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Improved operational lifetime of deep-red phosphorescent organic light-emitting diodes using a benzothienobenzothiophene (BTBT)-based p-type host material

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Abstract

Although deep-red organic light-emitting diodes (OLEDs) with emission peak wavelengths beyond 660 nm are attractive candidates as unique light sources for plant growth or health-monitoring systems, the research on these OLEDs is not advanced over those emitting in other visible spectral regions. Here, we demonstrate a highly efficient and very stable deep-red OLED based on a novel exciplex host system. The developed system achieves an external quantum efficiency of 12% and shows a long lifetime of nearly 1500 h at an initial luminance of approximately 300 cd cm⁻² (current density: 25 mA cm⁻²). These are the best performance parameters reported so far in the scientific literature for a deep-red OLED. Additionally, the effect of the p-type exciplex host material on the device performance is investigated. A device based on the benzothienobenzothiophene (BTBT)-based p-type host material with superior electrochemical and thermal stabilities provides higher efficiency and more than five times longer stability than that based on the conventional p-type host material, **NPD**.

Introduction

Recently, high-performance organic light-emitting devices (OLEDs) based on exciplex host systems have attracted attention because they enable the simultaneous realization of high efficiency, low drive voltage, and long lifetime.¹⁻³ From the viewpoint of material development, exciplex systems have more flexible and tunable optoelectronic properties than the conventional single host systems.³ When exciplex systems are used, one can simply focus only on one frontier molecular orbital (MO), the highest occupied MO (HOMO) or the lowest unoccupied MO (LUMO), level that is suitable for the used emitter, and two types of host materials, p-type and n-type hosts, can be combined at an appropriate ratio to maintain the carrier balance in the emission layer (EML). On the other hand, in a single host system, multiple functionalities should be installed in a single molecule, which is one of the biggest hurdles in the design and development of novel host materials; for example, the (i) HOMO/LUMO levels, (ii) triplet energy (E_T), (iii) chemical compatibility, and (iv) carrier mobilities of holes and electrons should be controlled to control the carrier balance with respect to the target emitter.⁴ Moreover, the exciplex host system provides many opportunities beyond those of a single host system for the realization of high-performance OLEDs, especially for narrow bandgap systems that emit in the deep-red region. For example, Fujii reported a deep-red OLED using an iridium-based emitter denoted as **(DPQ)₂Ir(acac)** with a maximum external quantum efficiency

($\eta_{\text{ext,max}}$) of 10.2%.⁵ They used a single host system based on a triazole derivative. Recently, Furue developed an efficient deep-red OLED with an $\eta_{\text{ext,max}}$ of 15% using a thermally activated delayed fluorescent emitter named as **DaCNBPz** combined with a wide-energy-gap single host system.⁶ Although these OLEDs showed $\eta_{\text{ext,max}}$ of more than 10%, severe roll-off and poor lifetimes are their critical drawbacks that should be overcome. Further, Sasabe and Kido recently reported deep-red OLEDs using an iridium-based emitter, denoted as **(DPQ)₂Ir(dpm)**, and an exciplex host system based on an arylamine-based p-type **NPD** host and a triazine-based n-type **DBT-TRZ** host, and realized high $\eta_{\text{ext,max}}$ of >15%, low efficiency roll-off, and long-term stability at high brightness.⁷ However, the chemical stability of the p-type host, **NPD** has been identified to be one of the critical issues that impede further improvements in the long-term stability of the OLED. In this context, we focused on the effect of different types of p-type exciplex host materials on the performance of deep-red OLEDs. We combined three types of p-type host materials with a triazine-based n-type host material, referred to as **DBT-TRZ** (see Fig. 1 for the molecular structures of the materials). Among the studied materials, the benzothienobenzothiophene (BTBT)-based p-type host material, referred to as **BTBTPDF**,⁸ showed higher efficiency and more than five times longer stability than those based on **NPD**.

Results and Discussion

Selection of p-type host materials and their optoelectronics properties

As mentioned in the introduction, we recently reported that the chemical stability of the conventional p-type host material, NPD, is one of the critical bottlenecks that prevent further improvement of the long-term stability of the device. Here, we investigated the effect of the type of p-type host material on the deep-red OLED performance. For this, we selected three types of p-type host materials: **NPD**, **BTBTPDF**, and **DBTPB**⁹ (Fig. 1). All these materials exhibit long-term stability in conventional multilayer OLEDs. First, we conducted density functional theory (DFT) calculations to estimate the HOMO/LUMO distributions and E_T levels (**Figure 1**). Whereas the HOMOs are located on the entire molecule for these p-type host materials, the LUMOs are located on the naphthyl moieties in the case of **NPD**, DBT and biphenyl moieties in the case of **DBTPB**, and BTBT and biphenyl moieties in the case of **BTBTPDF**. The E_T levels of these hosts were calculated to be greater than 2.33 eV, sufficiently large to confine the triplet excitons of the emitter, **(DPQ)₂Ir(dpm)** ($E_T = 1.95$ eV).⁷ It has been reported that arylamine derivatives have a small bond dissociation energy (BDE) of the C–N bond toward the anion states, and this small BDE is detrimental to the long-term stability of the final

