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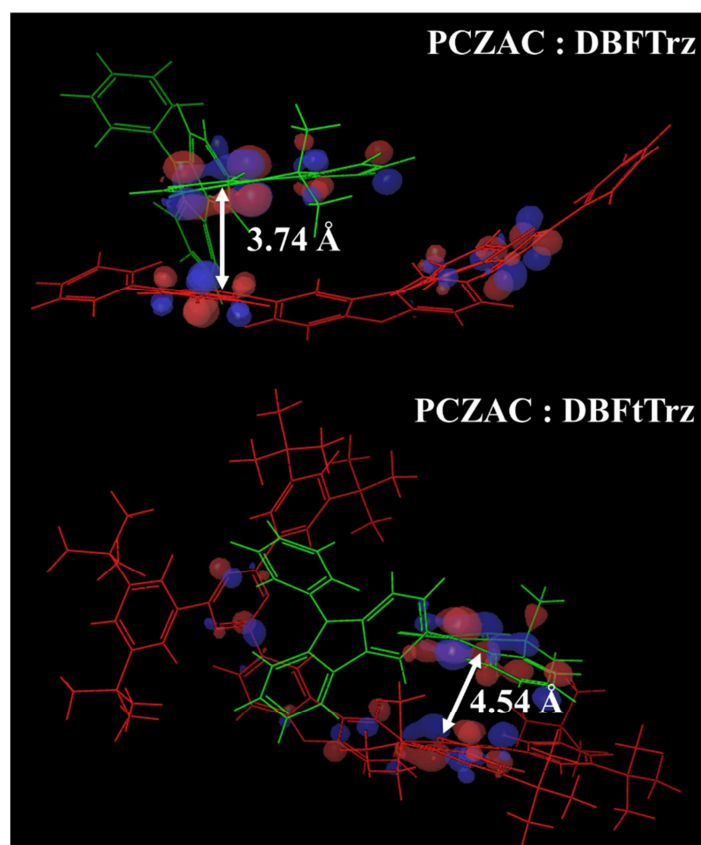
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## Design approach of exciplexes enhancing the singlet and triplet energy by managing electron transport type host

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### Abstract

A high singlet energy and triplet energy exciplex host was developed by synthesizing an electron transport type host with a controlled lowest unoccupied molecular orbital (LUMO) level and intermolecular interaction. A diphenyltriazine derived host was designed by substituting t-butyl functional moieties to the electron transporting core structure to make the LUMO shallow for high exciplex emission energy. An exciplex host with a singlet energy of 3.49 eV and a triplet energy of 3.02 eV was derived by mixing the t-butyl modified diphenyltriazine type host with a hole transport type host. The comparison of the newly developed t-butyl modified host with a previous host without the t-butyl group clarified that the t-butyl group had a singlet and triplet energy boosting effect. A high external quantum efficiency of 17.3% was demonstrated in the blue phosphorescent device using the high triplet energy exciplex host.

Keywords : exciplex, host, singlet energy, triplet energy, efficiency

## Introduction

An exciplex is a kind of material class which forms an intermolecular charge transfer complex after excitation by absorbing light. Generally, a hole transport type material is mixed with an electron transport type material to make the exciplex. In the exciplex emission process, electrons are excited from a ground state to an excited state by light absorption in the hole transport type material and then the excited electrons are transferred to an adjacent electron transport type material, which radiatively decays to the ground state of the hole transport type material. Therefore, the emission energy of the exciplex is dependent on the highest occupied molecular orbital (HOMO) of the hole transport type material and the lowest unoccupied molecular orbital (LUMO) of the electron transport type material, and exciton binding energy between holes and electrons in the exciplex.<sup>[1-2]</sup>

The exciplex has been widely used as the host of phosphorescent organic light-emitting diodes (OLEDs) because of high efficiency and low driving voltage merited by the exciplex host compared to conventional host. However, the exciplex host development was mostly focused on red and green phosphorescent OLEDs<sup>[3-14]</sup> rather than blue phosphorescent OLEDs<sup>[15-22]</sup> because it was difficult to increase the singlet and triplet energy of the exciplex host. Until now, only several high triplet energy exciplex hosts compatible with blue triplet emitters are available. Kido group reported a blue exciplex of a carbazole host and diphenylsulfone host<sup>[15]</sup>, Kim group demonstrated a blue exciplex of a carbazole host and a diphenylphosphine oxide host<sup>[17, 19]</sup>, Lee group developed an exciplex of a carbazole host and a diphenylphosphine oxide modified triazine host<sup>[22]</sup>, and our group explored an exciplex of a carbazole modified diphenylamine host and a diphenyltriazine host<sup>[20]</sup>. Other than these, no blue exciplex has been described in the literature. Therefore, it is essential to develop an exciplex for use in blue organic light-emitting diodes.

In this work, a design approach to increase the singlet and triplet energy of an exciplex host was explored by synthesizing a diphenyltriazine type electron transport type host which has an adjusted energy level and steric hindrance for high energy exciplex formation by sterically hindered t-butyl modification. It was described that the exciplex derived using the t-butyl modified diphenyltriazine type host enabled energy transfer from the exciplex host to blue emitters and harvested singlet and triplet excitons of blue emitters.

## Results and discussion

The electron transport type host designed for high singlet and triplet energy was 2,8-bis(4,6-bis(3,5-di-tert-butylphenyl)-1,3,5-triazin-2-yl)dibenzo[b,d]furan (DBFtTrz) which has a dibenzofuran core structure, triazine electron transport unit, and a t-butyl modified phenyl unit surrounding the triazine unit. DBFtTrz was different from a previous 2,8-bis(4,6-diphenyl-1,3,5-triazin-2-yl)dibenzo[b,d]furan (DBFTrz)<sup>[25]</sup> host in that two t-butyl units were substituted at 3 and 5 positions of phenyl unit in the diphenyltriazine moiety. The role of the t-butyl units would be to shift the LUMO level of the host due to the electron donating function of the t-butyl unit and to interrupt intermolecular interaction by protecting aromatic building blocks. The shifted LUMO level would increase the emission energy of the exciplex host by enlarging HOMO-LUMO offset and the suppressed intermolecular interaction may have the same effect on the emission energy by decreasing exciton binding energy.

The synthesis of DBFtTrz was carried out by Suzuki coupling reaction between 2,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[b,d]furan and 2-chloro-4,6-bis(3,5-di-tert-butylphenyl)-1,3,5-triazine prepared by Grignard reaction of 1,3-di-tert-butyl-5-chlorobenzene and cyanuric chloride. The synthesis scheme of DBFtTrz is shown in **Scheme 1**. Recrystallization and column chromatography purification of the crude product provided a

pure product at a production yield of 81% and vacuum sublimation produced a highly pure final product.

Ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) emission behaviors of DBFtTrz were measured for basic photophysical analysis. **Figure 1** shows UV-vis absorption spectra, fluorescence at room temperature and phosphorescence at 77 K. The phosphorescence was observed from 426 nm and the triplet energy was 2.91 eV from the first phosphorescence peak. Peak position of fluorescence was 387 nm, which corresponded to a singlet energy of 3.20 eV. UV-vis absorption spectra estimated the HOMO-LUMO gap from the edge of the absorption spectra. The HOMO-LUMO gap of the DBFtTrz was 3.59 eV. Energy levels of DBFtTrz were determined from the HOMO gathered from electrochemical cyclic voltammetry (CV) measurement and UV-vis absorption gap. The UV-vis and CV data of DBFtTrz offered the HOMO/LUMO of -6.59/-3.00 eV, which was relatively shallow compare to -6.64/-3.07 eV of DBFTrz without the t-butyl blocking groups. The t-butyl blocking groups made the energy level shallow due to electron donating character of the t-butyl functional group. Therefore, the DBFtTrz would generate high energy exciplex as an electron transport type host compared to DBFTrz because the HOMO-LUMO offset between two hosts in the exciplex would be increased.

