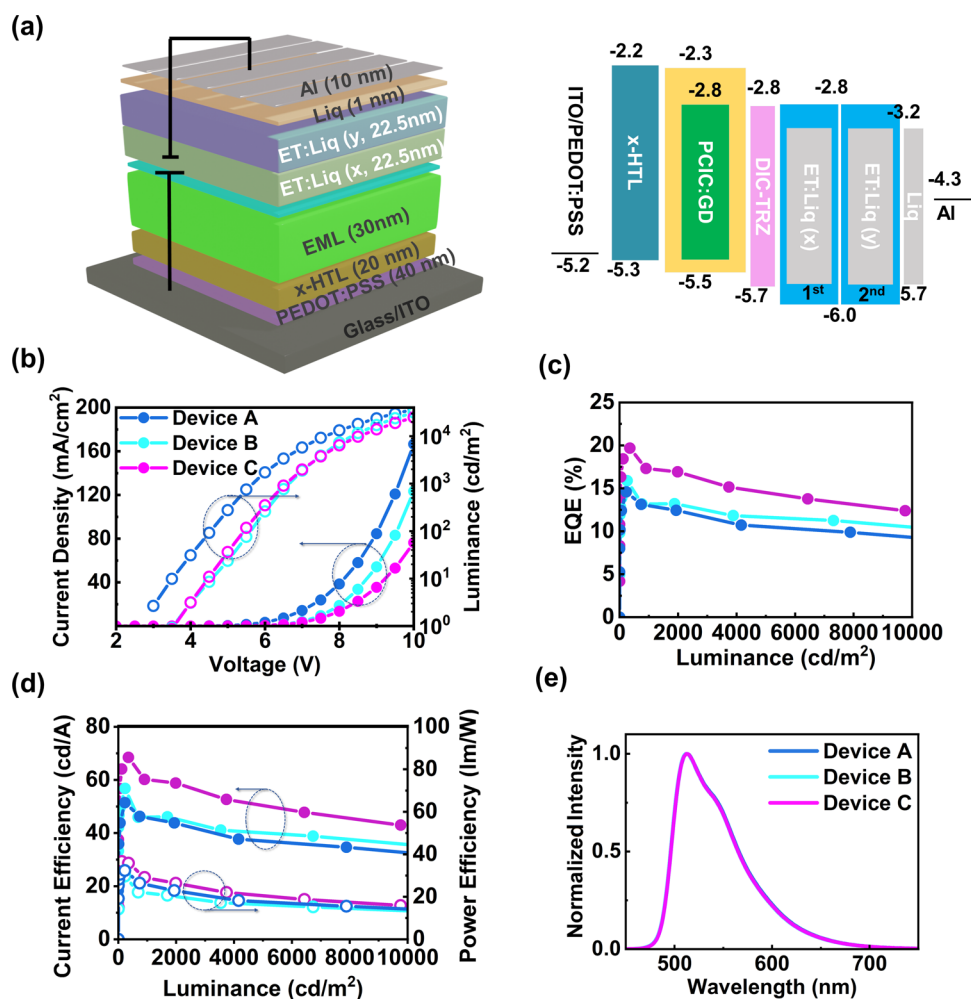


Figure 2. (a) Device structure with stacked layers and the energy diagram. (b) Current density–voltage–luminance, (c) external quantum efficiency (EQE)–luminance, (d) current efficiency–luminance–power efficiency, and (e) electroluminescence spectra of investigated devices.

then annealed at 105 °C for 15 min. The next step included evaporation of all of the remaining materials under a vacuum pressure of about 10^{-7} Torr. 5 nm of DIC-TRZ was evaporated on top of the EML, and then the blends of ET and Liq with different Liq concentrations were deposited as sETL or dETL. Finally, Liq and Al were respectively deposited as an electron injection layer and a cathode.

2.3. Measurement. Current density–voltage–luminance (J – V – L) characteristics were measured by a power supplier (Keithley SMU 2635A) and a luminance meter (Minolta CS-2000A) instrument. An impedance analyzer (Solartron Impedance/Gain-Phase Analyzer SI 1260) combined with a dielectric interface (Solartron 1296) was used to measure the impedance characteristics of devices. We measured the capacitance–frequency characteristics from 1 to 10^6 Hz with the amplitude of the alternating voltage set to 0.1 V for all measurements presented here. The bond dissociation energy (BDE), permanent dipole moment, and electrostatic potential were calculated by molecular simulation using density functional theory (DFT) with the Schrödinger Materials Science program. In addition, all spectra of LDI–TOF mass spectroscopy were acquired using an IDSys Premier LDI TOF Mass Spectrometer (ASTA, Suwon, South Korea) equipped with a high-resolution camera and a 343 nm Yb:YAG UV laser. The spectra were obtained in negative mode.

3. RESULTS AND DISCUSSION

3.1. Charge Accumulated/Trapped at the Interface within dETL. A dETL consists of two adjacent ETLs, each of which is a blend of ET and Liq at different concentrations.

Changing Liq concentration would result in a change in charge transport ability as well.²⁶ To analyze these changes, the following electron-only devices (EODs) with different concentrations of Liq in dETL were fabricated and then characterized by impedance spectroscopy (IS, Figure 1).

EOD A: ITO/Yb (1.3 nm)/ET:Liq (3:1) (45 nm)/Liq (1 nm)/Al (100 nm).

EOD B: ITO/Yb (1.3 nm)/ET:Liq (1:1) (45 nm)/Liq (1 nm)/Al (100 nm).

EOD C: ITO/Yb (1.3 nm)/ET:Liq (1:2) (45 nm)/Liq (1 nm)/Al (100 nm).

