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공학석사학위논문

Host Structure Engineering in Organic Light-Emitting Diodes for Improved Stability and Efficiency

발광층의 호스트 구조 변경 평가를 통한
유기발광다이오드의 안정성 및 효율 개선 연구

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Abstract

Host Structure Engineering in Organic Light-Emitting Diodes for Improved Stability and Efficiency

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Organic light-emitting Diodes have been adopted multi-layer structure to improve performances. All the organic materials in each layer need to be chosen appropriately to achieve high charge balance factor, especially for the host material in emissive layer. The host material and structure plays an important role because it controls charge balance and recombination distribution, energy transfer to dopant.

Herein, the effect of exciplex forming host structure on organic light-emitting diodes (OLEDs) has investigated. The exciplex formation was observed by mixing two organic materials with strong hole transporting and strong electron transporting properties. Two different types of emitters are used to confirm the effect of exciplex type host structure, the one is green phosphorescent dopant of iridium(III)tris(2-phenylpyridine) ($\text{Ir}(\text{ppy})_3$) and the other one is green thermally

activated delayed fluorescent dopant of (4s,6s)-2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN). Tris(4-carbazoyl-9-ylphenyl)amine (TCTA) and 3',5'-Di(carbazol-9-yl)-[1,1'-biphenyl]-3,5-dicarbonitrile (DCzDCN) are used for exciplex forming host structure in mixing ratio of 50:50. For the 4CzIPN emitter, additional exciplex type host structure with 1,3-Bis(N-carbazolyl)benzene (mCP) and DCzDCN is carried out. The green phosphorescent device with exciplex forming host structure exhibited improved carrier injection property and charge balance, leading to higher power efficiency and longer lifetime. The green thermally activated delayed fluorescent device with exciplex type host structure also showed longer lifetime.

Keywords : organic light emitting diodes, emissive layer, host structure, exciplex type host, lifetime

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Chapter 1

Introduction

After Ching W. Tang group report the first Organic light emitting diode(OLED) device in 1987 [1], OLEDs have been dramatically developed for the past few decades and several OLED products have been commercially available throughout the display applications and solid state lightings.

Fluorescent materials are widely used until now, since the first OLED device. But fluorescent material harvest only singlet excitons which is one fourth of excitons because under electrical excitation, 25 percent of singlet excitons and 75 percent of triplet excitons are formed. So there have been many studies on organic materials besides fluorescent material to enhance device performance. As a result of that, Princeton group fabricate first phosphorescent OLED device in 1998 [2]. Phosphorescent materials include heavy metal on their material structure which lead to spin-orbit coupling when electronic transition occur, so it can harvest not only singlet excitons but also triplet excitons. By adopting phosphorescent materials,

internal electroluminescence efficiency could reach one hundred percent. Furthermore, Adachi group synthesize new material called thermally activated delayed fluorescence (TADF) [3]. This is basically fluorescent material, but it has small energy difference between singlet excited state and triplet excited state. Which means it is possible to emit light from triplet excitons based on up-conversion of excitons from triplet states into singlet states.

Structurally, the first OLED adopt bilayer structure which consist of hole transport layer (HTL) and emissive layer (EML) sandwiched between two electrodes. In case of bilayer structure, there is comparatively large injection barrier and it is hard to inject equal amount of holes and electrons in the EML because of different charge transport property. To realize high-performance OLEDs, the key parameters are charge balance with efficient charge injection and transport as well as efficient energy transfer in the emitting layer (EML). By introducing multilayer structure, it is possible to inject equal amount of both holes and electrons. But to get a high charge balance factor, it is necessary that all the injected carriers should form excitons, efficiently transferring the energy to the dopant. This charge balance, recombination distribution and energy transfer to the dopant can be manipulated by the host materials. Therefore the effective design of the host structure is one of the key factors to improve the device performance.

There have been many studies on designing the host structure for improving the performance of OLEDs. Some studies report on synthesizing new host materials with bipolar charge transport property and suitable energy levels [4]. But synthesizing a new material is a complicated and time consuming process. Alternative simple approach of modifying the host properties is mixing two different

types of host material [5-6]. When two host materials interact in the excited state to form an exciplex, efficient energy transfer to the dopant as well as reduction of driving voltage can be possible [7-8].

In this work, we have investigated the effect of exciplex forming host structure on the device performance of OLEDs doped with green phosphorescent dopant of iridium(III) tris[2-phenylpyridine] ($\text{Ir}(\text{ppy})_3$) and green thermally activated delayed fluorescent dopant of (4s,6s)-2,4,5,6-tetra(9H-carbazol-9-yl) isophthalonitrile (4CzIPN).

Chapter 2

Theory

2.1 Principles of Organic Light-Emitting Diodes

In the following, basic knowledge of organic semiconductor and OLED operating principles are treated. In addition, degradation of OLED will be discussed.

2.1.1 Organic Semiconductor

Organic semiconductor is compound whose molecules contain carbon and is formed strong intramolecular covalent bonds and weak intermolecular van der waals bonds. What organic semiconductor makes interest is that there is conjugated π -electron system in their skeletal structure. Organic semiconductors are based on the carbon atoms consists of mixture of s and p orbitals (hybrid orbitals) which form covalent σ -bonds and remaining electrons in p orbitals form π -bonds. σ -bond is symmetric molecular orbital with respect to rotation about the bond axis and it becomes π -bond when the phase changed. Backbone σ -bonds hold molecular

together to maintain structure and π -electrons in π -bonds are acting as free electrons. These π -electrons determine the intermolecular interactions which effect on the geometrically allowed molecular packing arrangements and most of electronic and optical properties.

Organic molecules in solid phase form molecular crystals with weak intermolecular interaction forces of van der waals type. Most of the organic crystals include more than one molecule in the unit cell and it usually form monoclinic or triclinic lattice structure to increase the packing density for minimization of the intermolecular potential. When organic molecules form thin films, there is quantitative and qualitative difference compared with inorganic molecules. This is because organic molecules are 'extended objects' which have internal degrees of freedom. That is, there is orientational degree of freedom that can change the molecular orientation during film growth and it lead to fundamental growth difference (Fig. 1). Interaction potential also plays an important role when it forms the film. For instance, if the molecule-molecule interaction is stronger than molecule-substrate interaction, the absorption of the molecule occurs in a standing geometry. And in opposite case, it occurs in lying geometry. Also, the size of the organic molecules and the unit cells are greater than that of typical substrates. This indicates that organic molecules are more likely to form translational domains and crystallize in low-symmetry structure which can lead to multiple domains [9].

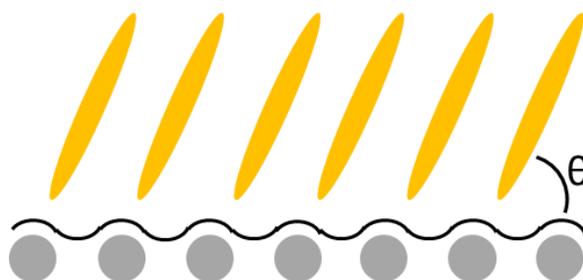


Figure 1. Orientational degree of freedom, potentially leading to orientational domains.

When organic molecules are formed, molecular orbitals formed by the overlap of atomic orbitals and it depends on their phase relationship. Bonding orbital means constructively overlapped molecular orbital with the bulk of the electron density located between two nuclei whose energy is lower than that of the original atomic orbital. On the contrary to bonding orbital, antibonding orbital is destructively overlapped molecular orbital which means atomic orbitals interact with each other out of phase. As molecule size gets bigger, the number of energy states of bonding, antibonding orbitals is increased according to phase relationship. It means there is decrease in the energy separation between molecular orbitals so it can form energy band (π -band, π^* -band). In other words, energy gap (HOMO-LUMO gap) will decrease by increasing π -conjugation length. This indicates that change of electrical and optical properties.

2.1.2 Operation of Organic Light-Emitting Diode

An OLED is a light-emitting diode which consists of semiconducting organic layers sandwiched between two electrodes. When the voltage is applied to the

electrodes, charges overpass injection barrier and move from the electrodes to organic layers. Injection barrier is due to energy level difference between electrodes and organic layers and also between organic layers. To minimize charge injection barrier, OLED device usually stack five different layers called HIL (Hole Injection Layer), HTL (Hole Transport Layer), EML (Emissive Layer), ETL (Electron Transport Layer), EIL (Electron Injection Layer). Basically, Holes are injected from anode and move along HOMO levels of HIL and HTL to EML and electrons are injected from cathode and move through LUMO levels of EIL and ETL to EML. So it is necessary to consider energy levels of each layer based on the electrons and holes path to minimize injection barrier.