As the DBFtTrz host was designed as an electron transport type host for exciplex host, it was mixed with a hole transport type 9,10-Dihydro-9,9-dimethyl-10-(9-phenyl-9H-carbazol-3-yl)-acridine (PCZAC)<sup>[26]</sup> host to develop a high emission energy exciplex. The exciplex emission of PCZAC:DBFtTrz host was compared with that of PCZAC:DBFTrz to understand the effect of t-butyl modification on the exciplex emission energy. Fluorescence and phosphorescence spectra of PCZAC:DBFtTrz and PCZAC:DBFTrz are shown in Figure 2. The fluorescence spectra of each material included in the exciplexes were added in Figure S1 in supporting information. Singlet energy and triplet energy were obtained from the onset

wavelength of the PL spectra at room temperature (fluorescence) and 77 K (phosphorescence). Overall, the onset wavelength of the PL spectra was shifted to short wavelength in the PCZAC:DBFtTrz exciplex. Singlet energy/triplet energy values of PCZAC:DBFtTrz and PCZAC:DBFTrz were 3.05/2.98 eV and 2.95/2.95 eV, respectively. Both singlet energy and triplet energy of the exciplex were increased by adopting the t-butyl modified DBFtTrz host instead of DBFTrz host. This can be correlated with the HOMO-LUMO offset and geometrical structure of the exciplex. The HOMO-LUMO offset of the exciplex is increased by the LUMO level shift in the DBFtTrz, which lead to large emission energy in the exciplex. In addition, the geometrical structure separating the aromatic units of PCZAC and DBFtTrz weakens the binding of two molecules, which decreases the exciton binding energy and increases the emission energy.

Molecular dynamics (MD) simulation was conducted with PCZAC: DBFTrz and PCZAC: DBFtTrz. After performing a MD simulation with a cubic structure consisting of two hosts, the trajectory distribution was visualized by DFT calculation. MD and DFT simulation results are shown in Figure 3. With the introduction of the t-butyl group, the distance between the HOMO dominant unit (acridine) of the donor forming the two exciplexes and the LUMO dominant unit (triazine) of the acceptor was affected. The distance between the acridine and triazine of PCZAC: DBFTrz was 3.74 Å, while that of PCZAC: DBFtTrz was 4.54 Å. This result suggests that the t-butyl group reduces the attractive interaction between the two host molecules constituting the exciplex, reduces the exciton binding of the exciplex and then shifts the emission wavelength to a short wavelength.

The singlet and triplet energy boosting effect of t-butyl modified DBFtTrz was validated by monitoring the emission spectrum of blue emitter doped exciplex. A common fluorescent emitter, TBPe, was a blue emitter to study the Forster energy transfer from the exciplex to the fluorescent emitter. The emission spectrum of the blue emitter doped PCZAC:DBFtTrz and

PCZAC:DBFTrz exciplexes is shown in Figure 4. It is clear from the emission spectrum that the emission of the TBPe doped PCZAC:DBFTrz is a mixed emission of exciplex and TBPe due to incomplete energy transfer, while that of TBPe doped PCZAC:DBFtTrz reflects TBPe emission due to efficient energy transfer. As the singlet energy of the PCZAC:DBFtTrz was higher than that of PCZAC:DBFTrz, the energy transfer from the exciplex host to the blue emitter was efficient in the DBFtTrz based exciplex.

The effect of the increased triplet energy in the DBFtTrz derived exciplex was confirmed using tris(4-carbazoyl9-ylphenyl)amine (TCTA):DBFtTrz exciplex. TCTA:DBFTrz was a reference exciplex and fac-tris(3-(1-(2,6-diisopropylphenyl)-1H-imidazol-2-yl)benzonitrile)Iridium ( $\text{Ir}(\text{CNpi})_3$ ) was a blue phosphorescent emitter to examine the effect of DBFtTrz. Emission spectra of the  $\text{Ir}(\text{CNpi})_3$  doped TCTA:DBFtTrz and TCTA:DBFTrz exciplexes are shown in Figure 5. As can be expected from the emission spectra, the emission of the  $\text{Ir}(\text{CNpi})_3$  doped TCTA:DBFtTrz is a pure emission of the phosphorescent emitter, but that of the  $\text{Ir}(\text{CNpi})_3$  doped TCTA:DBFTrz is a mixture of exciplex emission and  $\text{Ir}(\text{CNpi})_3$  emission, indicating incomplete energy transfer from the TCTA:DBFTrz exciplex to the  $\text{Ir}(\text{CNpi})_3$  emitter due to low triplet energy (2.90 eV at onset energy)<sup>[23]</sup>. This was also confirmed by the emission spectra of the TCTA:DBFTrz: $\text{Ir}(\text{CNpi})_3$  and TCTA:DBFtTrz: $\text{Ir}(\text{CNpi})_3$  devices in Figure S2. Pure  $\text{Ir}(\text{CNpi})_3$  emission was observed in the TCTA:DBFtTrz: $\text{Ir}(\text{CNpi})_3$  device, but complex emission of exciplex and  $\text{Ir}(\text{CNpi})_3$  was detected in the TCTA:DBFTrz: $\text{Ir}(\text{CNpi})_3$  device. The efficiency was also reduced by the incomplete energy transfer. The low triplet energy issue was overcome in the TCTA:DBFtTrz exciplex, which incurred pure  $\text{Ir}(\text{CNpi})_3$  emission by energy transfer. The singlet energy/triplet energy values of the TCTA:DBFTrz and TCTA:DBFtTrz were 2.95/2.81 eV and 3.17/2.92 eV, respectively. The singlet energy and triplet energy of the exciplexes are summarized in Table S1 in supporting information.



Encouraged by the complete triplet energy transfer from the DBFtTrz derived exciplex to a blue phosphorescent emitter, blue phosphorescent OLEDs were developed using high triplet energy exciplex hosts. Two exciplexes with the DBFtTrz platform, TCTA:DBFtTrz and 3,5-di(9H-carbazol-9-yl)-N,N-diphenylaniline (DCDPA):DBFtTrz, were applied as the hosts of Ir(CNpi)<sub>3</sub>. The singlet energy/triplet energy values of the TCTA:DBFtTrz and DCDPA:DBFtTrz exciplexes were 3.17/2.92 eV and 3.49/3.02 eV, respectively, as projected from the fluorescence and phosphorescence spectra in Figure 6. The emission energy was relatively high in the DCDPA:DBFtTrz exciplex. The two exciplexes showed rather large singlet energy-triplet energy splitting possibly due to weak binding of the two materials in the exciplexes, suggesting that they are not thermally activated delayed fluorescence type exciplexes. All PL spectra of the exciplexes are shown in Figure S3.

Device analysis data of the exciplex host based blue phosphorescent OLEDs are summarized in Figure 7. The current density (J) of the exciplex device was high in the TCTA:DBFtTrz device because of better hole injection property of TCTA than that of DCDPA as predicted from the energy level diagram in Figure 7 (a). Luminance (L) of the device also showed the same trend.

External quantum efficiency (EQE) data of the exciplex devices are shown in Figure 7 (c). The maximum EQEs of the exciplex devices were 12.3% and 17.3% in the TCTA:DBFtTrz and DCDPA:DBFtTrz devices, respectively. At 1,000 cd/m<sup>2</sup>, the EQEs were 9.1% and 12.0% in the TCTA:DBFtTrz and DCDPA:DBFtTrz devices, respectively. The EQE was rather high in the DCDPA:DBFtTrz exciplex device due to high triplet energy harvesting all triplet excitons of Ir(CNpi)<sub>3</sub>. This can be confirmed by the relatively low PL quantum yield of the Ir(CNpi)<sub>3</sub> doped TCTA: DBFtTrz (0.42) compared to that of the Ir(CNpi)<sub>3</sub> doped DCDPA: DBFtTrz (0.53). Moreover, balanced carrier density in the DCDPA:DBFtTrz device also contributed the relatively high EQE in the DCDPA:DBFtTrz device.