EOD D: ITO/Yb (1.3 nm)/ET:Liq (1:2) (22.5 nm)/ET:Liq (3:1) (22.5 nm)/Liq (1 nm)/Al (100 nm).

Figure 1b shows an energy diagram for electron trapping, while Figure 1c–e represents the calculated mobility of ETLs and IS results obtained from EODs with different ET:Liq ratios. The (1:1) ratio (EOD B) resulted in the highest electron mobility of $1.6 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (at $2.5 \times 10^5 \text{ V/cm}$), while increasing the Liq ratio to (1:2) (EOD C) led to a significant mobility decrease by about 1 order of magnitude ($1.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; Figure 1c). A reduction in mobility was also observed at the (3:1) ratio condition in EOD A ($6.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The resistance of dETL in EOD D also significantly increased compared to sETL in EOD B (Figure S1). Due to the deeper lowest unoccupied molecular orbital

Table 1. Summarized Performance of All Devices

device	V_{on}^a/V_{op}^b (V)	CE ^c /EQE ^d	CE/EQE	lifetime		CIE ^g (@1000 cd/m ²)
		max [cd/A]/[%]	1000 (cd/m ²) [cd/A]/[%]	LT95 ^e [h]	LT70 ^f [h]	
device A	2.7/5.6	51.5/14.5	45.7/13	0.9	9.5	(0.308, 0.621)
device B	3.5/6.5	56.8/15.9	46.0/13.1	1.9	9.5	(0.305, 0.620)
device C	3.5/6.5	68.5/19.7	60.1/17.3	2.7	13	(0.306, 0.621)

^aTurn-on voltage at 1 cd/m². ^bOperating voltage at 1000 cd/m². ^cCurrent efficiency. ^dExternal quantum efficiency. ^eLifetime at 95% of initial luminance. ^fLifetime at 70% of initial luminance. ^gCommission Internationale de l'Éclairage 1931.

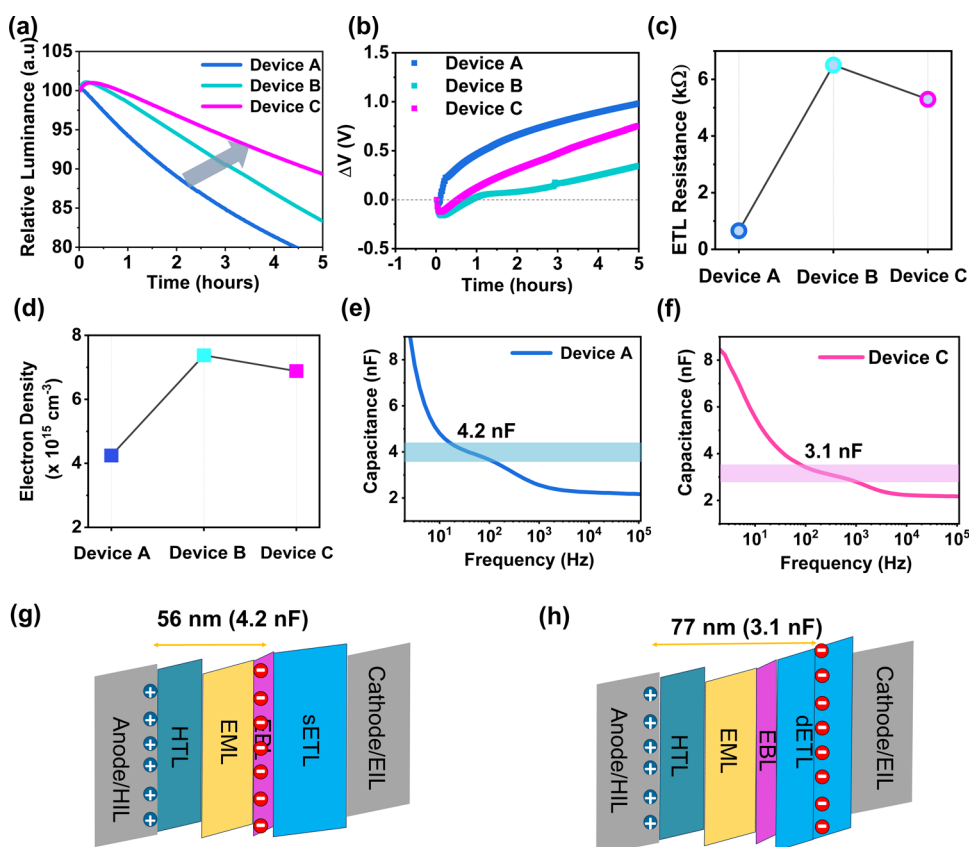


Figure 3. (a) Lifetimes of the three devices with an initial luminance of 1000 cd/m², and the overshooting effect observed in Devices B and C. (b) Driving voltage changes of the devices during the lifetime test. (c) The resistance of ETL obtained from fitting Cole–Cole plots of full devices. (d) Electron density inside the electron transport layer of devices. The resistance and electron density are calculated at 6 V. Capacitance–frequency characteristics of (e) Device A and (f) Device C showing plateaus at 5 V. Energy diagrams showing the trapped/accumulated electrons and holes on the anode side, which could result in plateau formation in the capacitance–frequency curve for (g) Device A and (h) Device C.

(LUMO) of Liq (−3.2 eV) compared to ET (−2.8 eV), electrons that were transported by ET will be trapped by the LUMO of Liq. In addition, the lower mobility of the constituent ETL (1:2) caused the accumulation of fast electrons coming from the constituent ETL (3:1). These trapped/accumulated electrons became immobile, leading to resistance increase and mobility decrease.