OLEDs.^{10–12} In this regard, we calculated and compared the BDEs of the C–N bond in the three host materials toward the anion states using Gaussian 09 at 298 K and 1 atm according to the reported method.¹¹ The C–N BDEs were calculated to be 1.62 eV for **NPD**, 1.64 eV for **DBTPB**, and 1.89 eV for **BTBTPDF** (**Table 1** and **Figure S1**). Thus, **BTBTPDF** has a relatively larger BDE than the other two. Then, we evaluated their optoelectronic properties in the solid state (**Table 1**). The three host materials have the same ionization potential (I_p) of -5.5 eV, as determined by photoelectron yield spectroscopy under a vacuum of 10^{-3} Pa. The UV-vis absorption edges of the p-type host were located at nearly the same wavelength of approximately 420 nm, which is equivalent to an optical energy gap (E_g) of approximately 2.9 to 3.0 eV. The E_g of **BTBTPDF** is slightly narrower than those of the other two p-type hosts, because the rigid and planar spirobifluorene unit has more extended π -conjugation than the biphenyl unit has. The electron affinities (E_a) were estimated from the I_p and E_g values to be -2.5 eV for **NPD**, -2.5 eV for **DBTPB**, and -2.6 eV for **BTBTPDF**. Further, all the host materials have similar E_T levels of 2.3–2.4 eV.^{8,9} As for the thermal properties, **BTBTPDF** has a much higher glass transition temperature (T_g) of 177 °C than **NPD** ($T_g = 100$ °C) and **DBTPB** ($T_g = 127$ °C), which is expected to prolong the device stability.

Photophysical properties of exciplex hosts

In order to confirm the formation of the exciplex, we recorded the UV-vis absorption and photoluminescence (PL) spectra of the co-deposited films of the three p-type host materials and the n-type host material, **DBT-TRZ** (1:1, molar ratio). For the co-deposited film of **BTBTPDF/DBT-TRZ**, no additional absorption peak derived from the charge-transfer (CT) complex was observed in the UV-vis absorption spectrum (**Figure 2(a)**). However, the PL spectrum of the co-deposited film showed a novel emission at 509 nm, which was not observed from the individual films of **BTBTPDF** and **DBT-TRZ** (**Figure 2(b)**). The novel emission can be attributed to the exciplex formation. This emission overlapped at approximately 500–520 nm with the UV-vis absorption band of the deep-red emitter, **(DPQ)₂Ir(dpm)**. Similarly, in the case of **DBTPB/DBT-TRZ**, a novel emission from the exciplex was observed at 522 nm, and this emission overlapped with the UV-vis absorption band of **(DPQ)₂Ir(dpm)** (**Figure S2**). Note that the exciplex emission from **NPD/DBT-TRZ** is reported to be located at 521 nm.⁷

We then evaluated the PL quantum yield (η_{PL}) values of the exciplex host films doped with 3 wt.% of the deep-red emitter, **(DPQ)₂Ir(dpm)**. The η_{PL} value was measured under N₂ flow and 330 nm excitation using an integrating sphere and a multichannel spectrometer as the optical detector. The η_{PL} values of the emitter-doped films were measured to be 48% for the film based on **BTBTPDF** and 52% for the film based on

DBTPB. These values are comparable to that of **NPD** ($\eta_{\text{PL}} = 50\%$) (**Table 1**). Accordingly, all these arylamine-based p-type host materials can form exciplexes with triphenyltriazine-based **DBT-TRZ**, and are expected to function as host materials for the deep-red emitter, **(DPQ)₂Ir(dpm)**.

