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Description	

High-current Injection and Transport on Order of kA/cm^2 in Organic Light-emitting Diodes Having Mixed Organic/Organic Heterojunction Interfaces

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We manufactured multilayer organic light-emitting diodes (OLEDs) with mixed organic/organic heterojunction interfaces composed of alpha-sexithiophene and phenyldipyranylphosphine oxide carrier-transporting layers. In the mixed-interface OLEDs, we achieved a low driving voltage of 3.6 V at a current flow of $100 \text{ mA}/\text{cm}^2$, which was caused by efficient carrier injection at the mixed interfaces. We investigated how much current can flow through these OLEDs with the aim of fabricating electrically pumped organic laser diodes. We found that an OLED of this type with a small active area of $625 \text{ }\mu\text{m}^2$ on a high-thermal-conductivity sapphire substrate can sustain high current densities of $1.1 \text{ kA}/\text{cm}^2$ and emits bright electroluminescence of $7.9 \text{ Mcd}/\text{m}^2$ under direct current.

KEYWORDS: organic light-emitting diode, organic/organic heterojunction interface, high current density, electrically pumped organic laser diode

Organic light-emitting diodes (OLEDs) fabricated using a wide variety of organic molecules have been intensively studied because of their high potential for use in low-cost, thin, flexible display, and light source applications.¹⁾ Various OLED characteristics, such as external quantum efficiency,^{2,3)} power conversion efficiency,^{3,4)} and lifetime,^{5,6)} have been greatly improved during the last decade. However, despite these improvements, the driving voltages of OLEDs are still much higher than those for inorganic LEDs. Reducing the required driving voltages in OLEDs to the corresponding exciton energies of organic emitters is crucial for further improving the OLED characteristics.^{4,5)}

There have been many reports on reducing driving voltages in OLEDs using doping organic hole-transporting layers (HTLs) and electron-transporting layers (ETLs) with *p*-type dopants, such as FeCl₃,⁷⁾ 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄-TCNQ),^{4,5,8)} and MoO₃,⁹⁾ and *n*-type dopants, such as Li,¹⁰⁾ 4-phenanthridinolato Li,¹¹⁾ and Cs,^{5,8,12)} which induce a marked increase in the electrical conductivity in these doped HTLs and ETLs. However, using these dopants makes the manufacture of OLED structures complicated and costly for most practical applications. To overcome this problem, we have shown that simply mixing organic/organic heterojunction interfaces leads to a reduction in driving voltage in OLEDs. Results of our studies indicate that the

mixing of heterojunction interfaces induces an increase in the contact areas of different types of organic molecules in the mixed regions, thereby improving the efficiency of carrier injection at these heterojunctions.

We fabricated four types of OLEDs, namely, (A), (B), (C), and (D) (see Fig. 1). Devices (A) and (B) consist of conventional *N*, *N'*-diphenyl-*N*, *N'*-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (α -NPD) HTLs and tris-(8-hydroxyquinoline) aluminum (Alq_3) ETLs, and (C) and (D) consist of α -sexithiophene (α -6T) HTLs⁸⁾ and phenyldipyrenylphosphine oxide (POPy_2) ETLs¹²⁾. In (B) and (D), 5-nm-thick organic/organic mixed layers with a mixing ratio of 50/50 mol% were inserted at the α -NPD/ POPy_2 , $\text{POPy}_2/\text{Alq}_3$, and α -6T/ α -NPD interfaces. The interface mixed device (D), with the α -6T HTL and POPy_2 ETL, exhibited a low driving voltage of 3.6 V at a current density of 100 mA/cm² and a high electroluminescence (EL) level at low driving voltages: 100 cd/m² at 2.4 V and 1,000 cd/m² at 2.8 V.