The degradation of ETLs was examined by simultaneously applying a current of 0.4 mA and 365 nm UV light to EOD B (sETL) and EOD D (dETL) for 7 h. The impedance rises only in EOD D, indicating serious degradation (Figure 1d,e), which could be due to degradation at the interface, where there are trapped/accumulated electrons. Nevertheless, we assumed that compared to the deterioration of EML, degradation at the transport layer has a less negative effect on the device lifetime.

3.2. Interfacial Charge-Induced Overshooting Effect.

OLEDs compositing dETL were then meticulously controlled by adjusting the Liq concentration in dETL. A reference device

with sETL was fabricated, and the same thickness was maintained in both cases to ensure an equivalent electric field across the devices. The detailed device structures are outlined below (Figure 2a).

Device A: ITO/PEDOT:PSS (40 nm)/x-HTL (20 nm)/EML (30 nm)/DIC-TRZ (5 nm)/ET:Liq (1:1, 45 nm)/Liq (1 nm)/Al (100 nm).

Device B: ITO/PEDOT:PSS (40 nm)/x-HTL (20 nm)/EML (30 nm)/DIC-TRZ (5 nm)/ET:Liq (1:1.5, 22.5 nm)/ET:Liq (2:1, 22.5 nm)/Liq (1 nm)/Al (100 nm).

Device C: ITO/PEDOT:PSS (40 nm)/x-HTL (20 nm)/EML (30 nm)/DIC-TRZ (5 nm)/ET:Liq (1:2, 22.5 nm)/ET:Liq (3:1, 22.5 nm)/Liq (1 nm)/Al (100 nm).

Here, we used a thin DIC-TRZ layer (triplet energy, $T_1 = 2.81 \text{ eV}$)²⁷ and a cross-linkable hole transport layer (x-HTL, $T_1 = 2.82 \text{ eV}$)²⁸ to confine the exciton inside the EML. The performances of the devices are shown in Figure 2b–e and Table 1. The maximum current efficiencies (CE_{max}) are 51.5,

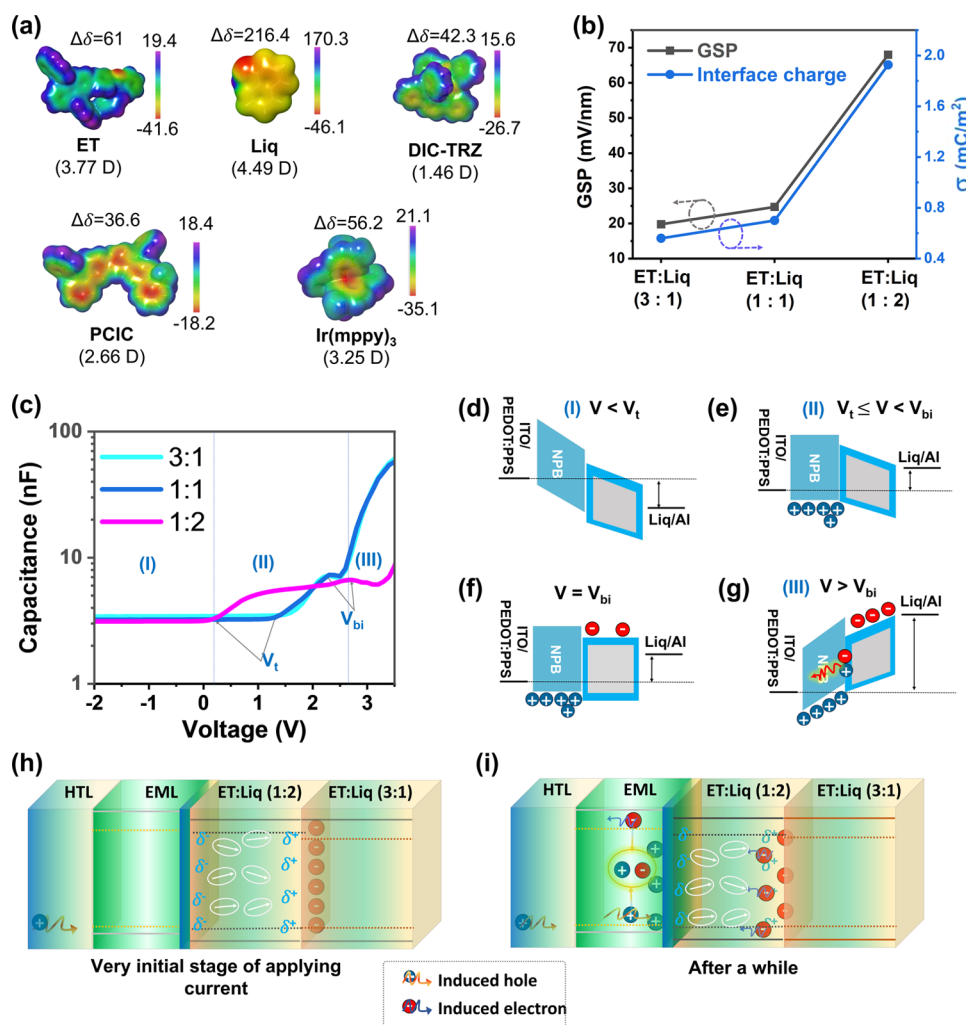


Figure 4. (a) Map volume for electrostatic potential with permanent dipole moment. (b) GSP and interfacial charge density (σ) of ETL layers. (c) Capacitance–voltage plots for the three devices having different ET:Liq ratios (3:1, 1:1, and 1:2). The blue dash lines to separate the regions are just for approximately defining regions (I), (II), and (III). Simplified band diagrams for different applied bias voltage V : (d) region (I): $V < V_t$, (e) region (II): $V_t < V < V_{bi}$, (f) $V = V_{bi}$, and (g) region (III): $V > V_{bi}$. (h) The trapped/accumulated electrons right after a constant current is applied to the device with dETL for the lifetime test (Device C). (i) The injections of electrons and holes were facilitated by strong GSP from ET:Liq (1:2).