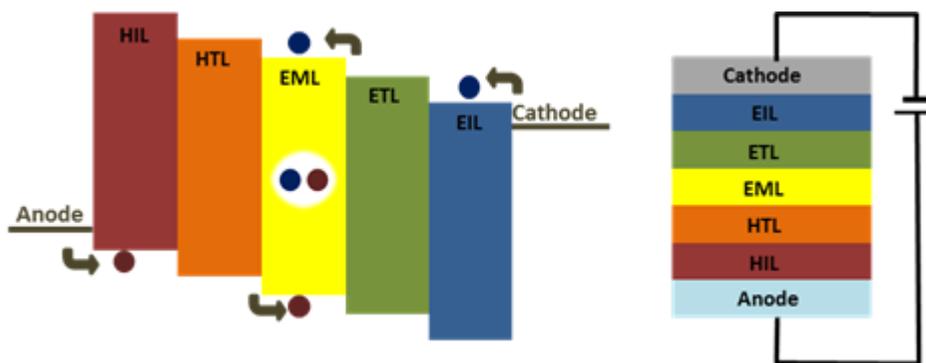


Figure 2. The typical multi-structure of OLEDs.

At the interface of electrodes and organic layers, energy barrier can be increased by interface dipoles which caused by interface interaction between metal or metal oxide and organic material. This energy barrier can be lower by doping n-type material on the interface of the EIL and cathode and p-type material on the interface of the HIL

and anode. It is also possible to lower the energy barrier by applying O₂ plasma treatment on the anode [10].

Electrostatic forces bring electrons and holes towards each other through the organic layers. Behavior of charges in the organic material is quite different with that in the inorganic material when it moves through layers. This is because of charge mobility in organic material is governed by hopping mechanism which is phonon assisted tunneling. It means charge moves by tunneling from one localized state to another when the electronic wave functions of the defect states are sufficiently overlapped. Which means transition rate is related with the position of the charge and energy of the localized state. This is to say that hopping depends on the structural disorder and the energetic disorder. Consequently, mobility of the organic materials is relatively small ($<0.1 \text{ cm}^2/\text{V}\cdot\text{s}$) compared to inorganic semiconductors ($100\text{-}10000 \text{ cm}^2/\text{V}\cdot\text{s}$).

Current flow of organic material follows SCLC (space-charge-limited current) model. This means current is limited by the charge transport in the bulk not by charge injection. When voltage is applied, charge carrier density is gradually decreased as the distance from the anode is increased. If the applied voltage is increased, near the anode, charge density is also increased and acting as a space charge. This indicates that there is virtual anode on the organic layer near the anode because of excess charges and effective thickness of organic layer becomes thinner than its own thickness. So charge transport in the organic layer is affected by space charge and it is given by Mott-Gurney law (no traps).

$$J = \frac{9}{8} \varepsilon \mu_p \frac{V^2}{d^3} \quad (2.1)$$

Where J is electric current density, ε is the dielectric constant of the solid, μ_p is the carrier mobility, V is applied voltage and d is the thickness of the organic layer.

When charge carriers reach the EML layer, they recombine forming exciton in the emissive layer. The decay of this excited state results in a relaxation of the energy levels of the electron, accompanied by emission of radiation with a frequency given by the energy gap between the HOMO and LUMO levels of the emitting molecules. There are certain rules for decay mechanism which is called selection rules. Enable the excitons to transit from the excited states to ground states, exciton need to satisfy two different selection rules. The first one is the symmetry selection rule ($\Delta l \pm 1$) and the other one is the spin selection rule ($\Delta S = 0$). Symmetry selection rule indicate that if there is center of symmetry, transitions within a given set of p or d orbitals are forbidden. Spin selection rule means that allowed transitions must involve the promotion of electrons without a change in their spin. Spin quantum number of ground state is zero and incase of singlet exciton and triplet exciton are zero and one, respectively. So, according to selection rule, emission from the triplet exciton is forbidden. But there is an exception if the molecule includes large atomic number atom such as heavy metal, it can emit the light even from the triplet excitons. This is because of the interaction between spin and its motion which allows the mixing of singlet and triplet states (spin-orbit coupling). Jablonski energy diagram is shown in Fig.3 which shows electronic states of a molecule and the transitions.

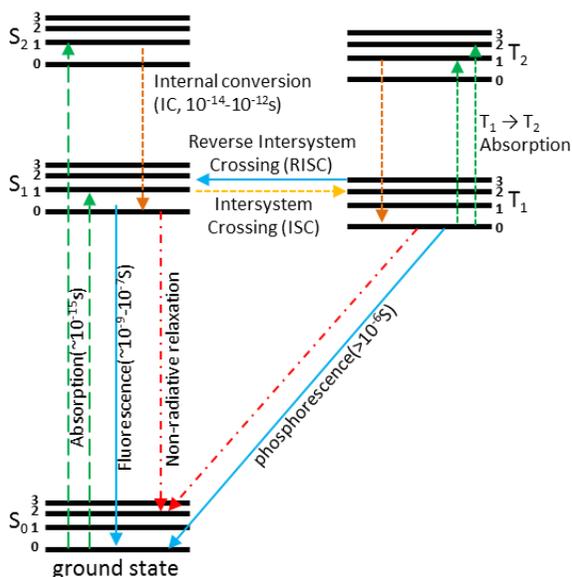


Figure 3. Jablonski diagram which shows electronic states of the transition.

2.1.3 Lifetime of OLEDs

Degradation of the OLED is caused by various internal and external mechanisms and is treated as the most serious issue because it causes the limited device lifetime. Extrinsic degradation is caused by light, enhanced temperature, process parameters, and so on. These give rise to number of degradation mechanisms such as photo-induced reactions, diffusion/migration of molecules, electrode deterioration, morphological changes and delamination, and so forth. Mechanisms of the intrinsic degradation are originated from excitons and charge carriers in the device. The typical mechanisms are exciton density caused reaction, electro/photo chemical reaction, migration and charge accumulation. As a perspective of effect on the OLED performances, degradation could result in voltage arises and luminance

decrease. Voltage arise is caused by electrode instability such as corrosion or work function degradation and decreasing charge transport property by formation of charge traps or instability of the radical cations and anions. Luminance decrease is caused by instability of excited states or formation of quenching centers that leads to decrease recombination efficiency [11].

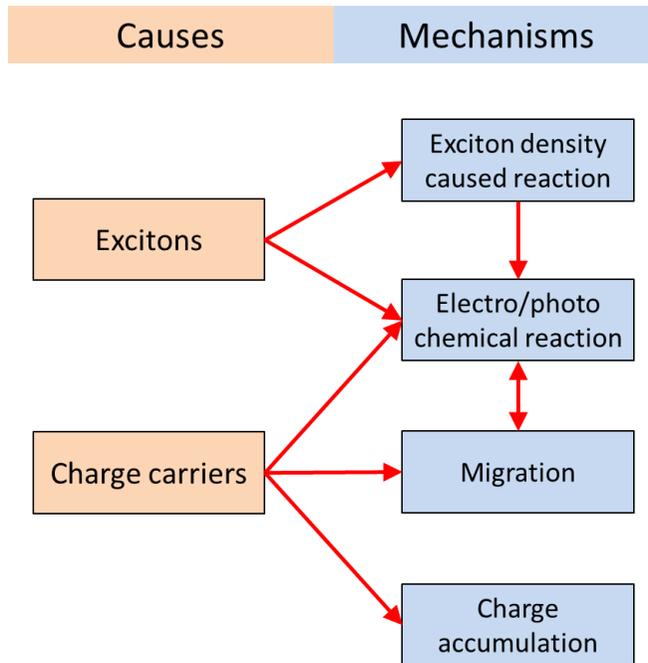


Figure 4. Intrinsic degradation mechanism of OLEDs

In regard to origin and effect of degradation as explained above, we can say that charge balance factor plays an important role in degradation of device as well. So, stability of the device can be improved by adopting suitable host structure because host structure can manages charge balance factor. Specifically, it is possible to inject equal amount of charges in EML with small energy barrier and transfer the energy to the dopant efficiently. And also host structure can act as a blocking layer and

prevent exciton quenching. These indicate that we can minimize excess charges and excitons which are not participate in light emitting and can lead to degradation of the device.