Device emission spectra at a luminance of 1,000 cd/m<sup>2</sup> are presented in Figure 7 (d). Exactly the same spectra were observed in the two exciplex devices because of energy transfer. The color coordinates of the Ir(CNpi)<sub>3</sub> doped TCTA:DBFtTrz and DCDPA:DBFtTrz devices were (0.16,0.24) and (0.15,0.23). The PL and EL emission spectra of the DCDPA:DBFtTrz:Ir(CNpi)<sub>3</sub> were quite similar as shown in Figure S4. Table 1 summarized the device results of the blue phosphorescent OLEDs.

## Conclusions

A singlet and triplet energy boosting host in the exciplex, DBFtTrz, was synthesized and emission behavior as the exciplex and the host in the blue phosphorescent OLEDs was investigated. The DBFtTrz based exciplex showed higher singlet and triplet energy than a similarly designed DBFTrz by the t-butyl functional unit and performed well as the electron transport type host in the exciplex host. Therefore, the t-butyl functional group based electron transport type host design would be useful to develop high energy exciplex host for blue OLEDs.

## Experimental

### General information

Cyanuric chloride and 1-bromo-3,5-di-tert-butylbenzene were purchased from TCI. Co. Mg turning was purchased from Sigma-Aldrich, Inc. Tetrakis(triphenylphosphine)palladium(0) (Pd(pph<sub>3</sub>)<sub>4</sub>) was purchased from Sunfine global Co. Ltd. Dichloromethane (MC) for high performance liquid chromatography and potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) were purchased from Duksan Sci. Co. Tetrahydrofuran (THF) was purchased from Samchun pure chemical Co. Ltd and distilled with sodium and calcium hydride.

The ultraviolet- visible (UV-Vis) spectra were measured to analyze absorption of compounds using a sample dissolved in refined THF. The photoluminescence (PL) was measured to analyze PL spectra of compounds dissolved in refined THF. Low temperature PL measurement was carried out at 77 k to measure triplet energy of compounds. The  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were recorded to identify the compounds. Samples were dissolved in deuterated dimethyl sulfoxide ( $\text{DMSO-d}_6$ ) for  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurement. The mass data were recorded by liquid chromatography-mass spectrometer (LC-MS) to measure the molecular weight of compounds.

## Synthesis

### **2-Chloro-4,6-bis(3,5-di-tert-butylphenyl)-1,3,5-triazine (1)**

2-Chloro-4,6-bis(3,5-di-tert-butylphenyl)-1,3,5-triazine was synthesized according to the synthetic method of 2-chloro-4,6-bis(3,5-di-tert-butylphenyl)-1,3,5-triazine<sup>[24]</sup> using 8.00 g (35.6 mmol) of 1-bromo-3,5-di-tert-butylbenzene. Purification by column chromatography (dichloromethane : n-hexane (1:4)) and drying afforded a white powder as a product (8.13 g, 72 % yield).

### **2,8-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[*b,d*]furan (2)**

2,8-Diboronic ester dibenzofuran was synthesized according to the synthetic method of previous research<sup>[25]</sup>. Crude product was purified by column chromatography (dichloromethane:n-hexane (1:4)) and complete drying afforded a white product (12.2 g, 64.4% yield).

**2,8-Bis(4,6-bis(3,5-di-tert-butylphenyl)-1,3,5-triazin-2-yl)dibenzo[b,d]furan (DBFtTrz)**

Compound **1** (4.92 g, 10.0 mmol), Compound **2** (2.0 g, 4.8 mmol), Pd(pph<sub>3</sub>)<sub>4</sub> (0.17 g, 0.144 mmol) and K<sub>2</sub>CO<sub>3</sub> (2.0 g, 14.4 mmol) were stirred in a two-neck round-bottomed flask filled with THF (100 ml) under a nitrogen atmosphere. The solution was refluxed overnight. Cooling of the mixture followed by extraction using dichloromethane and distilled water, separation of the dichloromethane layer, and evaporation of the solvent afforded a crude product. Crude product was purified by column chromatography (dichloromethane:n-hexane (1:2)) and vacuum sublimation, yielding a white product (4.2 g, 81% yield) with a purity of 99.5% from high performance column chromatography analysis.

<sup>1</sup>H NMR (500 MHz, dimethylsulfoxide-d<sub>6</sub>): δ 9.324 (s, 2H), 8.964-8.943 (d, 2H, J=10.5 Hz), 8.682 (s, 8H), 7.855-7.837 (d, 2H, J=9.0 Hz), 7.721 (s, 4H), 1.468 (s, 72H). <sup>13</sup>C NMR (125 MHz, dimethylsulfoxide-d<sub>6</sub>): δ 172.50, 172.41, 159.66, 151.44, 135.88, 132.82, 129.77, 127.12, 124.86, 123.36, 122.28, 112.27, MS (API-) m/z: 1080.5 [(M + H)].

**Molecular dynamics simulations**

The MD simulation and minimization process to investigate the geometry between the two molecules was performed using the desmond tool and the jaguar tool, which are the modules of the schrodinger material science suite. In addition, Equilibration simulations are performed on the NPT ensemble via the Nose-Hoover chain and the Martyna-Tobias-Klein method. The simulation box was set as a buffer with a boundary distance of 10 Å and cut-off when it exceeded.

**Device fabrication and characterization**

All organic materials except for poly(3,4-ethylenedioxythiophene):poly (styrene sulfonate (PEDOT: PSS) used in OLED devices were vacuum deposited at a pressure of  $1.0 \times 10^{-7}$  Torr. The device structure is indium tin oxide (50 nm) / PEDOT:PSS (40 nm)/1,1-bis(4-bis(4methylphenyl)aminophenyl)-cyclohexane (TAPC) (20 nm)/ 1,3-bis(N-carbazolyl)benzene (mCP) (10 nm)/ exciplex hosts:Ir(CNpi)<sub>3</sub> (30 nm:5 wt%)/diphenyl-4-triphenylsilylphenyl-phosphine oxide (TSPO1) (5 nm)/1,3,5-tris(1-phenyl-1Hbenzimidazol-2-yl)benzene (TPBi) (30 nm)/LiF (1 nm)/Al (200 nm). The ratio of the two hosts constituting the exciplex was 50:50. Chemical structures of the materials are displayed in Figure S5 in supporting information. Electrical and optical analysis was performed using a Keithley 2400 source measurement tool and a CS2000 spectroradiometer.

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**List of table**

Table 1. Summary of the device results of the blue phosphorescent OLEDs.

Table 1. Summary of the device results of the blue phosphorescent OLEDs.