Device Performances

To investigate the effect of the exciplex hosts on the device performance, we fabricated three types of OLEDs using the **(DPQ)₂Ir(dpm)**-doped exciplex hosts as EMLs and compared their performances. The device performances are summarized in **Table 2**. In these devices, we used 1,4-di(1,10-phenanthroline-2-yl)benzene (**DPB**)¹³ as an electron transporter and 8-quinolinolitolithium (**Liq**) as an electron-injection layer. The structures of the devices are as follows: ITO (130 nm)/triphenylamine-containing polymer¹⁴: 4-isopropyl-4-methyldiphenyl-iodonium tetrakis(pentafluorophenyl)borate (**PPBI**) (20 nm)/ **NPD** (20 nm) / p-type host:**DBT-TRZ** doped with 3 wt.% **(DPQ)₂Ir(dpm)** (p:n = 1:1 molar ratio) (40 nm) / **DBT-TRZ** (20 nm) / **DPB** (30 nm) / 20 wt.% **Liq**-doped **DPB** (20 nm) / **Liq** (1 nm) / Al (80 nm). The energy diagram and chemical structures of the materials used in the device are shown in **Fig. 3**. The electroluminescence (EL) spectra of the devices at 25 mA cm⁻² current density showed deep-red emission with an EL peak

at 675 nm and a weak emission peak at approximately 500–550 nm from the exciplex host in the **NPD**-based devices, suggesting insufficient energy transfer from the exciplex host to the emitter when compared with those from **BTBTPDF** and **DBTPB** to the emitter. The CIE coordinates at 100 cd m⁻² are (0.70, 0.29) for the **NPD**-based device, (0.72, 0.28) for the **DBTPB**-based device, and (0.72, 0.28) for the **BTBTPDF**-based device (**Fig. 4(a)**). Among the three hosts, **BTBTPDF** clearly exhibited superior OLED performance with low power consumption (**Table 2**). According to the current density–voltage–luminance (*J–V–L*) characteristics displayed in **Fig. 4(b)**, the **BTBTPDF**-based device provided much greater current density than those based on **DBTPB** and **NPD**. In addition, the turn-on voltage (V_{on}) for the **BTBTPDF**-based device was recorded at 2.21 V, which is much lower than those of the **NPD**-based (3.45 V) and **DBTPB**-based (2.52 V) devices. The **BTBTPDF**-based device showed the highest η_{ext} of 14.4% at 100 cd m⁻² (**Fig. 4(c)**). Although these devices showed very high η_{ext} values of 14% with low turn-on voltages, insufficient energy transfer might limit their long-term stability, LT_{80} to below 200 h at the constant current density of 25 mA cm⁻² (**Fig. 4(d)**). Therefore, we further increased the emitter concentration from 3 wt% to 10 wt%. The EL spectra recorded at 25 mA cm⁻² showed deep-red emission without the emission from the exciplexes, indicating sufficient energy transfer from the exciplex host to the emitter (**Fig. 5(a)**). Among the studied hosts,

BTBTPDF achieved the highest current density and luminance at the same voltage, suggesting its superior hole injection and transport properties (**Fig. 5(b)**). The corresponding 10 wt% emitter-doped devices showed lower turn-on voltages while maintaining high η_{ext} values of over 12% (**Fig. 5(c)**). These η_{ext} values are lower than those of 3 wt%-doped devices mainly due to the lower η_{PL} values (**Table 1**). The operational stability of the device at a constant high current density of 25 mA cm⁻² is shown in **Fig. 5(d)**. An initial luminance (L_0) of 292 cd m⁻² for the **NPD**-based device, 290 cd m⁻² for the **DBTPB**-based device, and 310 cd m⁻² for the **BTBTPDF**-based device was observed at 25 mA cm⁻². As for the device lifetime, the **BTBTPDF**-based device exhibited five times longer lifetime than the one based on the conventional p-type host, **NPD**. This is among the best reported lifetime for a deep-red OLED so far.⁷ The LT_{80} was recorded to be 280 h for the **NPD**-based device, 750 h for the **DBTPB**-based device, and 1480 h for the **BTBTPDF**-based device.

Location of the emission zone toward longer operational stability

As shown in **Figure 5**, the studied hosts provided a longer operational lifetime at a higher current density. The η_{PL} values are similar at approximately 50%. Although the order of the BDE is almost same as that of the operational lifetime, the differences in the