The following is introducing two well-known decay models. The first model is based on the concept that degradation behavior is influenced by multiple independent mechanisms which lead to rapid initial luminance drop and more long term luminance decay of the lifetime curve. This is called multiple exponential decay model and is given by

$$\frac{L}{L_0} = ae^{-\alpha t} + be^{-\beta t} \quad (2.2)$$

Where L_0 is initial luminance and t is time, L is luminance after time t passes and a , b , α , β are fitting parameters. Another approach to degradation model is that the loss mechanisms are related to the accumulation of defects created which act as quenchers, non-radiative recombination centers, and deep charge traps. This is called stretched exponential decay and shown in eq. 2.3.

$$\frac{L}{L_0} = \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] \quad (2.3)$$

Where β , τ are fitting parameters, τ as a decay constant and β as a stretching factor. All the fitting parameters in the equation 2.2 and 2.3 are depending on the materials that used in device and device structure.

2.2 Characterization: Theory and Method

There are tens of powerful techniques to characterize OLED devices. Especially for the emission characteristics, electrical and optical techniques are used in this experiment.

2.2.1 Photoluminescence (PL)/ Electroluminescence (EL) Spectroscopy

Spectroscopic analysis is used to examine the wavelengths of emitted light which is the set of discrete wavelengths according to the materials that used in the OLED. This is called photoluminescence spectroscopy or electroluminescence spectroscopy in accordance with its excitation method.

Emission spectrum is well known method to characterize light emission property based on the materials and the path of the light. When exciton transition occurs from the high energy state to the low energy state, photon emit with certain frequency which is equal to the energy difference between the HOMO level and the LUMO level of the material. In other words, the peak wavelength of emitted light which corresponds to the color depends on the material of the emissive layer. The emitted light also affected by propagate path. When the light across the interfaces of the organic layers and electrodes, it refracted and reflected because of the different refractive index of each layers. During the propagation, some of the lights are superposed to form a different amplitude wave. This interference makes emission spectrum has not only different FWHM (Full Width Half Maximum) but also different peak wavelength. If two waves are in phase coherence and form constructive interference, the resultant light wave has greater amplitude, in other words, greater intensity of emitted light. In OLED, it mostly depends on total

organic layer thickness because organic materials have similar refractive index. It is known as micro-cavity effect.

There are two different types to excitation method of emission spectrum. Firstly, photoluminescence (PL) is light emission from photoexcitation by the absorption of the photons. Laser diodes are used to give photon energy on the OLED device. Basic information about the energy gap of the emissive layer is needed to choose proper laser diode which has to have enough energy for excitation. Secondly, electroluminescence (EL) is caused by radiative recombination of electrons and holes. When electric field applied on the device, electric current flows across the device, electrons and holes recombine and form excitons which release their energy as photons.

2.2.2 Current-Voltage-Luminance (I-V-L) Characteristics

Electrical characteristics and performances can be investigated by measuring Current-Voltage-Luminance. It gives us the information about current flow and luminance intensity at the given voltage. Measurement is usually performed by varying voltages and measure current and luminance in the meantime.

Basically, OLED is the current driving device which means luminance characteristics and performances are greatly depends on the electric current flows. Therefore, I-V-L represents basic OLED characteristics and some of characteristics are listed below which draw from I-V-L measurement.

1. Turn-on voltage / Driving voltage

Turn-on voltage is the voltage at the luminance of 1 cd/m^2 and driving voltage is the voltage at the certain luminance, for example, 1000 cd/m^2 . This tells us

that how much electrical energy will be needed to operate OLEDs. So, both turn on voltage and driving voltage are related with injection barriers and charge carrier transport property through the organic layers and also recombination process.

2. Current efficiency / Power efficiency

Current efficiency [cd/A] indicates that how many charges are transferred to emit lights out of the charge flow during the operation and can be calculated by dividing luminance [cd/m²] by current density [mA/Cm²].

Power efficiency [lm/W] is the ratio between the total luminous flux (lumen [lm]) emitted by OLED device and the total amount of input power [W] it consumes. Lumen is luminous energy per unit time.

3. External Quantum Efficiency

External Quantum Efficiency (EQE) is given by

$$\eta_{ext} = \eta_{int}\eta_p = \gamma\eta_r\eta_{PL}\eta_p \quad (2.4)$$

Where η_{ext} is external quantum efficiency, η_{int} is internal quantum efficiency, η_p is light out-coupling efficiency, η_{PL} is PL quantum efficiency, η_r is charge recombination efficiency, γ is charge balance factor. By adopting materials that has proper energy levels and transport property and applying suitable device architecture to inject equal amount of charges and recombine all the injected charges in the device, it is possible to achieve one hundred percent of charge balance factor. And also internal quantum efficiency could reach one hundred percent because phosphorescent material and Thermally Activated Delayed Fluorescent (TADF) material can harvest triplet excitons. The remained issue

to achieve high EQE is light out-coupling efficiency which is only about 17.5 percent for typical bottom emission device with ITO (Indium Tin Oxide) anode on the glass. This caused by waveguide of ITO and glass. To minimize the light loss by waveguide, we can apply different device structures, for instance, micro-lens or microsphere on the glass or aerogel or mesa structure between ITO and glass, etc.

Chapter 3

Experimental

3.1 Materials and Device Fabrications

The devices with different host structures were fabricated on indium tin oxide (ITO) substrate pre-cleaned by ultra-sonication in acetone, isopropanol and deionized water and dried in an oven for a day at 150 °C. Before the deposition of the organic materials, ITO substrates are ultraviolet-ozone (UVO) treated for 10 minutes.

The experiment were performed in two different types of dopant materials which are tris[2-phenylpyridinato-C 2 ,N] iridium(III) ($\text{Ir}(\text{ppy})_3$) as a green phosphorescent material and (4s,6s)-2,4,5,6-tetra(9H-carbazol-9-yl) isophthalonitrile (4CzIPN) as a +green thermally activated delayed fluorescent material. The hole injection and transport layers of MoO_3 (10 nm) and di-[4-(N,N-di-p-tolylamino)-phenyl]cyclohexane (TAPC, 50 nm) were used in all the devices with same

thickness and were deposited by thermal evaporation in high vacuum ($< 10^{-6}$ torr), respectively. The green phosphorescent and TADF emitting layer consist of single host (4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP), (Tris(4-carbazoyl-9-ylphenyl)amine) TCTA, (3',5'-Di(carbazol-9-yl)-[1,1'-biphenyl]-3,5-dicarbonitrile) DCzDCN) and mixed host (CBP:DCzDCN, TCTA:DCzDCN) doped with Ir(ppy)₃ and 4CzIPN, respectively. The mixing ratio of two materials in the mixed host was 50:50 and the doping concentration of Ir(ppy)₃ and 4CzIPN were 8 wt%. Additional experiment was performed for the 4CzIPN with single host 1,3-Bis(N-carbazolyl)benzene (mCP) and mixed host mCP:DCzDCN (50:50). The electron transporting layer of 2,2',2''-(1,3,5-benzenetriyl) tris-[1-phenyl-1H-benzimidazole] (TPBi, 40 nm) were deposited on top of the green emitting layer and followed by thin electron injecting layer of 8-hydroxyquinolatolithium (Liq) and Al cathode. The detail of the device structure is listed in table 1 and chemical structures in Fig. 5.

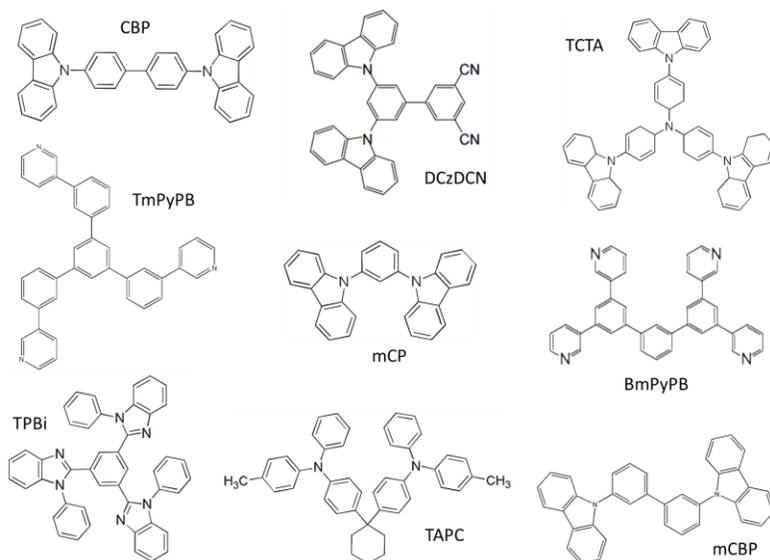


Figure 5. Chemical structures of organic materials.