A reduction in the driving voltage required for OLEDs is necessary for the development of electrically pumped organic laser diodes (OLDs). We previously estimated the threshold current density of amplified spontaneous emissions (ASEs) under electrical pumping to be 3.8 kA/cm² using an ASE threshold energy obtained in an optically pumped OLED.¹³⁾ For injecting high current densities into organic films, it

has been demonstrated that a reduction in the active area,¹⁴⁾ the use of high-thermal-conductivity substrates,¹⁵⁾ and a reduction in driving voltage⁸⁾ are effective owing to their ability to improve thermal management. In the latter part of this report, we discuss how much current can flow through the OLEDs we fabricated using these concepts. The mixed-interface device (D) with a small active area of $625\ \mu\text{m}^2$ on a high-thermal-conductivity sapphire substrate sustained a high current density of $1.1\ \text{kA/cm}^2$ and exhibited a high EL level of $7.9\ \text{Mcd/m}^2$.

Glass substrates coated with 100-nm-thick indium tin oxide (ITO) layers were used as hole-injecting electrodes. All the organic layers used were thermally evaporated in a vacuum on the precleaned ITO layers at an evaporation rate of $0.3\ \text{nm/s}$. We used green fluorescent 2,5-bis-[{bis-(4-methoxy-phenyl)-amino}-styryl]-terephthalonitrile (BST) molecules doped in a POPy₂ host layer at a concentration of 0.5 mol%, because BST-doped films show low optical ASE threshold energies on the order of $3.5\ \mu\text{J/cm}^2$.¹⁶⁾ An α -NPD layer with a large energy gap (2.9 eV) was inserted between the α -6T and POPy₂ layers in (C) and (D) to block electrons at the α -NPD/POPy₂ interfaces and prevent energy transfer from large-energy-gap POPy₂ (3.1 eV) to small-energy-gap α -6T (2.3 eV). To complete the devices, a bilayer cathode consisting of a 0.5-nm-thick LiF layer and a 100-nm-thick Al layer was vacuum-evaporated on the ETLs at an

evaporation rate of 0.02 nm/s for LiF and 0.1 nm/s for Al. The Al layer was patterned using a shadow mask with circular openings to define an active area of 785,000 μm^2 . With the aim of transporting high current densities in OLEDs, we reduced the active area of (D) from 785,000 to 625 μm^2 using photolithography.¹⁴⁾ We fabricated (D) on a high-thermal-conductivity sapphire substrate instead of on a low-thermal-conductivity glass substrate.¹⁵⁾ All the OLEDs were operated under a direct current condition to measure their room-temperature-current density-voltage-luminance (*J-V-L*) characteristics using a semiconductor parameter analyzer (E5250A, Agilent Technologies Inc.) and a calibrated silicon photodiode (1930-C, Newport Co.).

We observed a marked reduction in the driving voltage in the OLEDs that we manufactured using the interface mixing effect and α -6T HTLs and POPy₂ ETLs. The *J-V* characteristics of the OLEDs are shown in Fig. 2. The driving voltages for a current flow of 100 mA/cm² were 7.7 V for (A), 6.8 V for (B), 4.5 V for (C), and 3.6 V for (D). The driving voltage obtained in (D) is the lowest ever reported in OLEDs with undoped HTLs and ETLs.

The energy-level diagrams in the inset in Fig. 2 show the ionization potential energy (*IP*) and electron affinity (*EA*) values of the organic layers, which we measured to be -5.5 eV and -2.6 eV for α -NPD, -5.9 eV and -2.8 eV for POPy₂, -5.2 eV and -3.0 eV for

BST, -5.7 eV and -3.0 eV for Alq₃, and -5.1 eV and -2.8 eV for α -6T, respectively. These measurements were taken using an AC-1 photoelectron spectroscope (Rikenkeiki Co.) and by subtracting the optical absorption onset energies from the *IP* values. The work functions of the electrodes were -5.0 eV for ITO and -4.2 eV for Al using AC-1. On the basis of the energy-level diagrams, we calculated the heights of the heterojunction energy barriers in our OLEDs to be 0.4 eV at the α -NPD/POPy₂ and α -6T/ α -NPD interfaces and 0.2 eV at the POPy₂/Alq₃ interface. Generally, these heterojunction energy barriers lower carrier injection efficiency at the interfaces.¹⁷⁾ However, we demonstrated that using mixed organic/organic heterojunction interfaces results in a decrease in driving voltage by approximately 1 V. We attribute this to an increase in the contact areas of the different types of organic molecules in the mixed regions, leading to more efficient carrier injection at the heterojunctions. Moreover, the α -6T and POPy₂ layers can transport much higher current densities than the conventional α -NPD and Alq₃ layers,^{8,12)} which also contributes to a reduction in the required driving voltage in our OLEDs.