BDEs are not significantly large, especially between those of **NPD** and **DBTPB**, to explain the large differences in the device stability. Another important reason for the different operational stabilities could be the location of the emission zone, where interfaces such as HTL/EML¹⁰⁻¹² and/or EML/HBL¹⁵ play a critical role. To gain a deeper understanding of the operational lifetime, we fabricated three types of hole-only devices (HODs) without doping the emitter. The structures of the HODs are as follows: ITO (130 nm)/polymer buffer (20 nm)/**NPD** (20 nm) /p-type host:**DBT-TRZ** (p:n = 1:1 molar ratio) (40 nm)/**NPD** (70 nm) / Al (80 nm). According to the $J-V$ characteristics presented in **Figure S3**, the **BTBTPDF**-based device provided a significantly greater current density than those based on **NPD** and **DBTPB**. A similar tendency was observed for the three types of HODs doped with the emitter, **(DPQ)₂Ir(dpm)** (**Figure S4**). All these data suggest that the emission zone is located at the center-to-ETL side for the **BTBTPDF**-based device. In contrast, for the devices based on **DBTPB** and **NPD**, the emission zone is located at the HTL/EML interface. Therefore, electrons would be injected into the HTL, leading to a shorter operational lifetime in the case of **DBTPB**- and **NPD**-based devices because the HTL has low chemical stability against their anion state. To further confirm the location of the emission zone, we fabricated a series of partially **(DPQ)₂Ir(dpm)**-doped devices with the emissive layer structure: p-type host:**DBT-TRZ** doped with 3

wt.% **(DPQ)₂Ir(dpm)** (p:n = 1:1 molar ratio) (20 nm)/p-type host:**DBT-TRZ** (p:n = 1:1 molar ratio) (20 nm) (**Figure S5**). Among these devices, the **BTBTPDF**-based device showed much stronger exciplex emission compared with those with the other p-type hosts. This also suggests that the emission zone is located at the center-to-ETL side for the **BTBTPDF**-based device, and at the HTL/EML interface for the devices based on **DBTPB** and **NPD**. Consequently, the recombination zone should be preferably located at the center of the EML and not at the HTL/EML interface for realizing long-term stability.

Conclusion

We investigated the effect of different p-type host materials on the performance of deep-red OLEDs, and found that they play a critical role in the long-term stability of the device. Among the three p-type host materials studied, low-power-consuming deep red OLEDs were realized using **BTBTPDF** with $\eta_{\text{ext,max}}$ of 12% and an LT_{80} of nearly 1500 h at an initial luminance of approximately 300 cd cm⁻² (current density: 25 mA cm⁻²). These parameters are among the best reported so far in the scientific literature. It is clearly revealed that **BTBTPDF** has attractive features as a p-type host material, such as the highest T_g of 177 °C, aiding the realization of a thermally stable thin film, and a large

C–N BDE of 1.89 eV toward the anion state. In the case of the **(DPQ)₂Ir(dpm)**-based OLEDs, the **BTBTPDF/DBT-TRZ** exciplex host system exhibited the longest lifetime among the studied host materials owing to the preferable location of the recombination zone near the center-to-ETL side of the EML, which most likely prevents the chemical degradation of the HTL by the electron carriers. In the near future, we expect to realize high-performance and long-living phosphorescence and/or thermally activated delayed fluorescence OLEDs by combining **BTBTPDF** with a suitable n-type host material.

Supporting Information

Supporting information is available.

Acknowledgements

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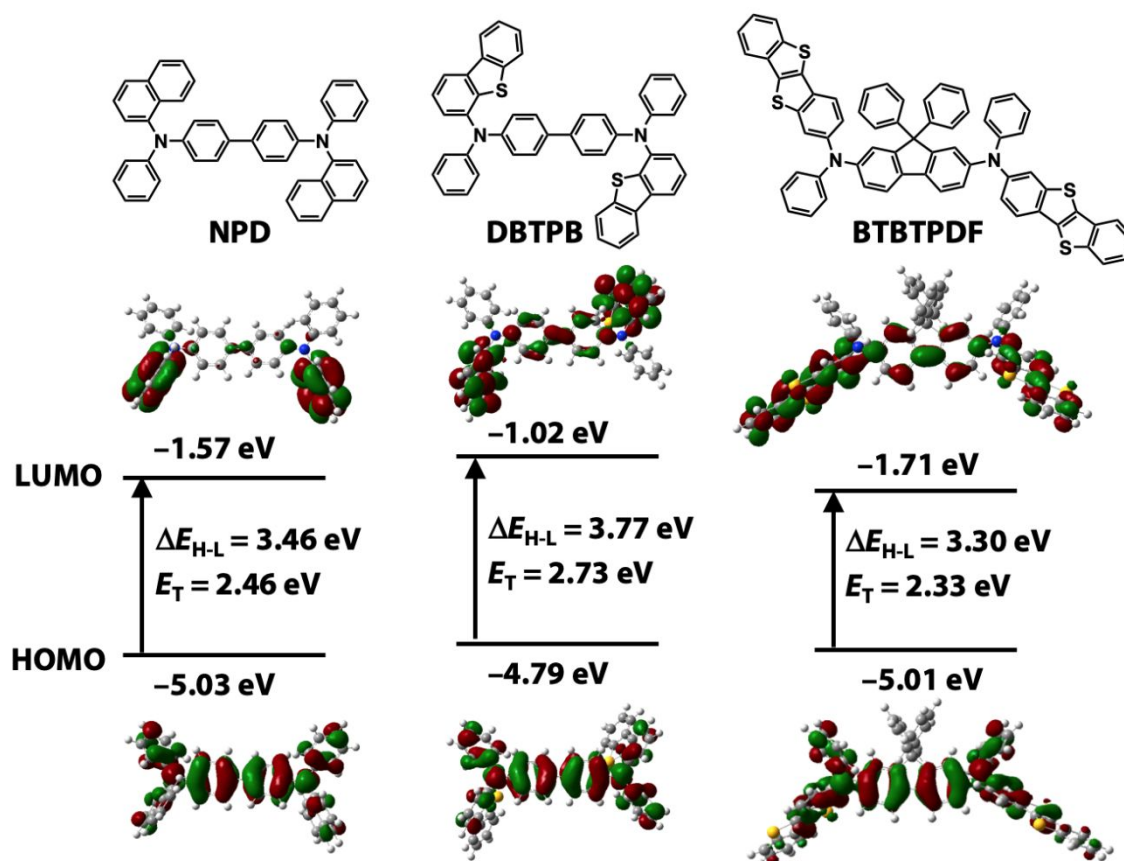