Table 1. Experiment conditions for EML and ETL

	EML	ETL
Green Phosphorescence	CBP :8wt% Ir(ppy)₃ (30nm)	TPBi (40nm)
	DCzDCN :8wt% Ir(ppy)₃ (30nm)	
	TCTA :8wt% Ir(ppy)₃ (30nm)	
	DCzDCN:CBP(1:1) :8wt% Ir(ppy)₃ (30nm)	
	DCzDCN:TCTA(1:1) :8wt% Ir(ppy)₃ (30nm)	
Green TADF	CBP :8wt% 4CzIPN (30nm)	
	DCzDCN :8wt% 4CzIPN (30nm)	
	TCTA :8wt% 4CzIPN (30nm)	
	DCzDCN:CBP(1:1) :8wt% 4CzIPN (30nm)	
	DCzDCN:TCTA(1:1) :8wt% 4CzIPN (30nm)	
	mCP :8wt% 4CzIPN (30nm)	
	mCP:DCzDCN :8wt% 4CzIPN (30nm)	

3.2 Measurement

The photoluminescence (PL) emission spectra of host materials were measured using 375nm laser as excitation source and an intensified charge-coupled device (ICCD) as a detector. The performances of the fabricated devices were measured using Keithley-236 as a source measurement, and Keithley-2000 as a multimeter and CS 2000 measurement unit for obtaining electroluminescence spectra.

Chapter 4

Results and Discussion

4.1 Performance of green phosphorescent device

To confirm the effect of exciplex forming host structure on the OLED device, green phosphorescent device were fabricated using Ir(ppy)₃ dopant which is widely used.

4.1.1 The host structure and property

Mixed host structure can be categorized in two types, the one is exciplex type and the other one is exciplex free type. When strong electron transport type and hole transport type host materials are mixed, there will be strong intermolecular interaction which lead to form exciplex. The biggest difference between two types of host structure is the emission process. The emission mechanism of exciplex type

host structure is energy transfer, while exciplex free type host structure is dominated by charge trapping [12].

Mixed host structure for phosphorescent dopant is carried out using CBP, TCTA, DCzDCN as a host material. The CBP is the typical host material for Ir(ppy)₃ emitter and has weak hole transport property. The TCTA is strong hole transport type material which is widely used. The DCzDCN shows bipolar charge transport property but stronger electron transport property than hole transport property based on its chemical structure. In other words, the DCzDCN contains Carbazole unit which has weak hole transport property, whereas Phthalonitrile unit has strong electron transport property [13]. So, CBP:DCzDCN host structure is used as an exciplex free type and TCTA:DCzDCN host structure is used as an exciplex type for the two types of mixed host structure.

Photoluminescence (PL) emission spectrum of two mixed host structures and three single host structures were measured to confirm the exciplex formation. The HOMO and the LUMO levels of each material are shown in Fig. 6. The DCzDCN has deepest HOMO level and LUMO level, so electrons are usually injected into DCzDCN and holes are usually injected into TCTA or CBP. For the TCTA:DCzDCN host structure, we can expect the formation of exciplex between HOMO level of TCTA and LUMO level of DCzDCN.

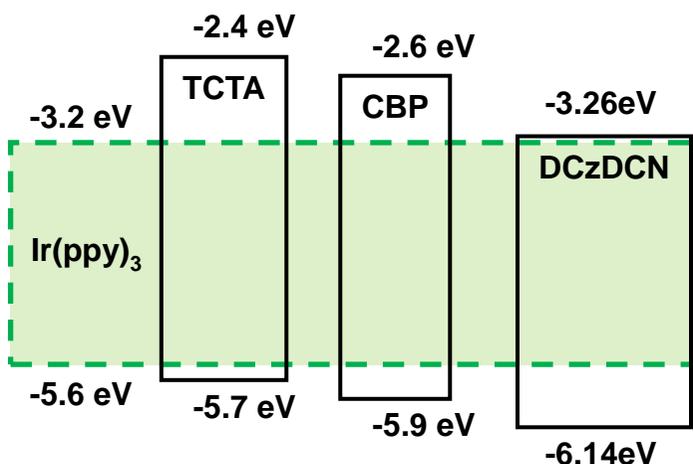


Figure 6. Schematic energy diagram for host materials along with HOMO and LUMO levels of Ir(ppy)₃ (dashed line).

Fig.7. (a) shows PL spectrum of exciplex free type host structure and (b) shows PL spectrum of exciplex type host structure. The PL emission of TCTA:DCzDCN host structure exhibited red-shifted broad PL spectrum compared to that of TCTA and DCzDCN, indicating successful exciplex formation between TCTA and DCzDCN. The peak wavelength of TCTA:DCzDCN was 510 nm(2.43 eV), well-matched with the energy level difference between the LUMO level of DCzDCN(3.26 eV) and the HOMO level of TCTA(5.7 eV), as shown in Fig.6. However, such red-shift of the PL spectrum was not observed in case of CBP:DCzDCN mixed host structure, indicating no exciplex formation.

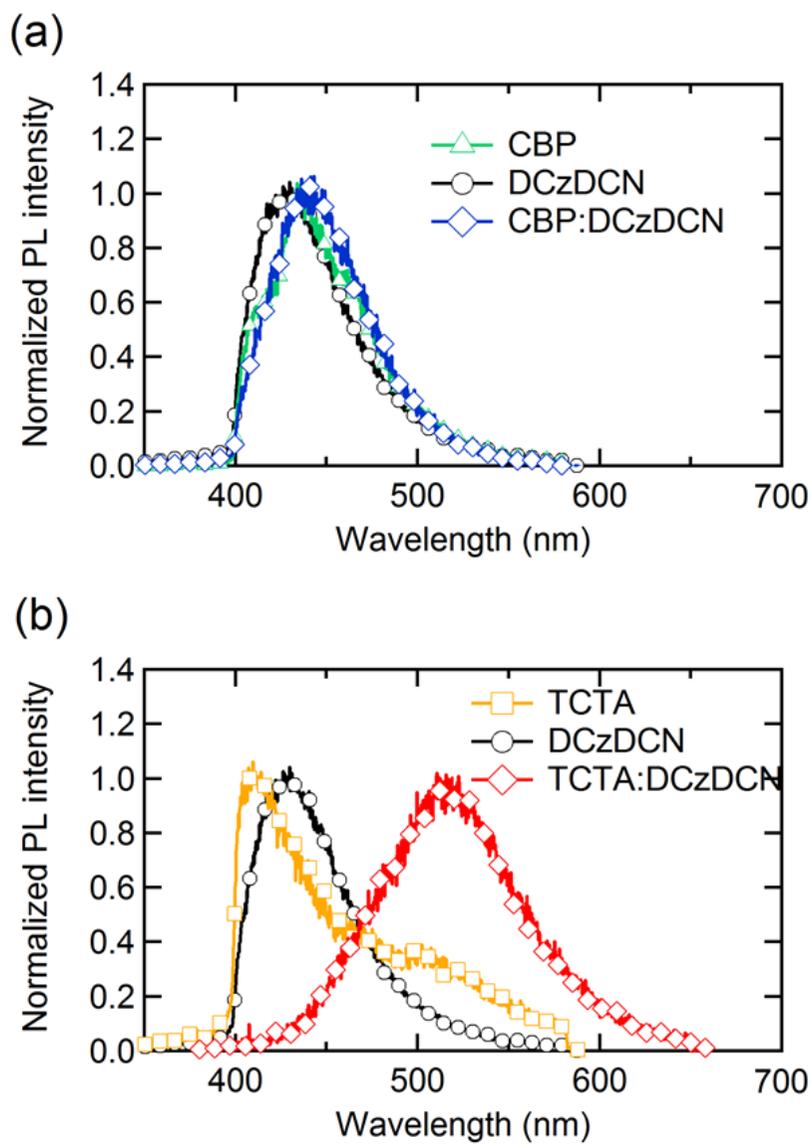


Figure 7. Normalized PL spectra of host thin films of (a) CBP, DCzDCN and CBP:DCzDCN, (b) TCTA, DCzDCN and TCTA:DCzDCN.