The external quantum efficiency-current density ($\eta_{\text{ext}}-J$) and power conversion efficiency-current density ($\eta_{\text{power}}-J$) characteristics of the OLEDs are shown in Fig. 3. The η_{ext} and η_{power} at a current density of 100 mA/cm² were 1.3% and 1.9 lm/W for (A),

1.6% and 2.7 lm/W for (B), 1.7% and 4.2 lm/W for (C), and 1.7% and 5.6 lm/W for (D).

Although the η_{ext} was almost unchanged in all the devices, the η_{power} increased by approximately 3-fold. This increase is due to a reduction in the driving voltage resulting from the use of mixed heterojunction interfaces composed of α -6T HTLs and POPy₂ ETLs, which have high carrier transport abilities.

The EL spectra of the OLEDs that were operated at a constant current density of 100 mA/cm² and the photoluminescence (PL) spectrum of a 0.5 mol%-BST-doped POPy₂ layer are shown in the inset in Fig. 3. We observed green EL from electrically excited BST molecules doped in the POPy₂ host layers. The EL peak maximum was approximately 550 nm for all the devices. Although a weak POPy₂ emission peak was observed at a shorter wavelength in the PL spectrum, this peak disappeared in the EL spectra, and all the EL spectra corresponded to the PL spectrum, suggesting that injected electrons and holes are predominantly trapped on BST molecules doped in the large-energy-gap POPy₂ layers, and are directly recombined on BST molecules to produce EL.

We fabricated (D) with a small active area of 625 μm^2 on a high-thermal-conductivity sapphire substrate to investigate its breakdown current density (J_{break}) and luminance (V_{break}). The J - V and L - J (η_{ext} - J) characteristics of several (D)s with different active

areas and substrates are shown in Figs. 4(a) and 4(b).

The breakdown current density and luminance level increased from 6.3 A/cm^2 (J_{break}) and 210 kcd/m^2 (L_{break}) to 120 A/cm^2 (J_{break}) and 1.3 Mcd/m^2 (L_{break}) when the active areas were reduced from $785,000$ to $625 \text{ }\mu\text{m}^2$. Moreover, by replacing the low-thermal-conductivity glass substrate with a high-thermal-conductivity sapphire substrate, we obtained a J_{break} of 1.1 kA/cm^2 and an L_{break} of 7.9 Mcd/m^2 , both of which are the highest values ever reported in OLEDs. When the devices were biased beyond the flat-band condition to cause carrier injection across interfacial energy barriers, the currents abruptly increased at $\approx 2 \text{ V}$. After this voltage, the J - V characteristics were controlled by a power law ($J \propto V^{5.4}$) in a wide current region of over five orders of magnitude [Fig. 4(a)]. Moreover, we observed a marked decrease in η_{ext} in a high-current region [Fig. 4(b)], which makes fabricating OLEDs difficult. One possible reason for this decreased η_{ext} is exciton quenching caused by injected charge carriers.¹⁸⁾ We are now working to solve this exciton quenching problem in order to enable the manufacture of electrically pumped OLEDs.

In summary, we achieved a reduction in driving voltage and an improvement in power conversion efficiency in OLEDs by mixing organic/organic heterojunction interfaces and using α -6T HTLs and POPy₂ ETLs with high carrier transport abilities.

The mixed-interface OLEDs had a low driving voltage of 3.6 V at a current density of 100 mA/cm² and a 3-fold improvement in power conversion efficiency when compared with a heterojunction OLED with conventional α -NPD HTLs and Alq₃ ETLs. This interface mixing method enables more efficient carrier injection at the organic/organic heterojunctions owing to an increase in the contact area of different types of organic molecules in the mixed regions. Moreover, we fabricated a mixed-interface OLED with an active area of 625 μm^2 on a high-thermal-conductivity sapphire substrate. This small-area OLED sustained an extremely high current density of 1.1 kA/cm² and exhibited a high EL level of 7.9 Mcd/m², which opens the door to the development of electrically pumped OLEDs. In a future study, we will analyze carrier injection mechanisms at mixed heterojunction interfaces using double-injection models.