Figure 1. Molecular structures of p-type host materials and the results of DFT calculation.

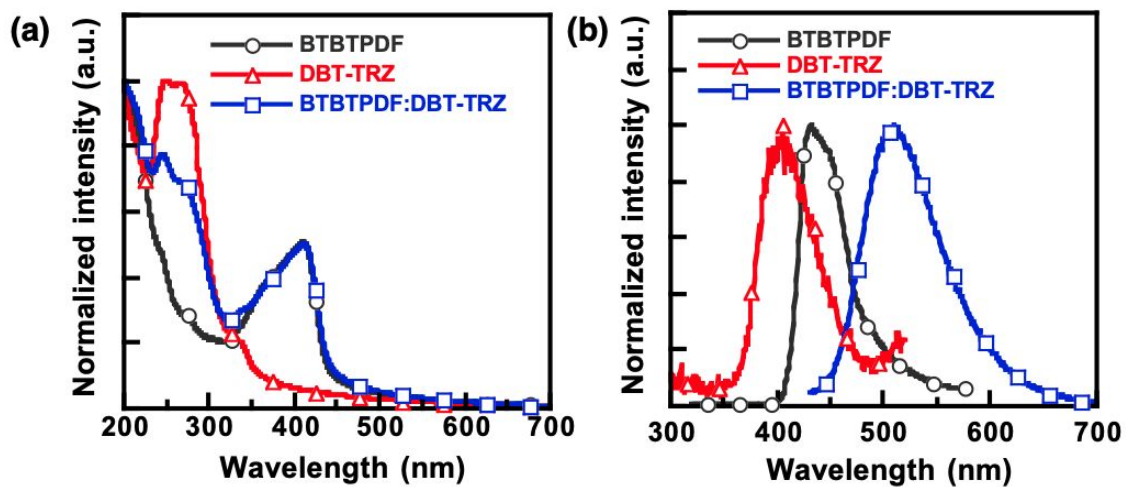


Figure 2. (a) Normalized UV-vis absorption spectra and (b) normalized PL spectra of the BTBTPDF and DBT-TRZ films, and BTBTPDF:DBT-TRZ (1:1, molar ratio) co-deposited film.