4.1.2 Characteristics of the green phosphorescence device

Green phosphorescence devices were fabricated with the structure of ITO(150nm)/MoO₃(10nm)/TAPC(50nm)/EML(30nm)/TPBi(40nm)/liq(3nm)/Al(1200nm) as in Fig.8(a).

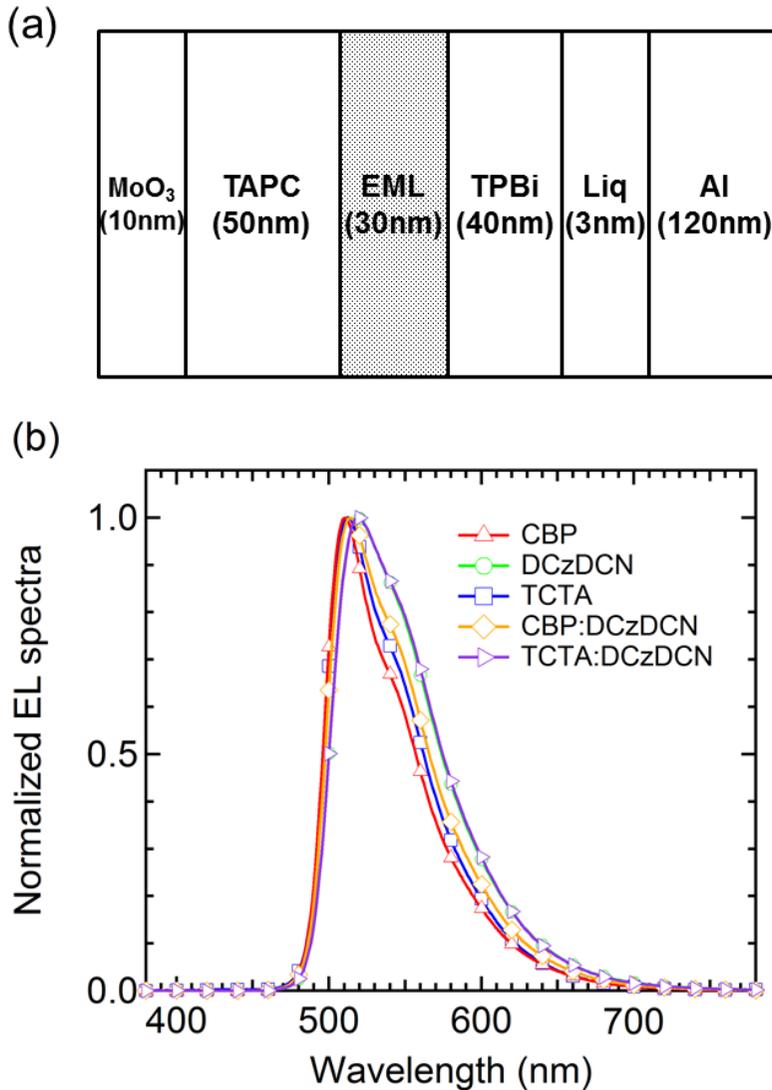


Figure 8. (a) Device structure, (b) Normalized EL spectra of the devices.

Electroluminescence emission spectrum of devices is measured to make sure that all the lights are emitted from Ir(ppy)₃ dopant. There is no peak lower than the wavelength of 500nm (Fig.8 (b)). This indicates that there is no emission from host materials, all the lights are from dopant.

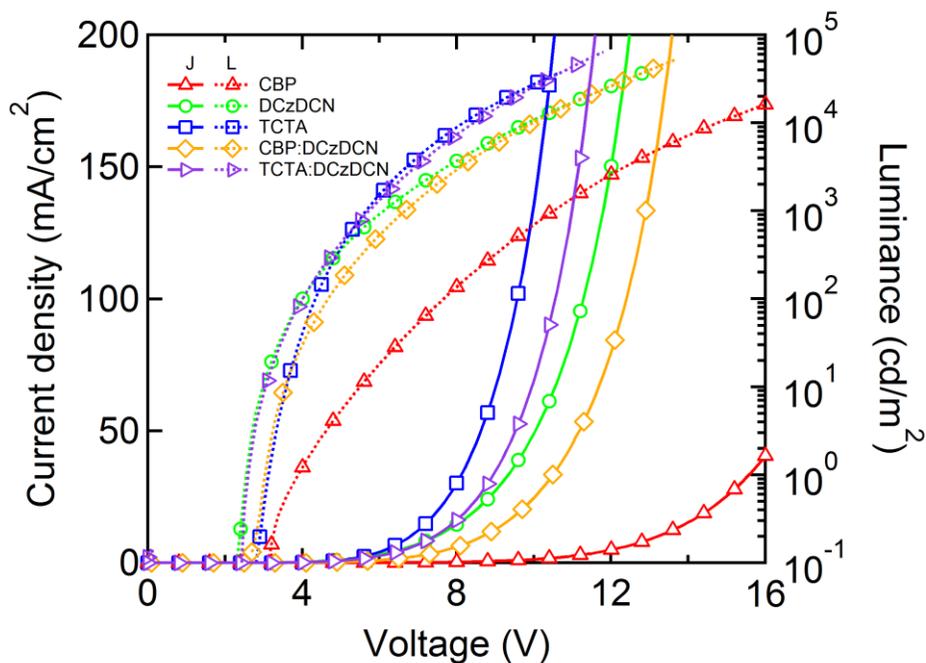


Figure 9. J–V–L characteristics of the devices with different host materials.

Figure 9 shows current density–voltage–luminance (J–V–L) characteristics of the devices with different host materials. The device with TCTA as host had the lowest driving voltage due to the small hole injection barrier between TAPC and TCTA (HOMO=0.2 eV). The current density and luminance of the device with TCTA:DCzDCN host was higher than that of the device with CBP:DCzDCN host because of better hole transporting properties of TCTA than CBP. The driving voltages at 1000 cd/m² of all devices are listed in table 2.

Power efficiency (PE) and external quantum efficiency (EQE) characteristics were shown in Figure 10. The EQE of TCTA:DCzDCN and CBP:DCzDCN is similar because they consist of both hole and electron transport type materials. These properties lead to efficient charge injection and transport with good electron-hole balance. However, in terms of power efficiency, TCTA:DCzDCN device had higher value than CBP:DCzDCN device due to low driving voltage coming from better hole transporting properties of TCTA.

In case of the single host structure, the EQE of CBP device is similar with mixed host devices because of its good charge balance with moderate electron and hole transport property. But Power efficiency of CBP device is lower because of relatively high charge injection barriers. In contrast with CBP, DCzDCN has strong electron transport property and TCTA has strong hole transport property, which lead to unbalance of charges. So, external quantum efficiency of DCzDCN and TCTA are lower than other devices.

Table 2. The summary of device performances with different host materials.

	EQE (%) @1000cd/m ²	PE (lm/W) @1000cd/m ²	Driving voltage (V) @1000cd/m ²	Lifetime (hr) @3000cd/m ² @T70
CBP	15.85	16.23	10.6	1.12
DCzDCN	8.01	14.67	6.2	12
TCTA	10.97	20.87	5.7	0.33
CBP:DCzDCN	14.82	24.29	6.7	18.3
TCTA:DCzDCN	14.27	28.03	5.8	29.3