56.8, and 68.5 cd/A for Devices A, B, and C, respectively. Compared to Device A, the current efficiency was enhanced by 110.2 and 133.0% for Devices B and C, respectively. The increase in EQE in Device C is believed to result from the reduced electron current injected into the EML, which improves charge balance and enhances efficient exciton recombination. Increasing the Liq concentration in the first ETL next to the DIC-TRZ resulted in decreasing current density from 7.3 through 1.67 to 1.5 mA/cm² (at 6.5 V), respectively, for Devices A, B, and C, which could be ascribed to the trapped/accumulated electrons within dETL. Trapped-filled limited voltages (V_{TFL}) of 0.69, 0.75, and 1.3 V were measured for dETL in Devices A, B, and C, respectively (Figure S2). The higher V_{TFL} indicates a greater amount of traps presented in the devices. The low LUMO level of Liq in the ET:Liq (1:2) layer (Device C) acts as a trap, and the higher concentration of Liq increases the number of traps, thereby raising the V_{TFL} . This, in turn, effectively slows the electron flow into the emitting layer. However, further adding Liq to the first ETL or using sETL with different ET:Liq ratios did not increase the device performance (Figures S3, S4,

Tables S1 and S2), indicating that Device C has the optimal condition for dETL.

Importantly, an overshooting effect was observed during the initial stage of the lifetime test, in which the luminance increased at the constant applied current (Figure 3a and Table 1). This enables an enhancement of LT95 by 233 and 300%, respectively, for Devices B and C. The short lifetimes of these devices are expected due to the unavoidable characteristics of s-OLEDs, such as the presence of solvent or interface mixing that causes exciton quenching.^{2,9,28–31}

To investigate the overshooting effect and device performance improvement, IS was employed to analyze the variations of resistance and electron density inside ETLs (Figures S5 and 3 and Table S3). Each layer in the device was assigned to one resistance–capacitance (RC) element. The details of the electrical circuit used to obtain resistance and electron density are described in the Supporting Information (SI). The resistance significantly increased when changing from sETL to dETL, resulting from the immobile electrons trapped and accumulated at the interface within dETL. The trapped and accumulated electrons are caused by the mismatch in

mobilities and LUMO levels between ET and Liq (0.4 eV). Alternating the Liq concentration in the dETLs led to the discontinuous distribution of ET and Liq across the interface. Electrons carried by the LUMO of ET will be slowed down and trapped by the deeper LUMO of Liq when encountering the interface (Figure 1b).

A correlation among the following four quantities: resistance, the electron density of dETL, the intensity of the overshooting peak, and driving voltage during the lifetime test was observed (Figure 3a–3d). The higher resistance and electron density in dETL gave rise to a greater increase in overshooting peak intensity and a greater decrease in driving voltage as well. In other words, the observed overshooting effect could be directly related to trapped/accumulated electrons inside dETL, which caused the resistance increase.

The evidence of trapped/accumulated electrons is depicted in Figure 3e,f, and the plateaus at different capacitances (4.2 nF for Device A and 3.1 nF for Device C) were found in the capacitance–frequency plots of the two devices. These plateaus could be attributed to the existence of charge traps or accumulation, as reported in many other studies.^{32,33} The location of trapped/accumulated electrons was estimated by calculating the distances between these electrons and positive charges on the anode side (Supporting Information (SI)). Those distances were 56 nm (Device A) and 77 nm (Device C), which were approximately the thickness of organic layers from HIL/HTL to the EML/EBL interface (Device A) and to the interface inside dETL (Device C), respectively (Figure 3g,h).

To further understand the origin of the overshooting effect, the GSP, induced by the SOP of ETLs, was analyzed. The density functional theory (DFT) simulation for electrostatic potential (ESP) and PDM was performed to first estimate the polarity of the molecules (Figure 4a). Among them, Liq shows the largest difference between the minimum and maximum ESP ($\Delta\delta = 216.4$) and the relatively highest PDM of 4.49 D. The intrinsic interfacial charge density (σ) and the GSP of the ETL with various Liq doping ratios were then determined through impedance spectroscopy measurements on simplified bilayer devices: ITO/PEDOT:PSS (40 nm)/NPB (50 nm)/ET:Liq (50 nm)/Liq (1 nm)/Al (100 nm), where the ET:Liq ratios are 3:1, 1:1 and 1:2 (Figure 4b–4g). Here, NPB was used due to nonpolar characteristics, which are advantageous for accurately determining the intrinsic σ and GSP of the ETL.³⁴

Figure 4c,d displays the capacitance–voltage plot and simplified band diagrams at various applied forward bias voltages. In region I, where $V < V_t$, no charge carrier injection occurs, resulting in the measured capacitance being equivalent to the geometric capacitance of the device (Figure 4d). As the voltage increases, the slope decreases until the flat-band condition for NPB is reached ($V = V_t$), allowing holes to be injected. In the range of $V_t \leq V < V_{bi}$ (region II), holes accumulate at the NPB/ETL interface, leaving the ETL as the primary capacitor, with the capacitance determined by the ETL thickness (Figure 4e). At $V = V_{bi}$, the flat-band condition for the ETL is achieved, enabling electron injection into the device (Figure 4f). For $V > V_{bi}$ (region III), both hole and electron injection occur, leading to exciton formation and light emission (Figure 4g). This results in an initial strong increase, followed by a subsequent drop in capacitance. The absence of simultaneous hole and electron injection ($V_t \neq V_{bi}$) indicates

the presence of an interfacial charge, and a GSP, induced by SOP, was determined by^{35,36}

$$\sigma = \frac{C_{\text{ETL}}}{A}(V_t - V_{bi}) \quad (1)$$

$$\text{GSP} = \frac{C_{\text{ETL}}}{A\epsilon_r\epsilon_0}(V_t - V_{bi}) \quad (2)$$

where ϵ_0 is the vacuum permittivity, $\epsilon_r \cong 3.2$, $A = 9 \text{ mm}^2$, and C_{ETL} is the capacitance of ETL. The calculation data for interfacial charge density σ and GSP are shown in Table 2 and