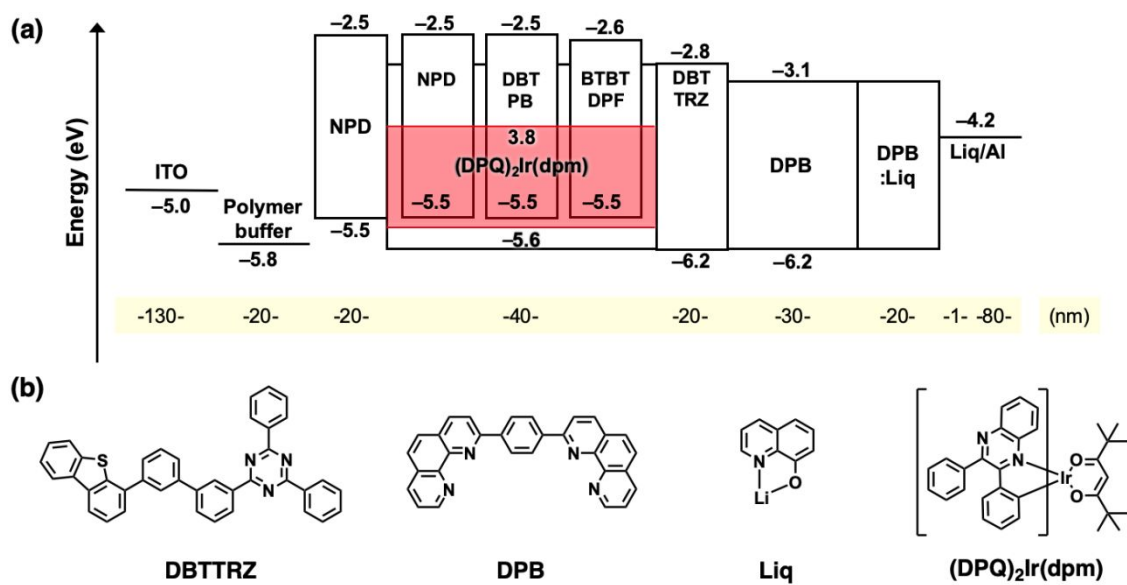


Figure 3. (a) Schematic of the device structure and the energy levels of the device. (b) Chemical structure of the materials.

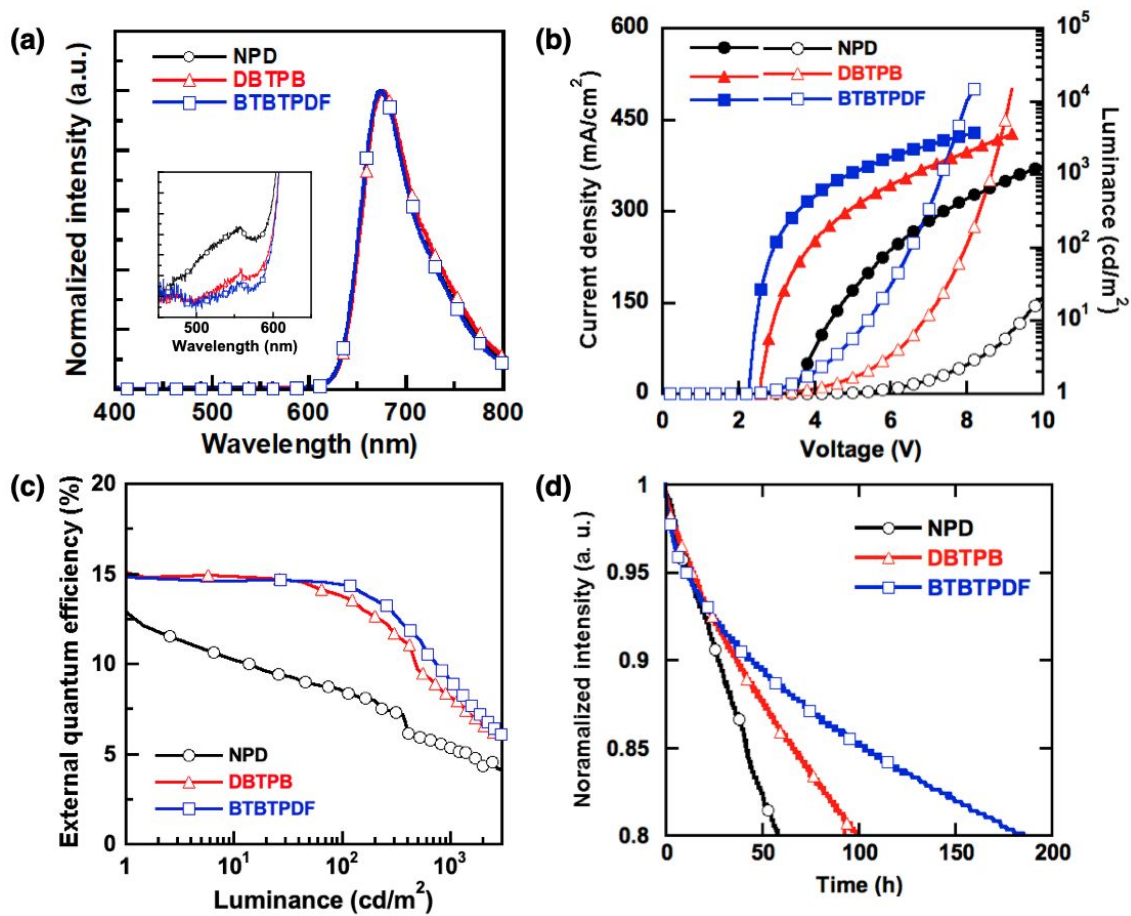


Figure 4. Performances of devices doped with 3 wt.% of the emitter: (a) EL spectra, (b) $J-V-L$ characteristics, (c) $\eta_{\text{ext}}-L$ characteristics, and (d) operational stability. In the lifetime measurement, the current density was maintained constant at 25 mA cm^{-2} .