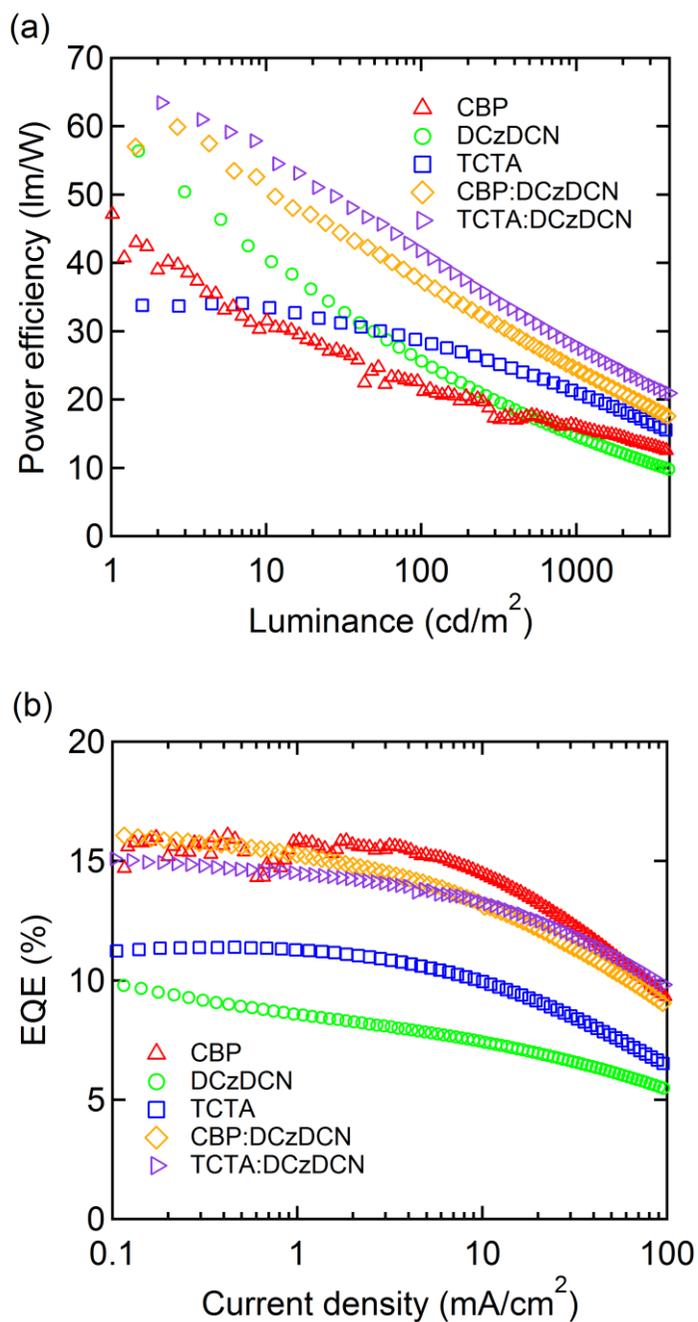


Figure 10. (a) Power efficiency–luminance characteristics and (b) External quantum efficiency–current density characteristics of the green phosphorescent OLEDs

Lifetime of the devices were measured at 3000cd/m². The long lifetime of the device with DCzDCN compared to that of CBP and TCTA comes from effective charge confinement, high glass transition temperature, and good charge transport properties of DCzDCN [12]. The lifetime of the device with mixed host structure was longer than that of device with DCzDCN as a host. This is attributed to the mixing of hole transporting materials with DCzDCN leading to improved charge injection and exciton confining properties. Especially, the improved lifetime of the device with TCTA:DCzDCN as host can be explained by its low driving voltage.

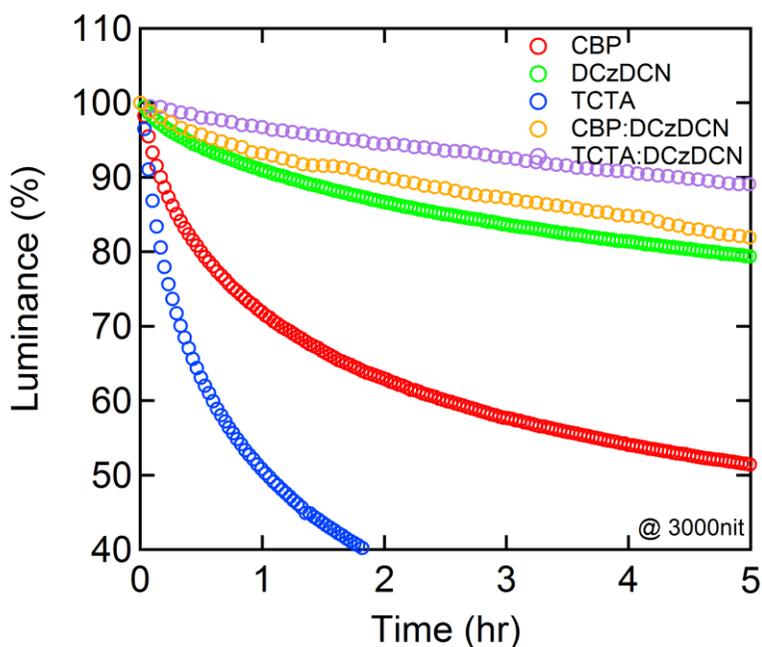


Figure 11. The lifetime of the devices at initial luminance 3000 cd/m².

4.2 Performance of green TADF device

4.2.1 The host structure for TADF material

Thermally activated delayed fluorescent materials have small energy difference between singlet energy level and triplet energy level (small ΔE_{st}). In other words, TADF materials have high triplet energy level while they are maintaining singlet energy level.

To achieve high device performance, the host materials for TADF emitter need to satisfy additional requirements. The HOMO and LUMO levels of TADF materials are usually deeper than phosphorescent material, so host materials for TADF emitter also need to have deep HOMO, LUMO levels. In addition, to suppress exciton quenching, it is necessary to have higher singlet and triplet energy level than singlet energy level of TADF emitter. The DCzDCN contains carbazole unit and phthalonitril unit connected with a phenyl linkage. This donor-acceptor structure allows DCzDCN to meet the requirements mentioned above.

In this experiment, DCzDCN is used as an electron transport type host material, and mixed with TCTA or mCP for exciplex type host structure. And, also, fabricate CBP:DCzDCN mixed host device for exciplex free type host structure. The schematic energy diagram of host materials is in Fig. 12.

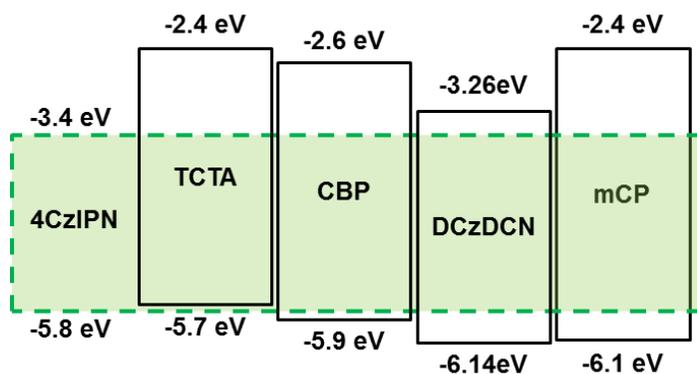


Figure 12. Schematic energy diagram for host materials along with HOMO and LUMO levels of 4CzIPN (dashed line).

4.2.2 Characteristics of the green TADF device

Green TADF devices were fabricated as the same device structure of green phosphorescence device but with different EML composition.

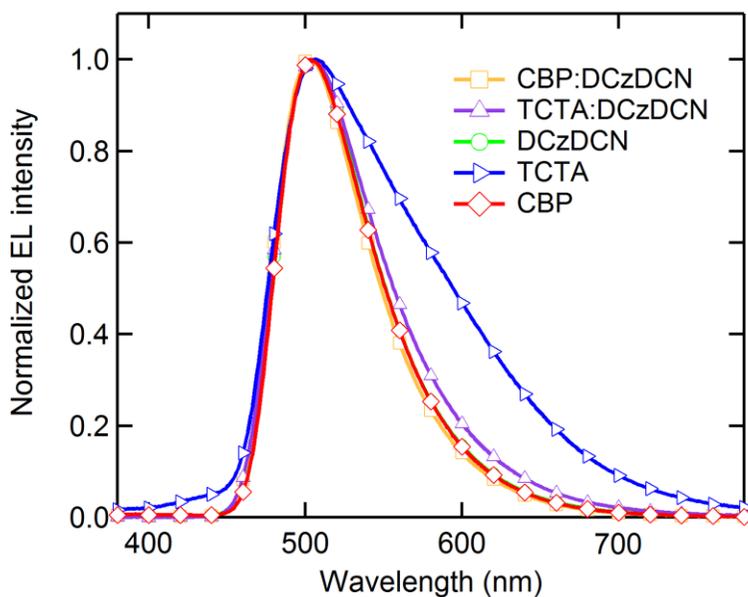


Figure 13. Normalized electroluminescence spectrums of 4CzIPN devices.

Electroluminescence spectrum is measured to confirm the emission light of the devices is coming out from emitter material. All the devices show typical 4CzIPN emission which has peak wavelength at 502nm. However, device which contains TCTA exhibits extra tail at long wavelength (Fig. 13.). This is because of exciplex formation between TCTA and 4CzIPN [14].