	Driving Voltage <sup>*</sup> [V]	QE* [%]	QE <sub>MAX</sub> [%]	CIE x <sup>*</sup>	CIE y <sup>*</sup>
<b>TCTA:DBFtTrz</b>	5.5	9.1	12.3	0.16	0.24
<b>DCDPA:DBFtTrz</b>	5.9	12.0	17.3	0.15	0.23

QE: external quantum efficiency  
<sup>\*</sup> : Data at a luminance of 1000 cd/m<sup>2</sup>

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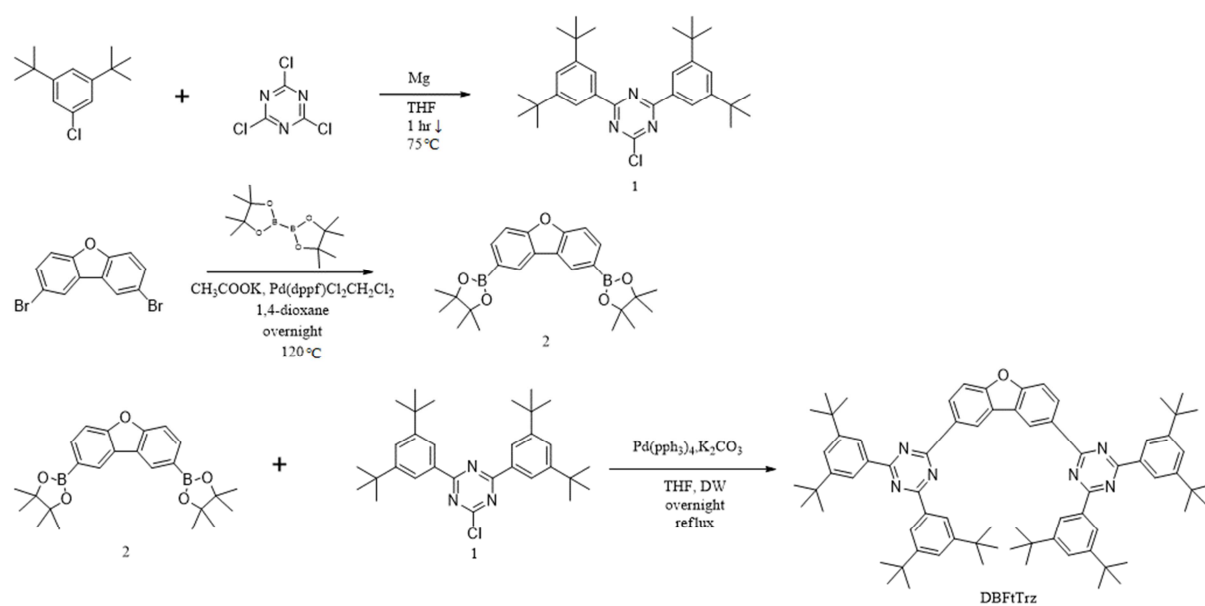
Figure 4. The emission spectrum of TBPe doped PCZAC:DBFtTrz (a) and PCZAC:DBFtTrz (b).

Figure 5. Emission spectra of the Ir(CNpi)<sub>3</sub> doped TCTA:DBFtTrz (a) and TCTA:DBFtTrz exciplexes (b).

Figure 6. Fluorescence and phosphorescence spectra of TCTA:DBFtTrz (a) and DCDPA:DBFtTrz (b) exciplexes

Figure 7. Device configuration (a), current density-voltage-luminance curves (b), EQE-current density curves (c), and EL spectra of the exciplex devices.

Scheme 1.



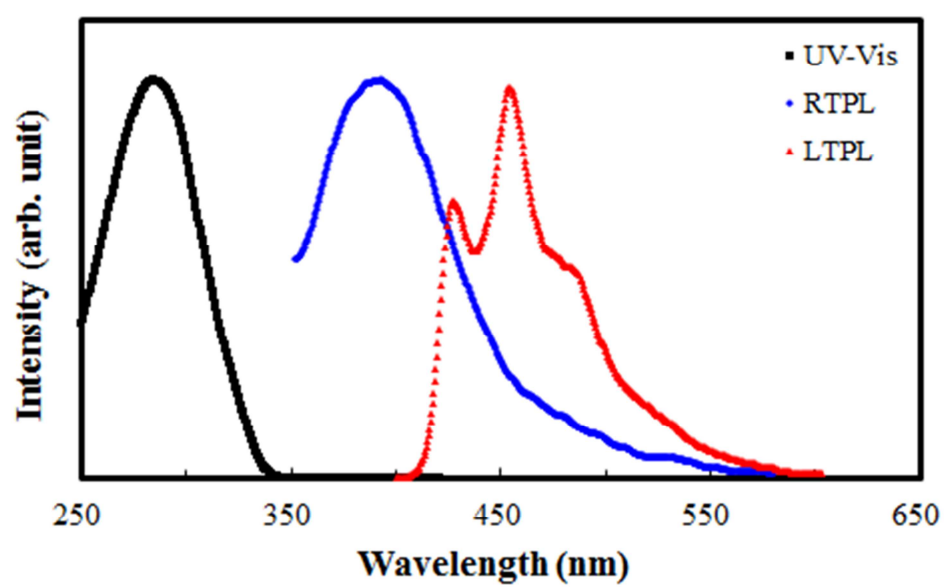


Figure 1.

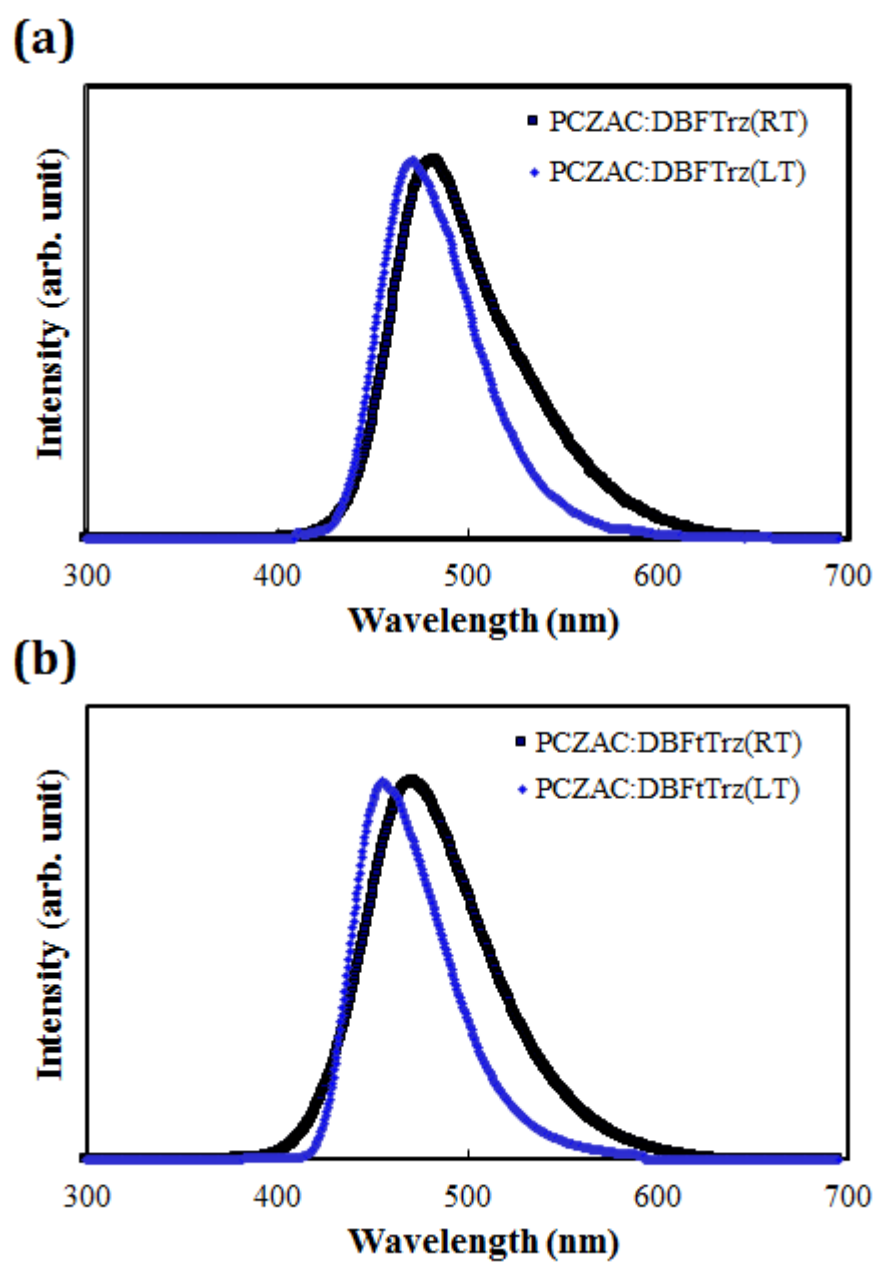


Figure 2.