Table 2. Summary of Calculation for C_{ETL} , σ , and GSP of ET:Liq at Various Concentrations of Liq Using Equations 1 and 2^a

ET:Liq	C_{ETL} (F)	V_t (V)	V_{bi} (V)	σ (mC/m ²)	GSP (mV/nm)
3:1	7.2×10^{-9}	1.5	2.2	0.6	19.8
1:1	7.0×10^{-9}	1.4	2.3	0.7	24.7
1:2	6.8×10^{-9}	0.15	2.7	1.9	68.0

^a C_{ETL} : ETL capacitance, V_t : transition voltage, V_{bi} : built-in voltage, σ : interfacial charge density, and GSP: giant surface potential.

Figure 4b. Increasing the Liq concentration, which has the highest PDM, leads to a rise in interfacial charge density (from 0.6 to 0.7 to 1.9 mC/m²) and GSP (from 19.8 to 24.7 to 68 mV/nm). The early hole injection observed under the (1:2) condition can be attributed to the stronger GSP, which generates an internal electric field, thereby facilitating more hole injection at lower voltages.

At the initial stage of the lifetime test for a full device having dETL, where a constant current is applied, part of the injected electrons accumulate or are trapped at the interface within the dETL. This prompts the injection of additional electrons to maintain the constant current flowing into the device. Sequentially, the highest GSP generated in ET:Liq (1:2) could facilitate the injection of the accumulated electrons or the detrapping process of trapped electrons to move toward the EML, leading to an increase in current flowing and hence reducing the applied voltage (Figures 3b and 4g,h). Additionally, this high GSP could further induce the injection of holes, evidenced by the lower V_t for the (1:2) condition, which finally recombined with injected electrons, resulting in increasing luminance observed in the overshooting effect.

Nevertheless, the SOP of ETL is commonly considered a source of exciton–polaron quenching due to the hole accumulation at the EML interface.^{37,38} To address this, appropriate device structures and material designs are to be implemented. For instance, using n-type host materials can simultaneously reduce hole accumulation at the EML/ETL (or EML/EBL) interface due to its weak hole transport ability, while the holes moving toward the ETL side due to SOP could help to broaden the recombination zone and improve the charge balance. Similarly, optimizing the charge transport properties of the HTL and ETL, among other factors, also plays an important role.

3.3. Molecular Dissociation at the Interface by LDI–TOF. To define the most possible fragments of the dissociated molecules after the lifetime test, the bond dissociation energy (BDE) was calculated through Schrodinger simulation software (Figures S6 and 5a–5c).⁹ Despite the high BDE of C–C bonds in the molecules, most of the C–N bonds possess quite low BDE values, which are supposed to be susceptible to