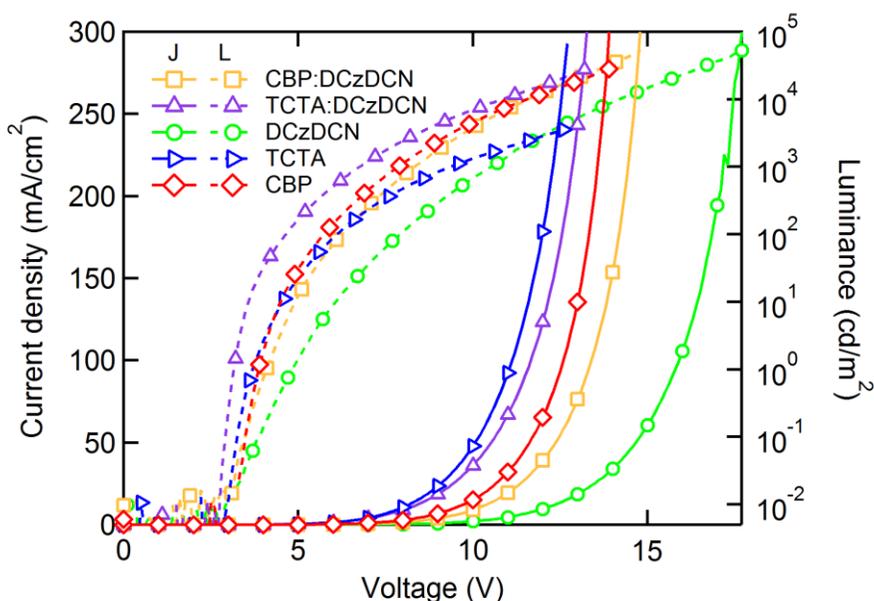


Figure 14. Current-Voltage-Luminance characteristics of 4CzIPN devices with different host structure.

Current-Voltage-Luminance characteristics are shown in Fig. 14. The device with the TCTA has lower current density than the TCTA:DCzDCN device at the same voltage despite of it has lowest driving voltage. This is because of better charge balance of the TCTA:DCzDCN device. The TCTA:DCzDCN device has better J-V-L characteristics than CBP:DCzDCN because of smaller hole injection barrier.

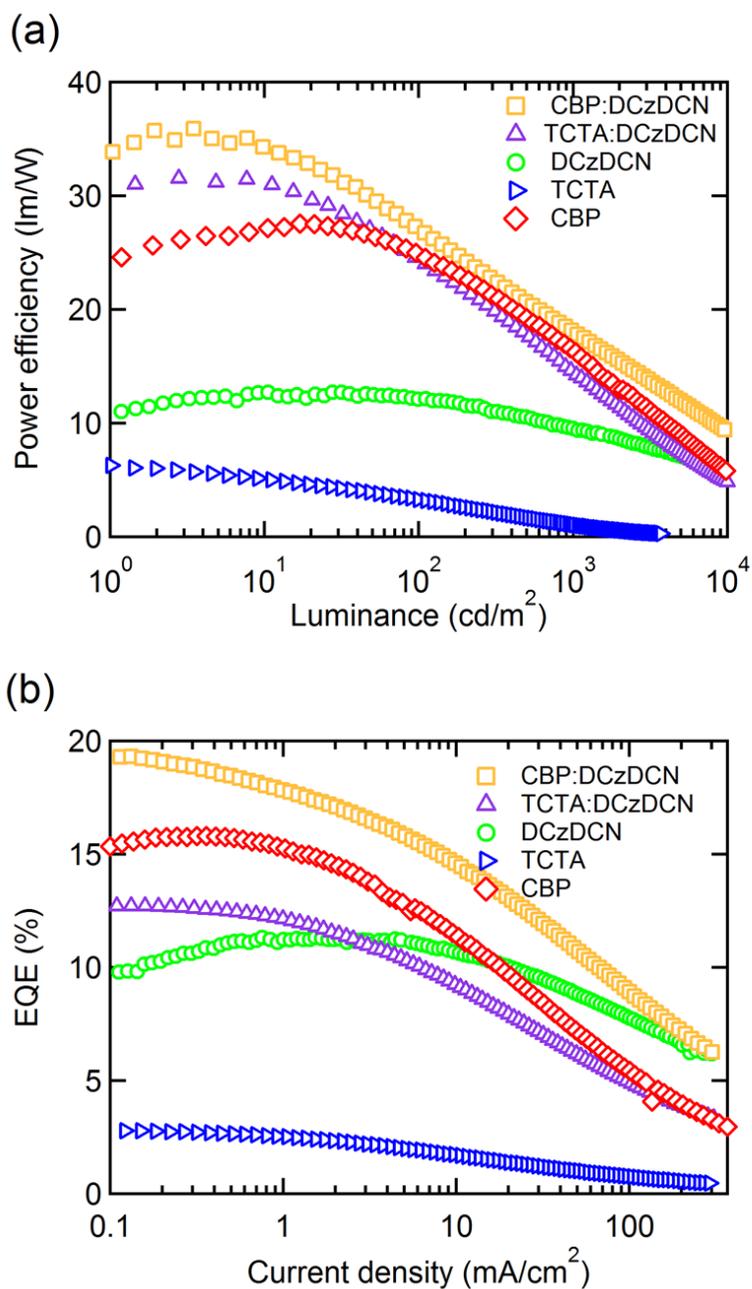


Figure 15. (a)Power efficiency characteristics, (b)External quantum efficiency characteristics of the TADF devices

Fig. 15 shows power efficiency and external quantum efficiency of the devices with different host structure and the summary of all the characteristics shown in table3. Mixed host structures usually have better efficiency because of good charge balance coming from small injection barrier and good hole and electron transport properties. For this reason, CBP:DCzDCN device has better power and external quantum efficiency than single host devices. In case of TCTA:DCzDCN, external quantum efficiency is lower than CBP and DCzDCN device at over the current density of $3\text{mA}/\text{cm}^2$. This can be presumed by the exciton quenching in the emissive layer because of the HOMO level of the TCTA which is shallower than 4CzIPN. However, the lifetime of the TCTA:DCzDCN is the better than other devices, which means the formation of exciplex still gives good effect on the device.

Based on the experiment results, additional experiment is carried out using the mCP which has deeper HOMO level than the 4CzIPN (See the Fig. 12.). The device is fabricated with CBP single host as a reference device, and with mCP:DCzDCN mixed host as a exciplex forming host structure. Also, the mCP single host structure device is fabricated for comparison.

Table 3. The summary of characteristics of TADF devices.

	EQE (%) @1000cd/m²	PE (lm/W) @1000cd/m²	Driving voltage (V) @1000cd/m²	Lifetime (hr) @3000cd/m² @T70
CBP	14.2	16.24	7.9	0.696
DCzDCN	11.2	9.54	10.5	-
TCTA	1.22	1.08	9.4	0.0495
CBP:DCzDCN	16.9	18.2	8.4	1.44
TCTA:DCzDCN	10.8	14.26	6.7	1.55

Electroluminescence spectrums of devices are almost same (See the Fig.16). This indicates that there is no undesirable emission from host materials and no exciplex formation between the dopant and host materials.

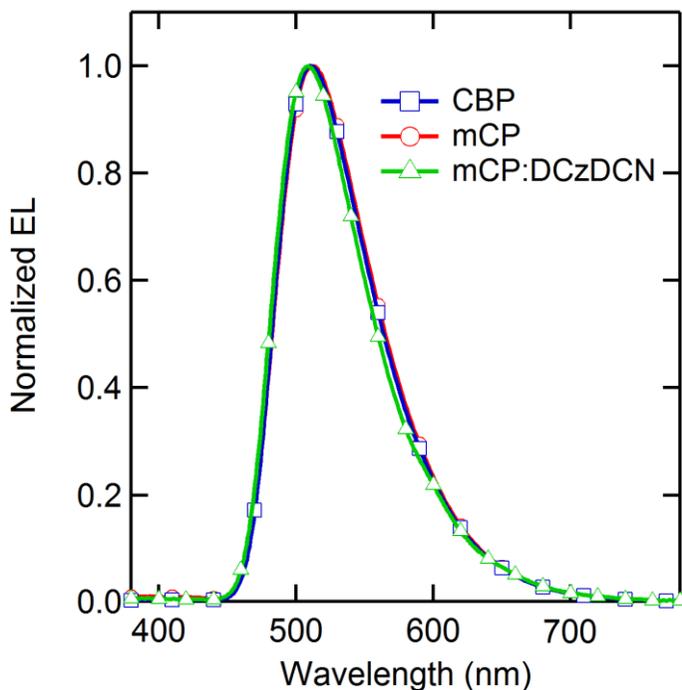


Figure 16. Normalized electroluminescence spectrum of the TADF device with CBP, mCP and mCP:DCzDCN as a host.