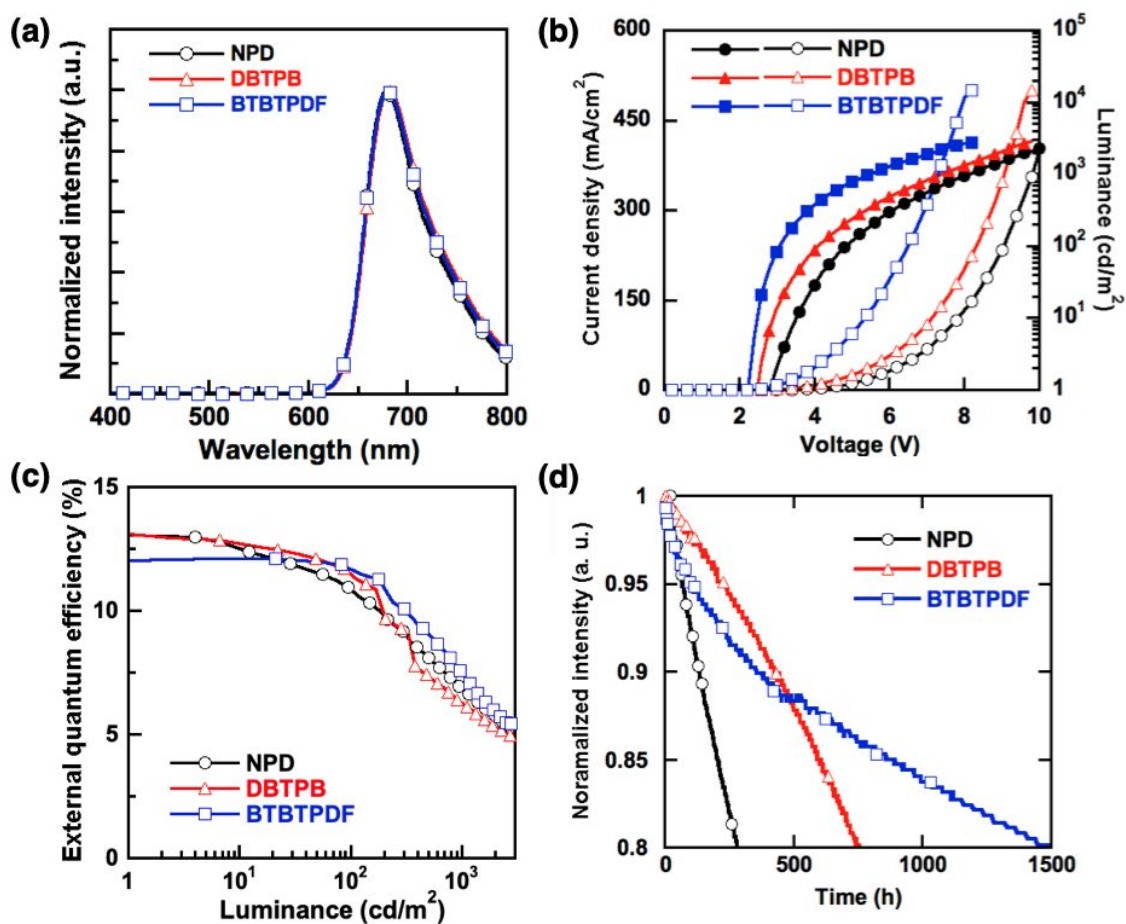


Figure 5. Performances of devices doped with 10 wt.% of the emitter: (a) EL spectra, (b) $J-V-L$ characteristics, (c) $\eta_{\text{ext}}-L$ characteristics, and (d) operational stability. In the lifetime measurement, the current density was maintained constant at 25 mA cm^{-2} .