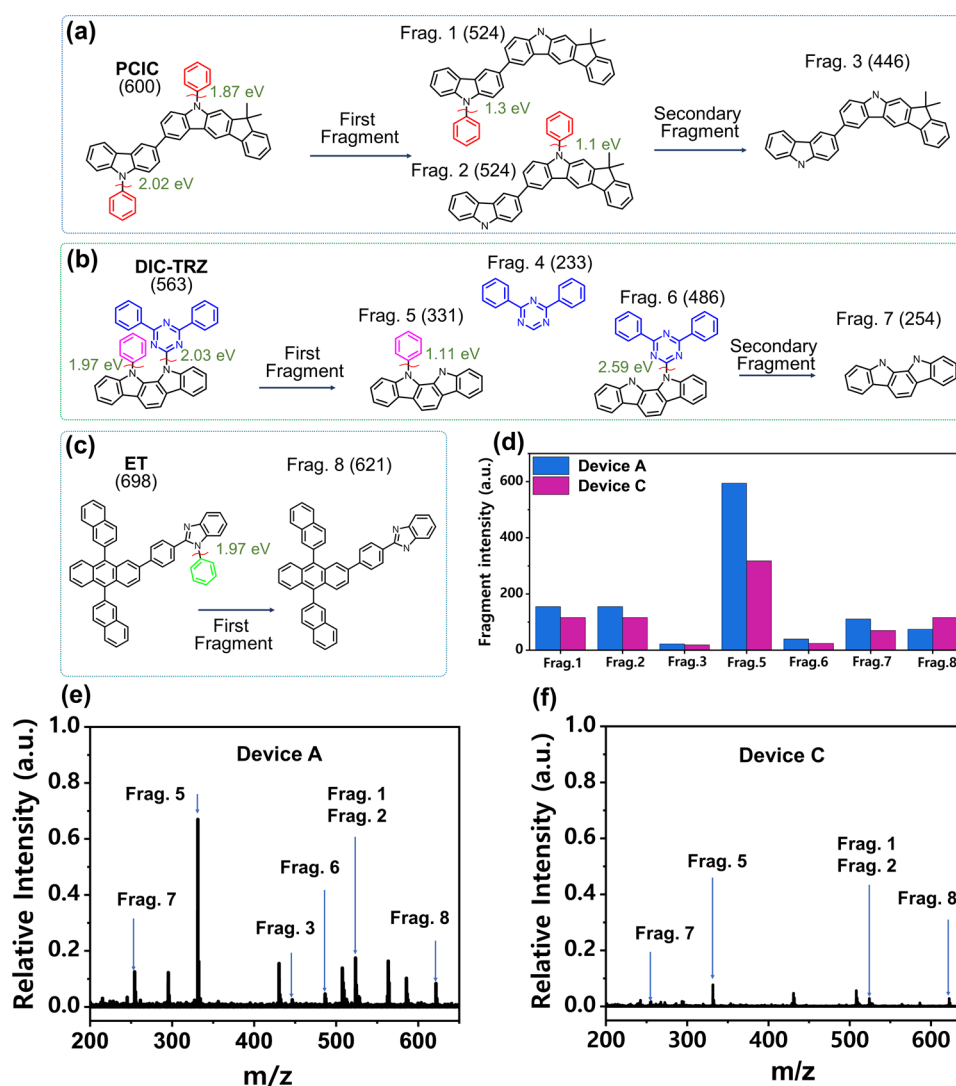


Figure 5. Fragmentations with m/z and BDE (eV) of (a) PCIC, (b) DIC-TRZ, and (c) ET. The DBE is assigned to each bond corresponding to the energy necessary to break that bond, forming further fragments. (d) Comparison of fragment intensity between degraded Device A and degraded Device C. Normalized LDI-TOF mass spectra of the degraded device: (e) Device A and (f) Device C.

dissociation under current-driven conditions. The dopant Ir(mppy)₃ shows quite a high BDE of 3.21 eV, implying its high stability. The low BDE of some first fragments made them possible to be further dissociated to form secondary fragmentation. Laser desorption/ionization–time-of-flight (LDI-TOF) mass spectroscopy was then used to detect the possible fragments of the molecules in degraded devices (Figure 5d,e). Most of the possible fragments were observed in Device A at higher intensity compared to Device C (Figure 5f). The observation of all of the possible fragments in both devices is possibly attributed to the long-time operation or high-intensity laser beam used in LDI-TOF. Nevertheless, comparing the fragment intensity in both devices would be meaningful to reveal how severely the molecules were degraded.

The fundamental and secondary fragments of DIC-RZ and PCIC (Frag. 1 → Frag. 7) were all found to be more overwhelmingly abundant in Device A compared to Device C (Figure 5f and Table 3). Frag. 1 and Frag. 2 ($m/z = 524$) and Frag. 3 ($m/z = 446$) for PCIC were detected at higher intensities of 155 and 22 in Device A compared to 116 and 19 in Device C, respectively. Frag. 5 ($m/z = 331$), Frag. 6 ($m/z =$

Table 3. Intensity of Observed Fragments from Device A and Device C after Degradation

molecule	fragmentation	m/z	intensity (au)	
			device A	device C
PCIC	frag. 1 + frag. 2	524	155	116
	frag. 3 (secondary)	446	22	19
	frag. 5	331	594	318
DIC-TRZ	frag. 6 (secondary)	486	40	24
	frag. 7	254	111	70
ET	frag. 8	621	74	116

486), and Frag. 7 ($m/z = 254$) for DIC-TRZ were also found at higher intensities of 594, 40, and 111 in Device A, while those in Device C were only 318, 24, and 70, respectively. This could come from the high stress at the interface of the EML/DIC-TRZ in Device A, as electrons quickly accumulate and quench excitons around that interface. In contrast, Frag. 8 ($m/z = 621$) of ET was detected at a lower intensity in Device A (intensity = 74) than in Device C (intensity = 116), implying that the degradation happened more severely at dETL due to accumulated/trapped electrons at the interface inside dETL. In

other words, avoiding the degradation of materials at the EML interface could elongate the stability of the device.

4. CONCLUSIONS

In conclusion, we have achieved a lifetime enhancement in its initial stage for solution-processed OLEDs through a phenomenon called the overshooting effect. This helped to suppress initial degradation and enhance the LT95 by 300% and efficiency by 130%. This improvement was achieved by implementing a dETL composed of ET and Liq. The mismatch in charge mobility and LUMO level of Liq and ET creates a charge trap inside dETL, slowing down electron current and preventing charge accumulation at the EML interface. A giant surface potential was generated at the surface of a constituent ETL that contains a higher concentration of Liq with high polarity. This giant surface potential simultaneously promoted the injection of trapped/accumulated electrons through the interface within dETL and the injection of holes from the anode, generating more exciton recombination events and ultimately enhancing efficiency by 133.0% and lifetime LT95 (luminance drops by 5%) by 300% with an overshooting effect. Additionally, the degradation at the emitting layer was mitigated by shifting the degradation zone to the dETL, which was evidenced by laser desorption/ionization–time-of-flight (LDI–TOF) mass spectroscopy.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.4c11945>.

Additional experimental details; methods including photographs of the experimental setup; and simulation data (PDF)