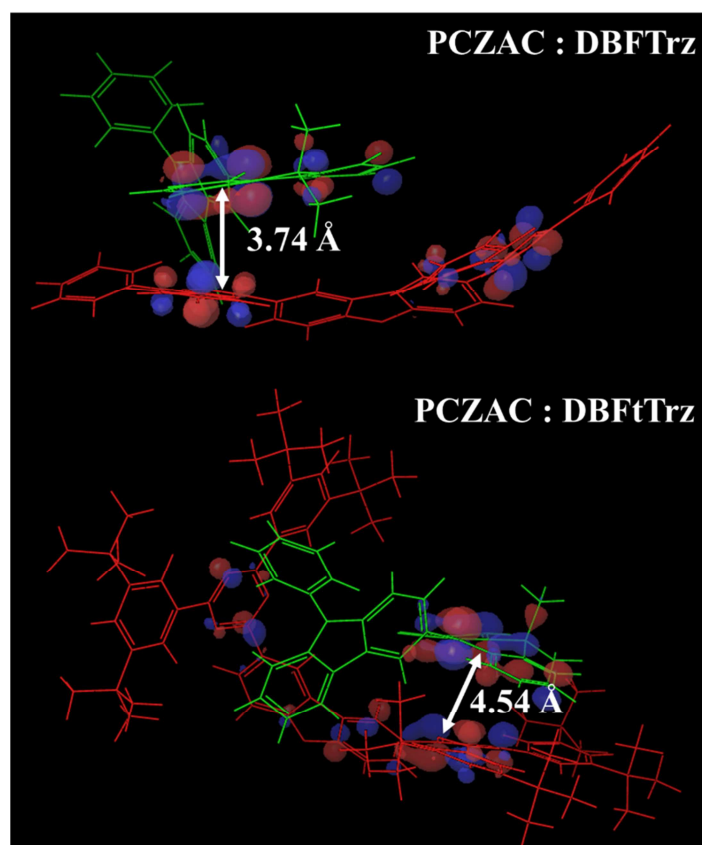


Figure 3.

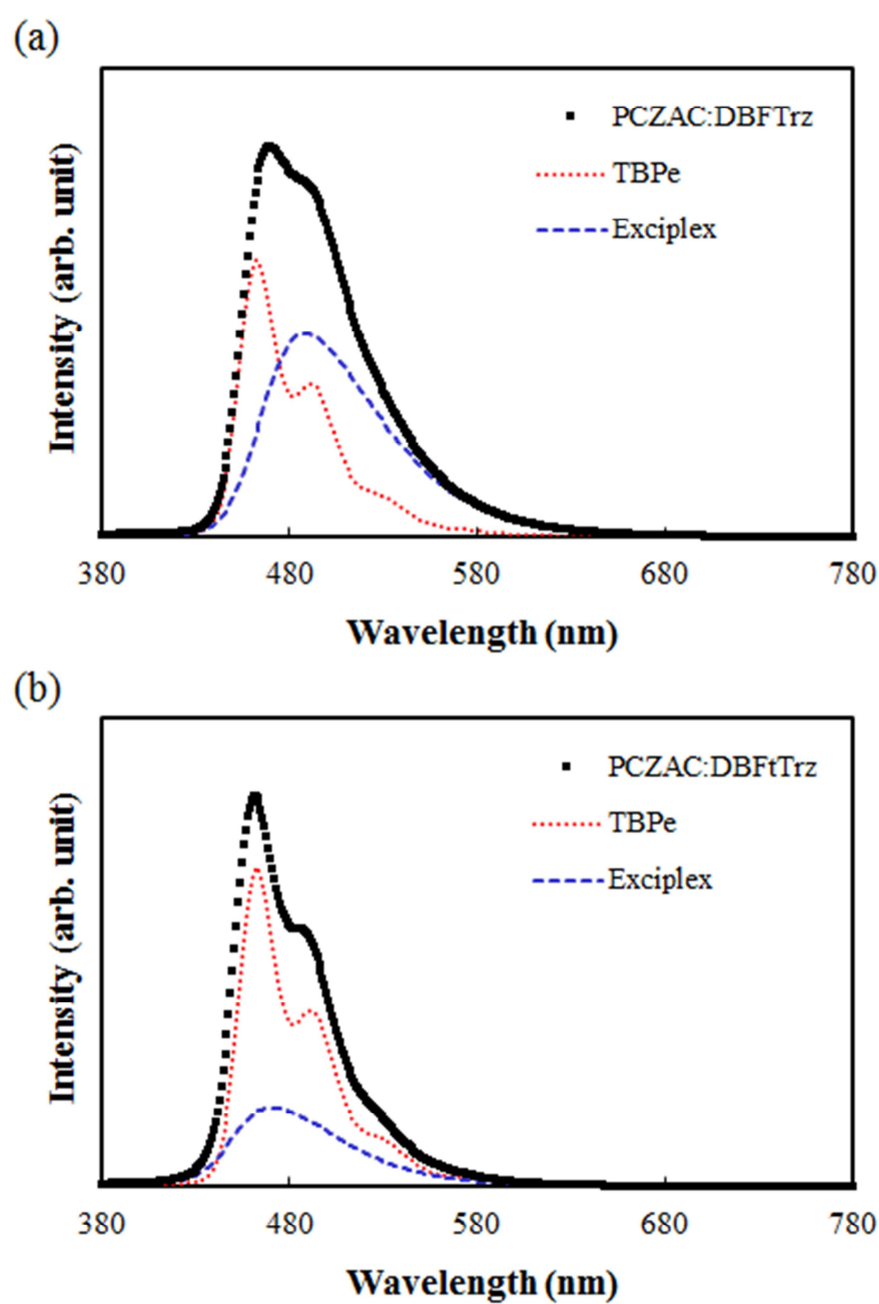


Figure 4.