Table 1. Properties of p-type host materials

p-type host	Mw	T_g^a (°C)	$I_p^b/E_g^c/E_a^d$ (eV)	BDE _{C-N} ^e (eV)	η_{PL}^f (%)
NPD	588.7	100	-5.5/3.0/-2.5	1.62	50/43
DBTPB	700.2	127	-5.5/3.0/-2.5	1.64	52/43
BTBTPDF	977.3	177	-5.5/2.9/-2.6	1.89	48/41

a) Measured by DSC. b) Determined by photoelectron yield spectroscopy. c) Taken as the point of intersection of the normalized absorption spectra. d) Calculated using I_p and E_g . e) The bond dissociation energy (BDE) of the C–N bond of the arylamine moiety was calculated according to the energy associated with the corresponding hemolytic cleavage of the single bond in the gas phase. f) η_{PL} values of 3 and 10 wt.% **(DPQ)₂Ir(dpm)**-doped p-type host: **DBT-TRZ**.

Table 2. Summary of OLED performances (at 3 wt.% emitter doping)

p-type host	$V_{on}/\eta_{p,on}/\eta_{c,on}/\eta_{ext,on}^{[a]}$ [V/lm W ⁻¹ /cd A ⁻¹ / %]	$V_{100}/\eta_{p,100}/\eta_{c,100}/\eta_{ext,100}^{[b]}$ [V/lm W ⁻¹ /cd A ⁻¹ / %]	$V_{1000}/\eta_{p,1000}/\eta_{c,1000}/\eta_{ext,1000}^{[c]}$ [V/lm W ⁻¹ /cd A ⁻¹ / %]	$LT_{80}^{[d]}$ [h]
NPD	3.45/1.54/1.68/13.0	6.07/0.58/1.12/8.51	9.37/0.29/0.87/5.38	58
DBTPB	2.52/2.12/1.69/15.4	3.85/1.25/1.54/13.8	6.59/0.50/1.05/8.15	100
BTBTPDF	2.21/2.59/1.82/14.9	2.93/1.89/1.76/14.4	4.90/0.76/1.19/9.07	184

[a] Voltage (V), power efficiency (η_p), current efficiency (η_c), and external quantum efficiency (η_{ext}) at 1 cd m⁻². [b] V , $\eta_{p,100}$, $\eta_{c,100}$, and $\eta_{ext,100}$ at 100 cd m⁻². [c] V , $\eta_{p,1000}$, $\eta_{c,1000}$, and $\eta_{ext,1000}$ at 1000 cd m⁻². [d] Operational lifetime at 80% of the initial luminance at the current density of 25 mA cm⁻².

Table 3. Summary of OLED performances (at 10 wt.% emitter doping)

p-type host	$V_{on}/\eta_{p,on}/\eta_{c,on}/\eta_{ext,on}^{[a]}$ [V/lm W ⁻¹ /cd A ⁻¹ / %]	$V_{100}/\eta_{p,100}/\eta_{c,100}/\eta_{ext,100}^{[b]}$ [V/lm W ⁻¹ /cd A ⁻¹ / %]	$V_{1000}/\eta_{p,1000}/\eta_{c,1000}/\eta_{ext,1000}^{[c]}$ [V/lm W ⁻¹ /cd A ⁻¹ / %]	$LT_{80}^{[d]}$ [h]
NPD	2.82/1.46/1.31/13.1	4.84/0.70/1.08/10.9	8.10/0.28/0.71/6.86	280
DBTPB	2.44/1.50/1.17/13.2	4.11/0.79/1.03/11.5	7.40/0.30/0.71/6.26	750
BTBTPDF	2.20/1.58/1.11/12.0	3.08/1.12/1.10/11.7	5.46/0.44/0.77/7.48	1480

[a] Voltage (V), power efficiency (η_p), current efficiency (η_c), and external quantum efficiency (η_{ext}) at 1 cd m⁻². [b] V , $\eta_{p,100}$, $\eta_{c,100}$, and $\eta_{ext,100}$ at 100 cd m⁻². [c] V , $\eta_{p,1000}$, $\eta_{c,1000}$, and $\eta_{ext,1000}$ at 1000 cd m⁻². [d] Operational lifetime at 80% of the initial luminance at the current density of 25 mA cm⁻².

Improved operational lifetime of deep-red phosphorescent organic light-emitting diodes using a benzothienobenzothiophene (BTBT)-based p-type host material

Graphical Abstract: Highly efficient and stable deep red OLED exhibiting external quantum efficiency of 12 % and long lifetime of nearly 1500 hours at the initial luminance of approximately 300 cd m^{-2} (at 25 mA cm^{-2}) is successfully realized by use of BTBT-based p-type host material. This result is higher efficiency and over x5 longer stability than those based on the conventional p-type host material, NPD.

Keyword: photochemistry; organic light-emitting device; solid-state emission; phosphorescence; exciplex

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