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Notes

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■ REFERENCES

- (1) Lee, S.; Ha, H.; Lee, J. Y.; Shon, H. K.; Lee, T. G.; Suh, M. C.; Park, Y. Degradation Mechanism of Solution-Processed Organic Light-Emitting Diodes: Sputter Depth-Profile Study. *Appl. Surf. Sci.* **2021**, *564*, No. 150402.
- (2) Lee, S. J.; Kang, J. H.; Ahn, D. A.; Shon, H. K.; Lee, T. G.; Park, S. K.; Suh, M. C.; Park, Y. Sputter Depth-Profile Study of Accelerated Interface Mixing by Thermal Annealing in Solution-Processed Organic Light-Emitting Diodes. *Adv. Mater. Interfaces* **2018**, *6*, No. 1801627.
- (3) Giebink, N. C.; D'Andrade, B. W.; Weaver, M. S.; Mackenzie, P. B.; Brown, J. J.; Thompson, M. E.; Thompson, M. E.; Forrest, S. R. Intrinsic Luminance Loss in Phosphorescent Small-Molecule Organic Light Emitting Devices Due to Bimolecular Annihilation Reactions. *J. Appl. Phys.* **2008**, *103*, No. 044509.
- (4) Sandanayaka, A. S. D.; Matsushima, T.; Adachi, C. Degradation Mechanisms of Organic Light-Emitting Diodes Based on Thermally Activated Delayed Fluorescence Molecules. *J. Phys. Chem. C* **2015**, *119*, 23845–23851.
- (5) Kondakov, D. Y. Role of Chemical Reactions of Arylamine Hole Transport Materials in Operational Degradation of Organic Light-Emitting Devices. *J. Appl. Phys.* **2008**, *104*, No. 084520.
- (6) Scholz, S.; Kondakov, D.; Lüssem, B.; Leo, K. Degradation Mechanisms and Reactions in Organic Light-Emitting Devices. *Chem. Rev.* **2015**, *115*, 8449–8503.
- (7) Ingram, G. L.; Zhao, Y.-B.; Lu, Z.-H. Exciton-Triggered Luminance Degradation of Organic Light-Emitting Diodes. *Org. Electron.* **2019**, *69*, 160–163.
- (8) Tyagi, P.; Srivastava, R.; Giri, L. I.; Tuli, S.; Lee, C. Degradation of Organic Light Emitting Diode: Heat Related Issues and Solutions. *Synth. Met.* **2016**, *216*, 40–50.
- (9) Le, T. N.; Park, E. Y.; Thangaraj, V.; Suh, M. C. Operational Lifetime Improvement of Solution-Processed OLEDs: Effect of Exciton Formation Region and Degradation Analysis by Impedance Spectroscopy. *Org. Electron.* **2021**, *99*, No. 106346.
- (10) Tsang, D. P.-K.; Matsushima, T.; Adachi, C. Operational Stability Enhancement in Organic Light-Emitting Diodes with Ultrathin Liq Interlayers. *Sci. Rep.* **2016**, *6*, No. 22463.
- (11) Takashima, D.; Takahashi, T.; Kawata, S.; Kido, J.; et al. Addition of Lithium 8-Quinolate into Polyethylenimine Electron-Injection Layer in OLEDs: Not Only Reducing Driving Voltage but Also Improving Device Lifetime. *ACS Appl. Mater. Interfaces* **2017**, *9*, 18113–18119.