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Figure captions

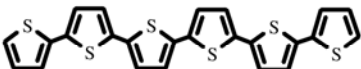
Fig. 1. Schematics of OLED structures and chemical structures of α -6T, BST, and POPy₂.

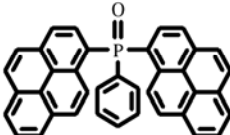
Fig. 2. J - V characteristics of (A), (B), (C), and (D). The inset shows the energy-level diagrams of these devices.

Fig. 3. η_{ext} - J and η_{power} - J characteristics of (A), (B), (C), and (D). The inset shows the EL spectra of these devices and the PL spectrum of a 0.5-mol%-BST-doped POPy₂ film.

Fig. 4. (a) J - V , (b) L - J , and η_{ext} - J characteristics of (D) with various active areas and substrates. The dotted line in (a) shows $J \propto V^{5.4}$.

Device (A)	Device (B)
Al (100 nm)	Al (100 nm)
LiF (0.5 nm)	LiF (0.5 nm)
Alq ₃ (30 nm)	Alq ₃ (25 nm)
0.5-mol%-BST-doped POPy ₂ (20 nm)	50-mol%-POPy ₂ -doped Alq ₃ (5 nm)
α -NPD (40 nm)	0.5-mol%-BST-doped POPy ₂ (20 nm)
ITO (100 nm)	50-mol%- α -NPD-doped POPy ₂ (5 nm)
Glass	α -NPD (35 nm)
	ITO (100 nm)
	Glass
Device (C)	Device (D)
Al (100 nm)	Al (100 nm)
LiF (0.5 nm)	LiF (0.5 nm)
POPy ₂ (30 nm)	POPy ₂ (30 nm)
0.5-mol%-BST-doped POPy ₂ (20 nm)	0.5-mol%-BST-doped POPy ₂ (20 nm)
α -NPD (20 nm)	50-mol%- α -NPD-doped POPy ₂ (5 nm)
α -6T (20 nm)	α -NPD (10 nm)
ITO (100 nm)	50-mol%- α -6T-doped α -NPD (5 nm)
Glass	α -6T (20 nm)
	ITO (100 nm)
	Glass


 α -6T


POPy₂

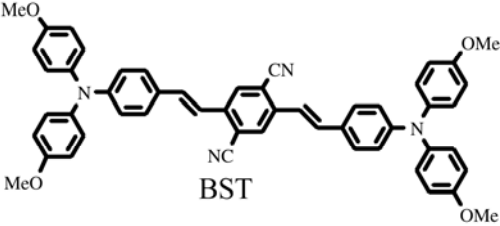

BST

Fig. 1.