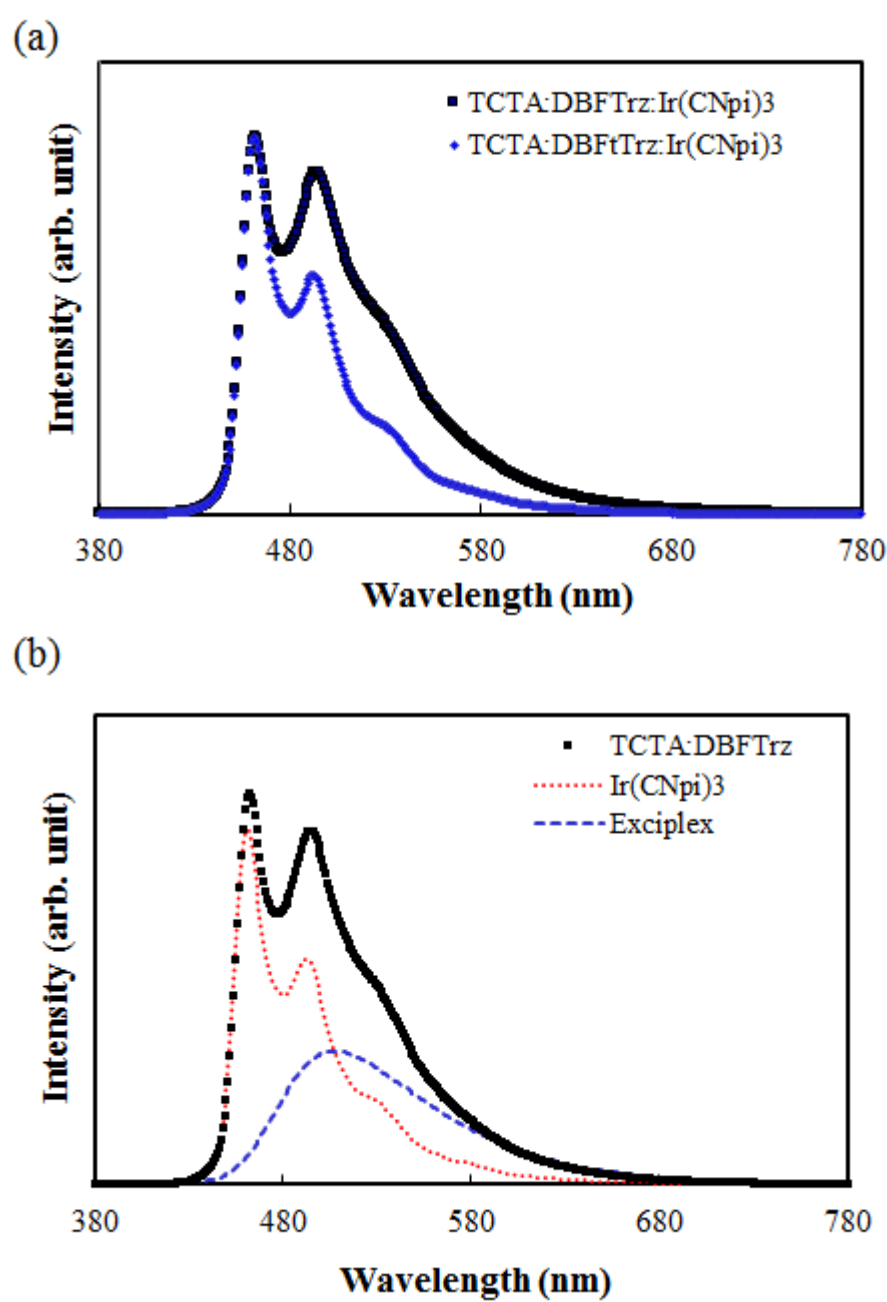


Figure 5.

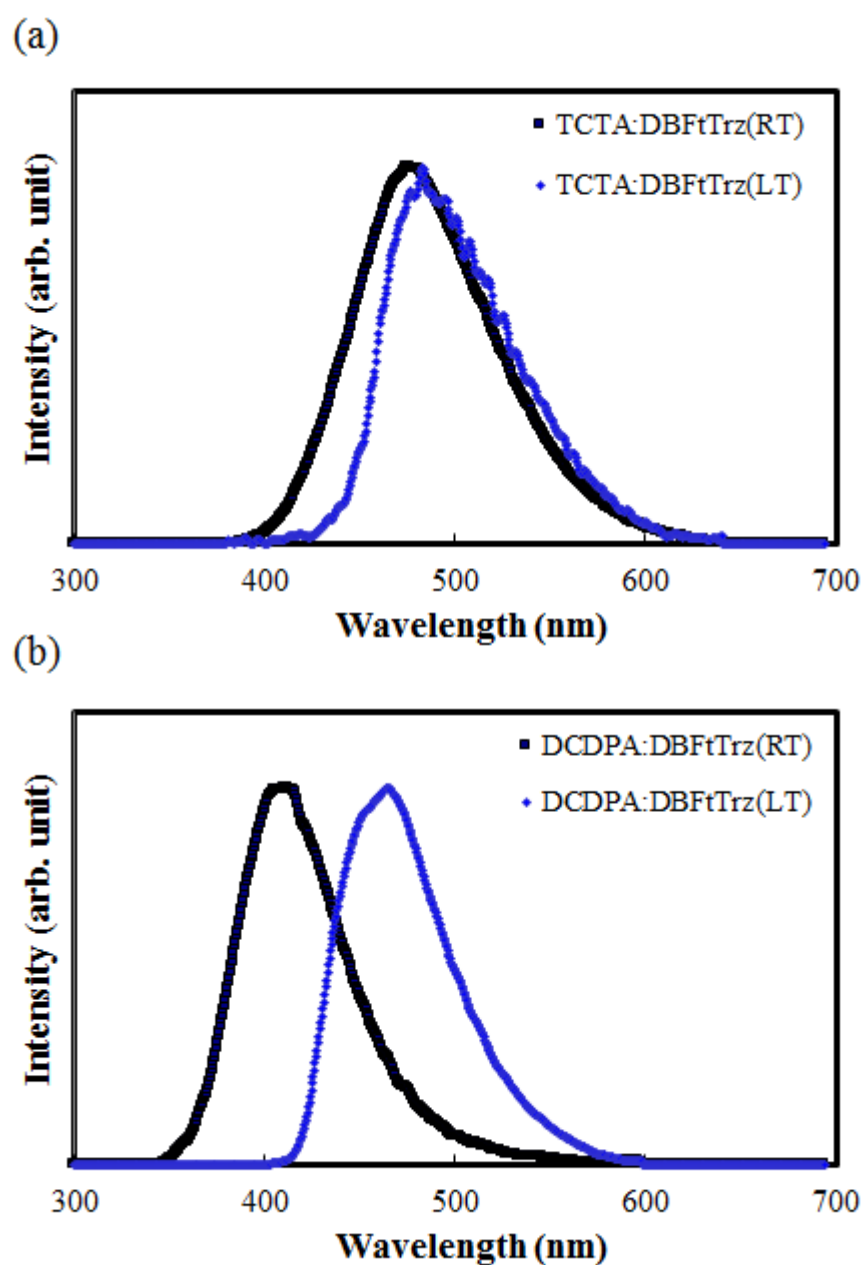


Figure 6.

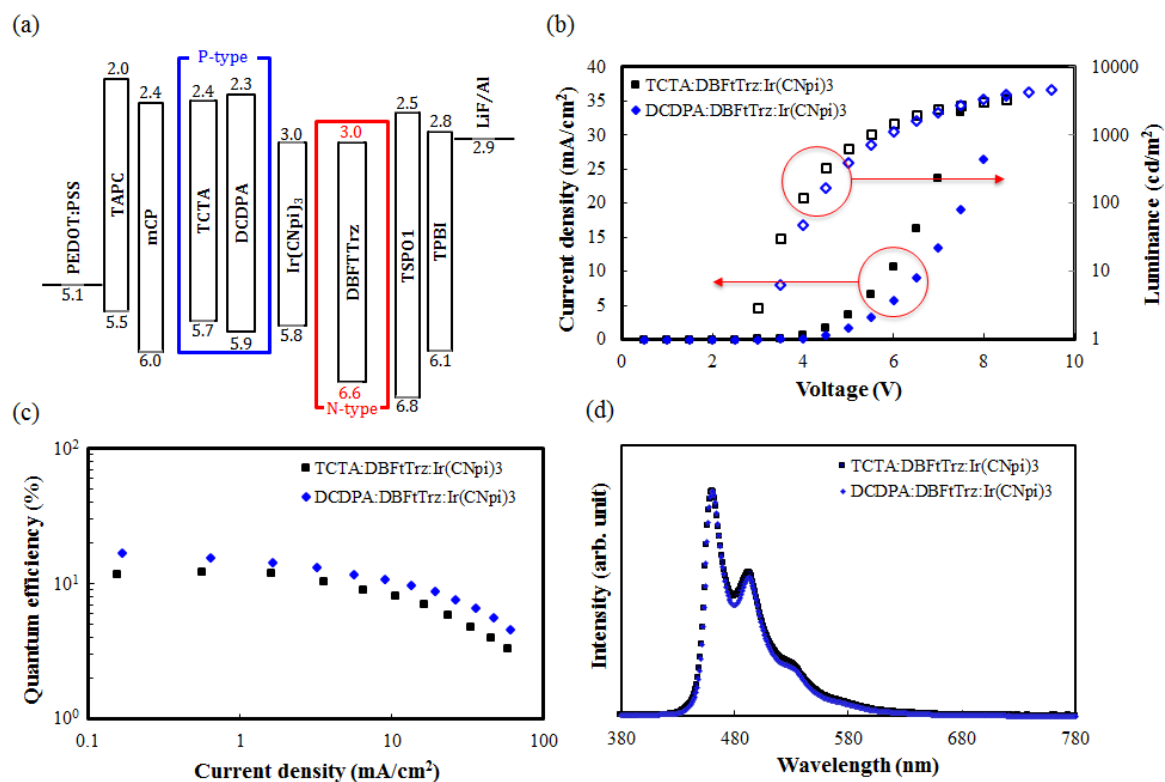


Figure 7.