- (12) Wang, J.; Zhang, M.; Zhang, Y.; Fu, J.; Qin, Y.; Li, R.; Chen, Y.; Lai, W.; Zhang, X.; Huang, W. Efficient Inverted Organic Light Emitting Devices Using a Charge-Generation Unit as Electron-Injection Layers. *Org. Electron.* **2021**, *96*, No. 106202.
- (13) Xu, W.-D.; Lai, W.-Y.; Hu, Q.; Teng, X. Y.; Zhang, Z.-W.; Huang, W. A Hydrophilic Monodisperse Conjugated Starburst Macromolecule with Multidimensional Topology as Electron Transport/Injection Layer for Organic Electronics. *Polym. Chem.* **2014**, *5*, 2942–2950.
- (14) Chen, Y.; Chu, S.; Li, R.; Qin, Y.; Xu, Y.; Zhang, X.; Wang, J.; Liu, M.; Lai, W.-Y.; Huang, W. Highly Efficient Inverted Organic Light Emitting Devices Adopting Solution-Processed Double Electron Injection Layers. *Org. Electron.* **2019**, *66*, 1–6.
- (15) Keum, C. M.; Kronenberg, N. M.; Murawski, C.; Yoshida, K.; Deng, Y.; Berz, C.; Li, W.; Wei, M.; Samuel, I. D. W.; Gather, M. C. The Role of Metallic Dopants in Improving the Thermal Stability of the Electron Transport Layer in Organic Light-Emitting Diodes. *Adv. Opt. Mater.* **2018**, *6*, No. 1800496.
- (16) Kwon, J. H.; Lee, J. Y. High Efficiency and Long Lifetime in Organic Light-Emitting Diodes Using Bilayer Electron Injection Structure. *Synth. Met.* **2009**, *159*, 1292–1294.
- (17) Choi, S. H.; Lee, S. J.; Lee, K. Y.; Yang, H. S.; Han, K.-I.; Kim, K. H.; Kim, S. D.; Bae, H. D.; Tak, Y. H. Improved Efficiency and Lifetime of Organic Light-Emitting Diode with Lithium-Quinolate-Doped Electron Transport Layer. *Jpn. J. Appl. Phys.* **2009**, *48*, No. 062101.
- (18) He, S.; Pakhomenko, E.; Holmes, R. J. Process Engineered Spontaneous Orientation Polarization in Organic Light-Emitting Devices. *ACS Appl. Mater. Interfaces* **2023**, *15*, 1652–1660.
- (19) Noguchi, Y.; Hofmann, A.; Brütting, W. Controlling Charge Accumulation Properties of Organic Light-Emitting Diodes Using Dipolar Doping of Hole Transport Layers. *Adv. Opt. Mater.* **2022**, *10*, No. 2201278.
- (20) Noguchi, Y.; Miyazaki, Y.; Tanaka, Y.; Sato, N.; Nakayama, Y.; Schmidt, T. D.; Brütting, W.; Ishii, H. Charge Accumulation at Organic Semiconductor Interfaces Due to a Permanent Dipole Moment and Its Orientational Order in Bilayer Devices. *J. Appl. Phys.* **2012**, *111*, No. 114508.
- (21) Yamanaka, T.; Nakanotani, H.; Adachi, C. The Role of Spontaneous Orientation Polarization on Charge Storage Behavior at an Interface Between Organic Semiconductor Layers. *J. Mater. Chem. C* **2024**, *12*, 1055.
- (22) Yamanaka, T.; Nakanotani, H.; Nakamoto, K.; Adachi, C. Electron Lifetime of Over One Month in Disordered Organic Solid-State Films. *Adv. Mater.* **2023**, *35*, No. 2210335.
- (23) Noguchi, Y.; Ishii, H.; Jäger, L.; Schmidt, T. D.; Brütting, W. Spontaneous Orientation Polarization in Organic Light-Emitting Diodes and Its Influence on Charge Injection, Accumulation, and Degradation Properties. In *Organic Semiconductors for Optoelectronics*; Wiley, 2021; pp 273–293.
- (24) Son, Y. H.; Boizot, J.; Kim, Y. J.; Park, M. J.; Song, W. J.; Lee, K. H.; Kwon, J. H. Efficiency Control of Organic Light-Emitting Diode for High Contrast Ratio Performance in Active Matrix Display Applications. *Curr. Appl. Phys.* **2014**, *14*, 697–701.
- (25) Jeon, S. K.; Lee, J. Y. Four Times Lifetime Improvement of Blue Phosphorescent Organic Light-Emitting Diodes by Managing Recombination Zone. *Org. Electron.* **2015**, *27*, 202–206.
- (26) Haq, K.-U.; Khan, M. A.; Jiang, X.; Zhang, Z.; Zhang, X.; Zhang, L.; Li, J. Estimation of Electron Mobility of N-Doped 4, 7-Diphenyl-1, 10-Phenanthroline Using Space-Charge-Limited Currents. *J. Semicond.* **2009**, *30*, No. 111103.
- (27) Zhang, D.; Duan, L.; Li, C.; Li, Y.; Li, H.; Zhang, D.; Qiu, Y. High-Efficiency Fluorescent Organic Light-Emitting Devices Using Sensitizing Hosts with a Small Singlet-Triplet Exchange Energy. *Adv. Mater.* **2014**, *26*, 5050–5055.
- (28) Ha, H.; Shim, Y. J.; Lee, D. H.; Park, E. Y.; Lee, I.-H.; Yoon, S.-K.; Suh, M. C. Highly Efficient Solution-Processed Organic Light-Emitting Diodes Containing a New Cross-Linkable Hole Transport Material Blended with Commercial Hole Transport Materials. *ACS Appl. Mater. Interfaces* **2021**, *13*, 21954–21963.
- (29) Kim, H. S.; Kang, J.-H.; Lee, D.; Kwak, S. K.; Ameen, S.; Lee, J.; Suh, M. C. The Behaviour of Solution-Processed Green Phosphorescent Organic Light Emitting Diodes with Undesirable Host Composition. *Org. Electron.* **2018**, *54*, 222–230.
- (30) He, Y.; Ji, M.; Hu, Y.; Yang, Q.; Yan, C.; Chen, Y.; Chang, S.; Lia, B.; Wang, J. Impact of Ferroelectricity on the Photodegradation of Charged Dye Species: Significance of Polarity Match. *J. Mater. Chem. C* **2018**, *6*, 774.
- (31) Park, S.-R.; Kang, J.-H.; Ahn, D. A.; Suh, M. C. A Cross-Linkable Hole Transport Material Having Improved Mobility Through a Semi-Interpenetrating Polymer Network Approach for Solution-Processed Green PhOLEDs. *J. Mater. Chem. C* **2018**, *6*, 7750.
- (32) Schmidt, T. D.; Jäger, L.; Noguchi, Y.; Ishii, H.; Brütting, W. Analyzing Degradation Effects of Organic Light-Emitting Diodes via Transient Optical and Electrical Measurements. *J. Appl. Phys.* **2015**, *117*, No. 215502.
- (33) Nowy, S.; Ren, W.; Wagner, J.; Weber, J. A.; Brütting, W. Impedance Spectroscopy of Organic Hetero-Layer OLEDs as a Probe for Charge Carrier Injection and Device Degradation. In *Organic Light Emitting Materials and Devices XIII*; SPIE, 2009; Vol. 7415, pp 79–90.
- (34) Jäger, L.; Schmidt, T. D.; Brütting, W. Manipulation and Control of the Interfacial Polarization in Organic Light-Emitting Diodes by Dipolar Doping. *AIP Adv.* **2016**, *6*, No. 095220.
- (35) Brütting, W.; Berleb, S.; Muckl, A. G. Device Physics of Organic Light-Emitting Diodes Based on Molecular Materials. *Org. Electron.* **2001**, *2*, 1–36.
- (36) Naqvi, B. A.; Schmid, M.; Crovini, E.; Sahay, P.; Naujoks, T.; Rodella, F.; Zhang, Z.; Strohrieg, P.; Bräse, S.; Z -Colman, E.; Brütting, W. What Controls the Orientation of TADF Emitters? *Front. Chem.* **2020**, *8*, 750.
- (37) Bangsund, J. S.; Van Sambeek, J. R.; Concannon, N. M.; Holmes, R. J. Sub-turn-on exciton quenching due to molecular orientation and polarization in organic light-emitting devices. *Sci. Adv.* **2020**, *6*, No. eabb2659.
- (38) Afolayan, E. O.; Dursun, I.; Lang, C.; Pakhomenko, E.; Kondakova, M.; Boroson, M.; Hickner, M.; Holmes, R. J.; Giebink, N. C. Reducing Spontaneous Orientational Polarization via Semiconductor Dilution Improves OLED Efficiency and Lifetime. *Phys. Rev. Appl.* **2022**, *17*, No. L051002.