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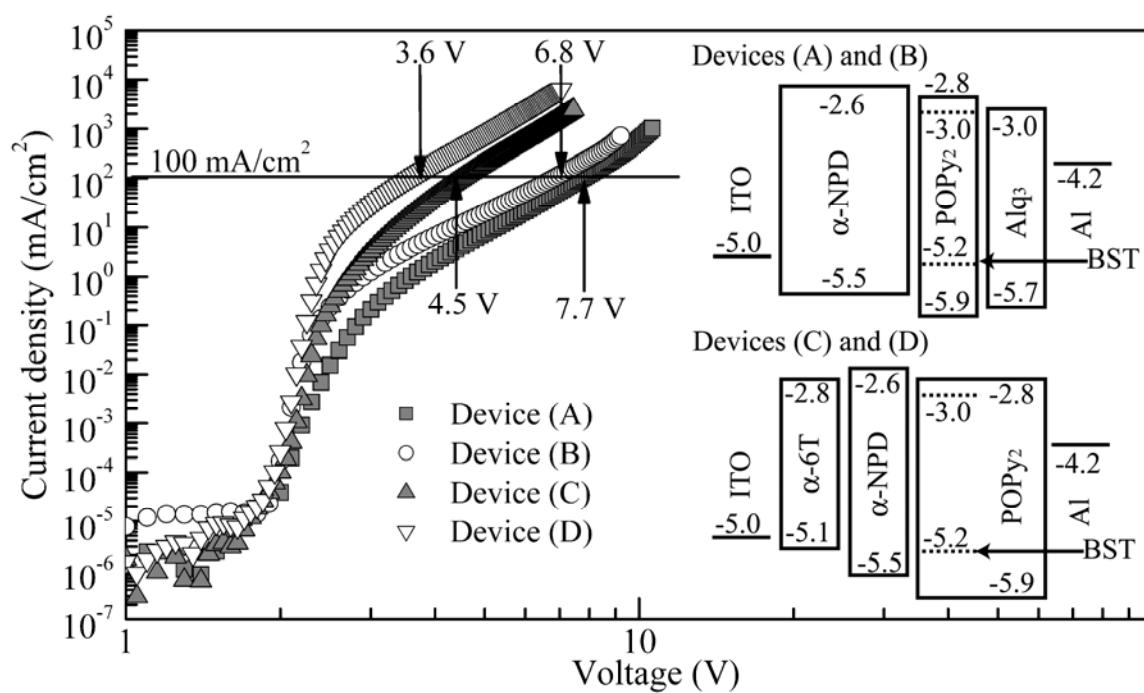


Fig. 2.

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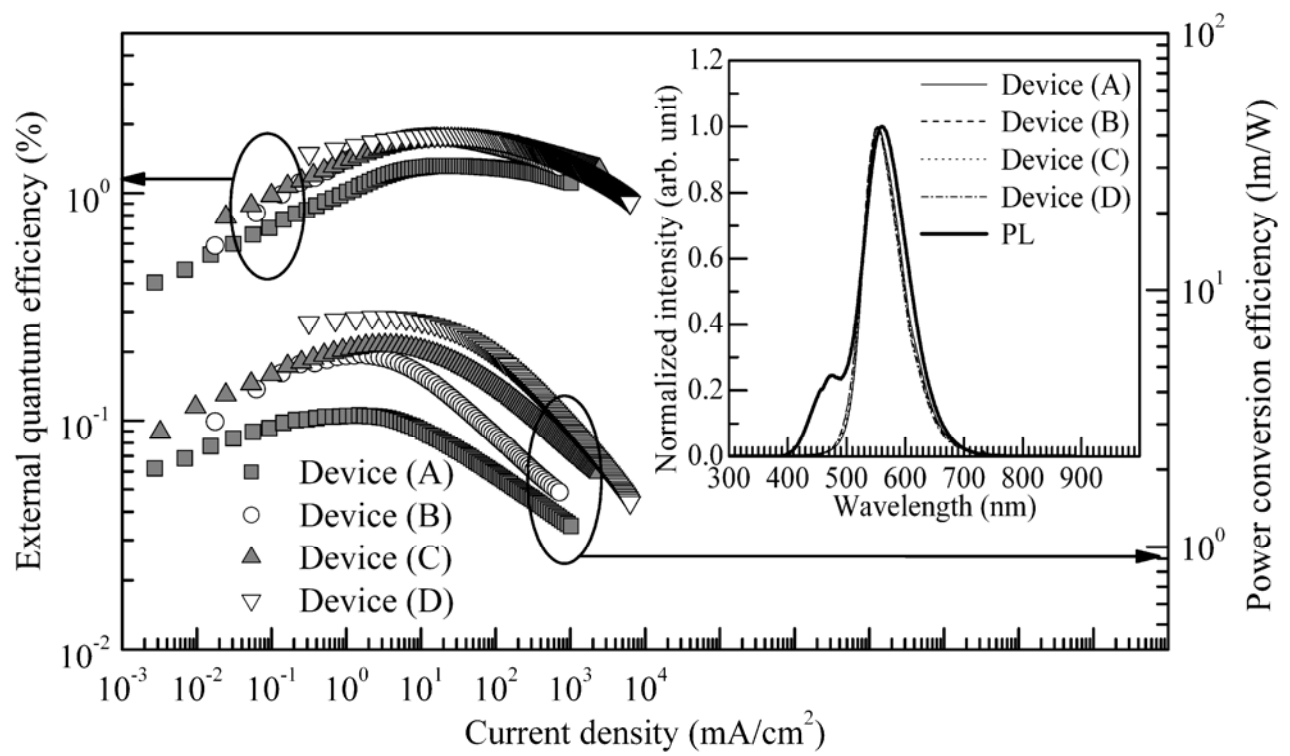