**Supporting information****Design approach of exciplexes enhancing the singlet and triplet energy by  
managing electron transport type host**

Sang Kyu Jeon, Ji Gwang Yu, Wook Song, Ha Lim Lee, Jun Yeob Lee\*

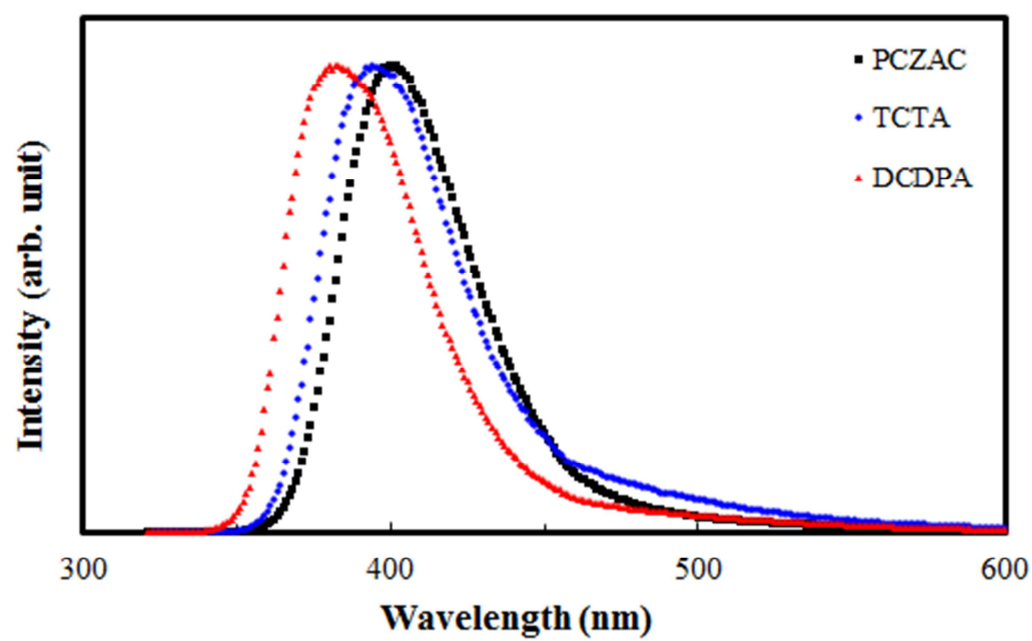
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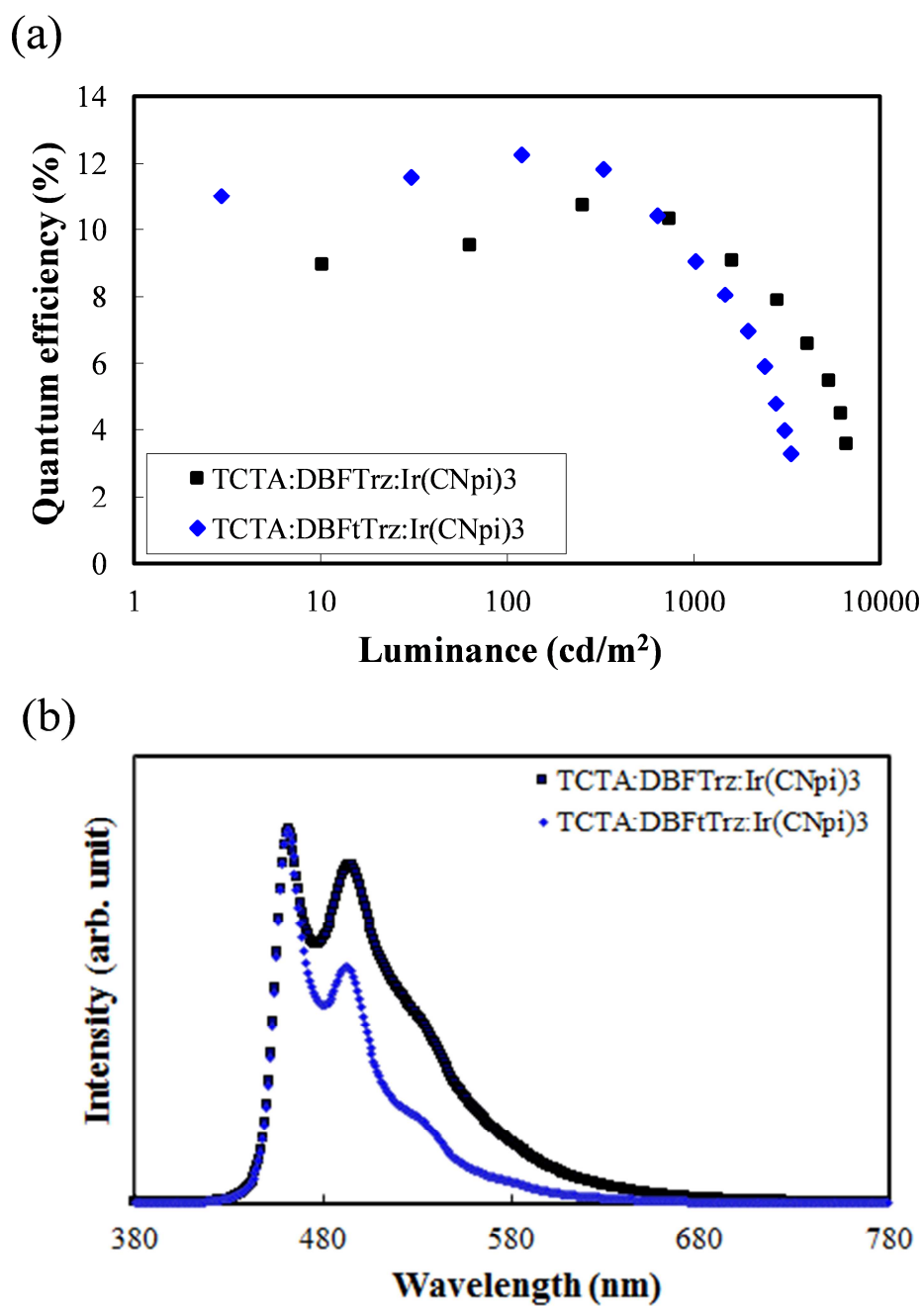
**Table S1.** Summary of photophysical properties of exciplexes.

	$\lambda_{\text{PL,peak}}$ (nm)	$S_1$ (eV)	$T_1$ (eV)
<b>PCZAC:DBFTrz</b>	483	2.95	2.95
<b>PCZAC:DBFtTrz</b>	469	3.05	2.98
<b>TCTA:DBFTrz</b>	505	2.95	2.81
<b>TCTA:DBFtTrz</b>	477	3.17	2.92
<b>DCDPA:DBFtTrz</b>	409	3.49	3.02

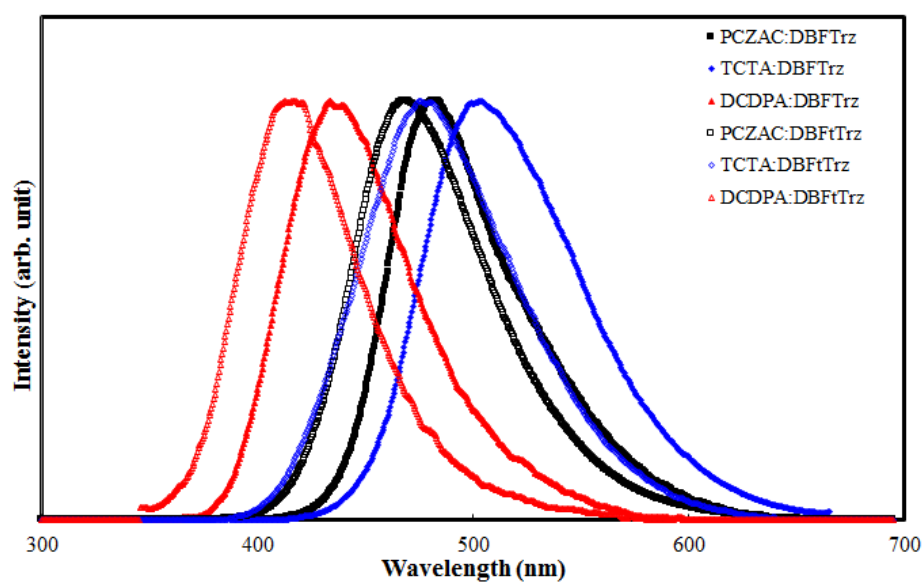
\* Singlet energy and triplet energy were calculated on the basis of spectrum onset.



**Figure S1.** PL spectra of PCZAC, TCTA and DCDPA films

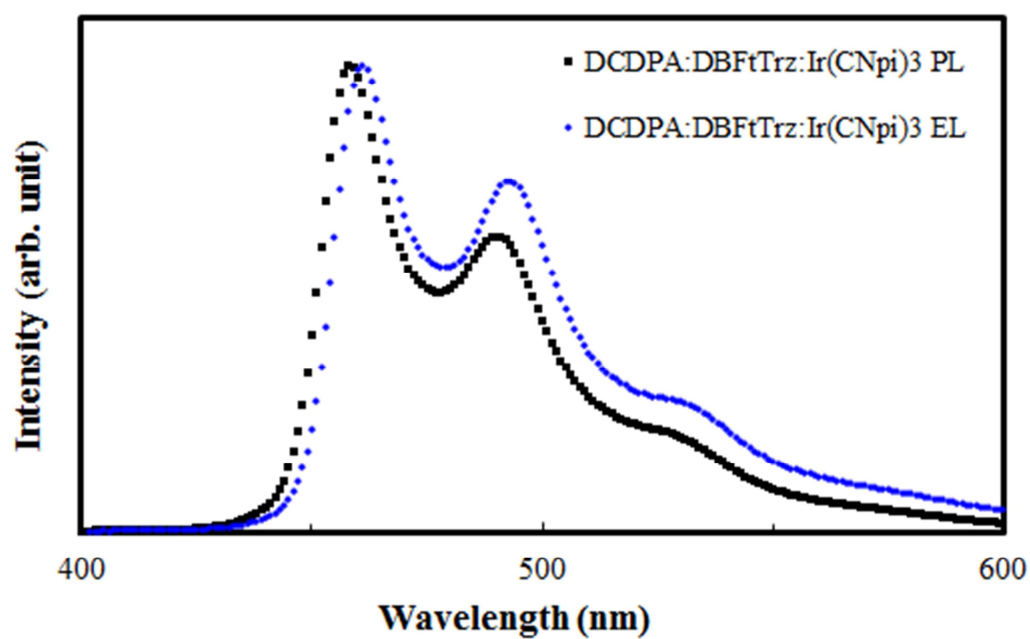


**Figure S2.** Quantum efficiency-luminance (a) and electroluminescence spectra (b) of the TCTA:DBFTrz:Ir(CNpi)<sub>3</sub> and TCTA:DBFtTrz:Ir(CNpi)<sub>3</sub> devices.

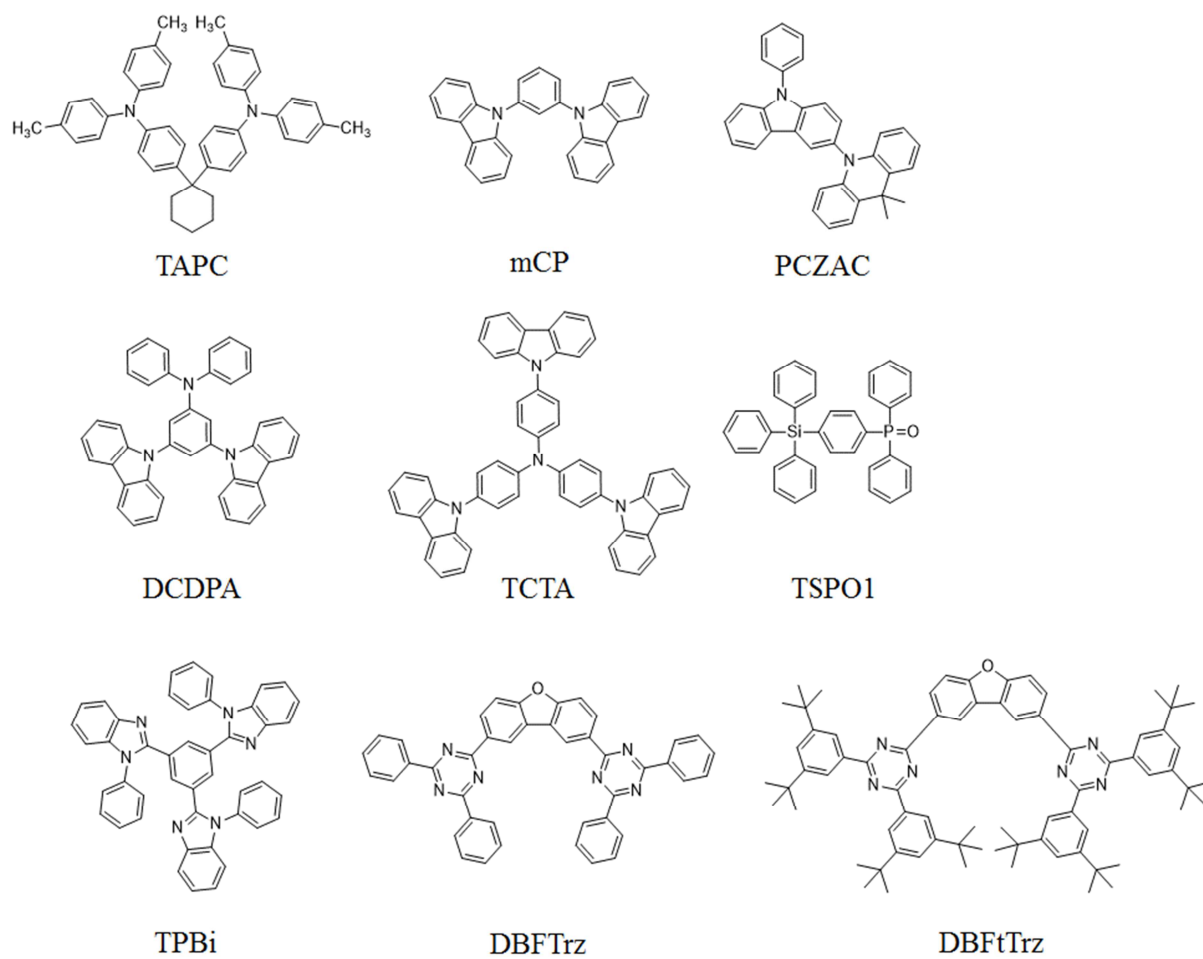


**Figure S3.** The PL spectra of exciplex films.





**Figure S4.** The PL spectra of the Ir(CNpi)<sub>3</sub> doped DCDPA:DBFtTrz film and EL spectra of DCDPA:DBFtTrz:Ir(CNpi)<sub>3</sub> device.



**Figure S5.** The chemical structure of the material used in the device

- High triplet energy exciplex for blue phosphorescent organic light-emitting diodes
- High triplet energy over 3.0 eV in the exciplex by managing the intermolecular interaction
- Triplet energy boosting effect by t-butyl substituent in the electron transport type host