Fig. 3.

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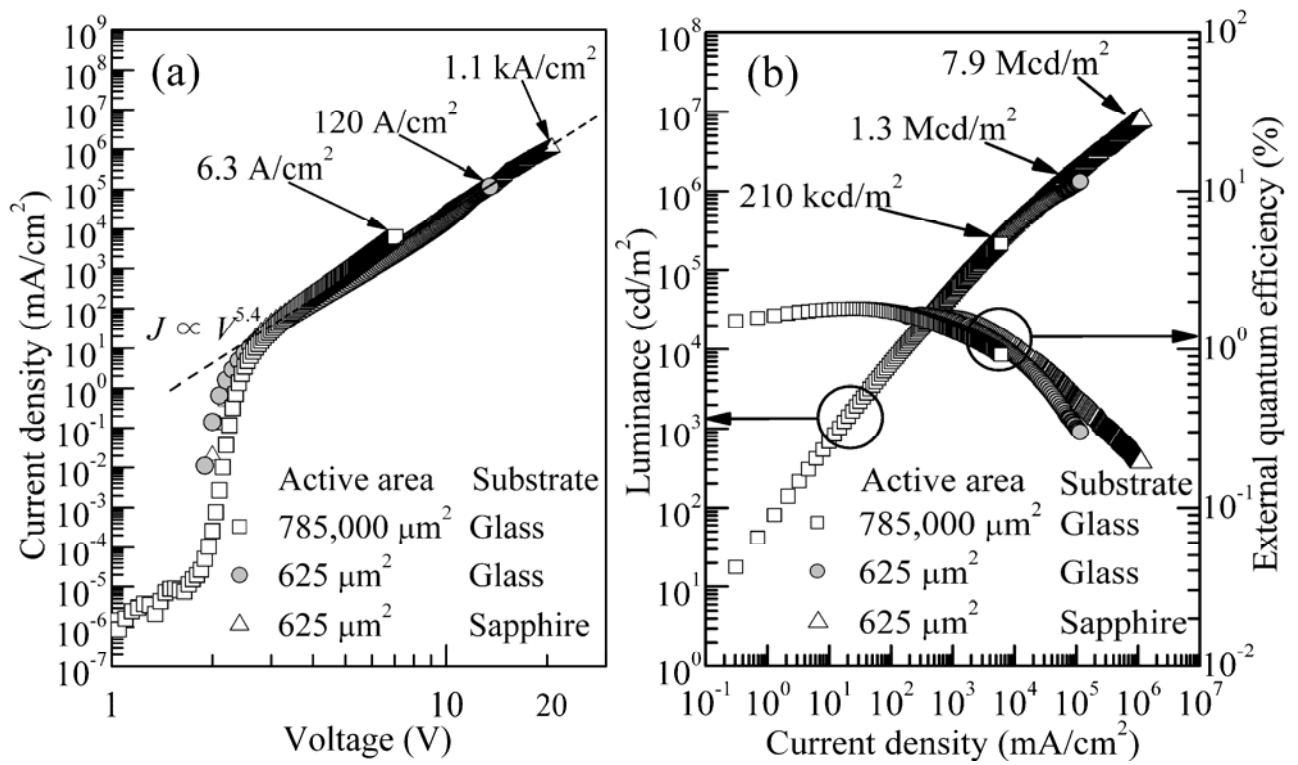


Fig. 4.

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