External quantum efficiency and Lifetime curves are shown in Fig.17 and Fig.18, respectively. External quantum efficiency of the mCP:DCzDCN device is not highest but the roll off of EQE exhibit better than other devices. This indicate that the mCP:DCzDCN device is more stable at the high current density, in other words, mCP:DCzDCN device is less likely to quench luminance species under the high charge density.

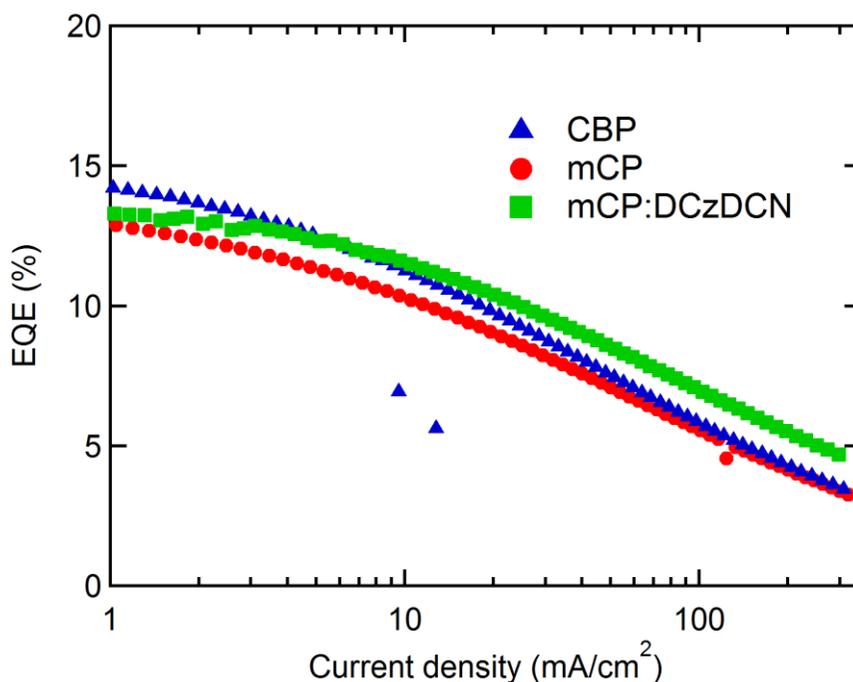


Figure 17. External quantum efficiency of the TADF device with CBP, mCP and mCP:DCzDCN as a host.

However, the deep HOMO level of mCP indicates high hole injection barrier which lead to high driving voltage and low power efficiency. Device characteristics are listed in table 4.

Table 4. The summary of characteristics of TADF device with CBP, mCP and mCP:DCzDCN as a host.

	EQE (%) @1000cd/m ²	PE (lm/W) @1000cd/m ²	Driving voltage (V) @1000cd/m ²	Lifetime (hr) @3000cd/m ² @T70
CBP	13.33	16.69	7.65	3.34
mCP	12.16	16.01	7.3	3.8
mCP:DCzDCN	12.58	14.36	8.15	8.83

The lifetime of mCP:DCzDCN device over 8hrs at the luminance of 3000 cd/m². This is the result from good charge balance and efficient energy transfer to the dopant as well.

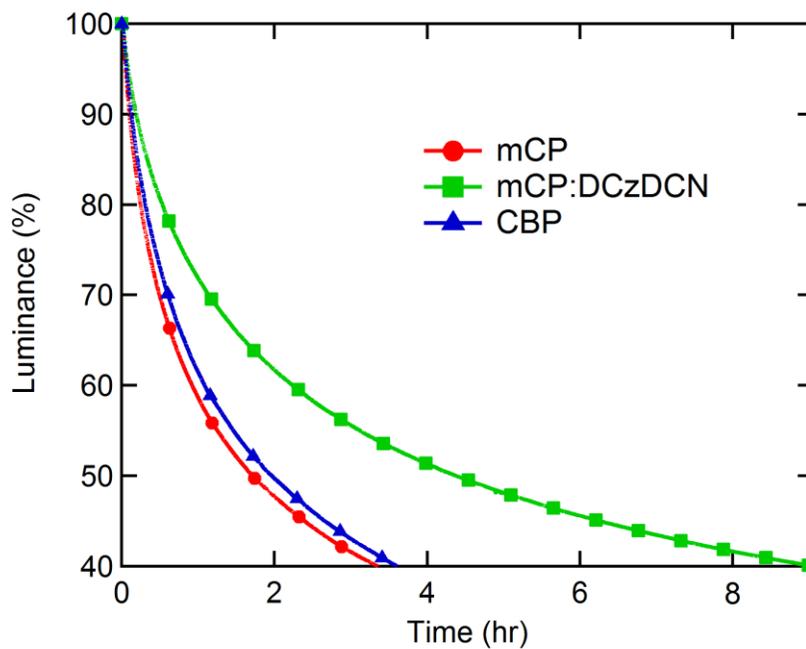


Figure 18. Lifetime of the TADF device with CBP, mCP and mCP:DCzDCN as a host.

Chapter 5

Conclusion

For the green phosphorescence device with Ir(ppy)₃ as dopant, the device performance was improved when it contains exciplex forming TCTA:DCzDCN. And compared with the reference device with CBP as host, the driving voltage was almost half and power efficiency was improved by a factor of 1.73. Also the operation lifetime of the device has improved 26 times and 1.6 times longer lifetime compared with reference device and exciplex-free mixed host structure device, respectively.

The efficiency of the TADF device with 4CzIPN as dopant was not the best when we used exciplex forming host structure. However, when we applied exciplex type host structures, they showed better stability compared with exciplex free type host structures. The operational lifetime of the device with TCTA:DCzDCN and mCP:DCzDCN as host were more than 2.2 times and 2.6 times longer than the device with CBP as host, respectively.

Therefore, the exciplex forming host structure is a good candidate for the stable device especially when one of the host materials has rather high triplet energy.

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초록 (Abstract in Korean)

지난 수십 년간 유기발광다이오드는 많은 발전을 이루어 왔으며 성능 향상을 위해 다층구조가 적용되어 왔다. 효과적인 성능의 유기발광다이오드를 제작하기 위해 각 층의 역할에 따라 적절한 유기재료들의 선택이 중요하다. 특히 발광층의 호스트 재료의 경우 매우 중요한 역할을 하는데 이는 전자와 정공의 비율, 재결합 분포, 도펀트 물질로의 에너지 전달을 호스트로 제어를 할 수 있기 때문이다.

본 논문에서는 엑시플렉스를 형성하는 호스트 구조가 유기발광다이오드의 성능에 미치는 영향에 대해 연구를 하였다. 강한 전자, 전공 수송 특성을 지니는 두 가지 호스트 물질 사이에서 엑시플렉스가 형성이 되는 것을 실험을 통해 확인을 하였고, 이를 바탕으로 서로 다른 두 도펀트 물질에 엑시플렉스를 형성하는 호스트를 적용하여 평가를 진행하였다. 도펀트 물질로는 녹색 인광 물질인 iridium(III)tris(2-phenylpyridine) (Ir(ppy)_3)과 녹색 지연형광 물질인 (4s,6s)-2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN)가 사용되었다. 엑시플렉스를 형성하는 호스트 물질의 경우 Tris(4-carbazoyl-9-ylphenyl)amine (TCTA) 와 3',5'-Di(carbazol-9-yl)-[1,1'-biphenyl]-3,5-dicarbonitrile (DCzDCN)을 50:50 비율로 증착하였다. 4CzIPN의 경우 추가적으로 1,3-Bis(N-carbazolyl)benzene (mCP):DCzDCN 조건에 대해서도 평가가 진행되었다. 디바이스 평가

결과 녹색 인광 디바이스는 엑시플렉스를 형성하는 호스트 구조를 적용하였을 때 전력효율이 좋은 긴 수명의 디바이스 특성을 나타내었고, 녹색 지연형광 디바이스도 역시 엑시플렉스를 형성하는 호스트 구조를 적용 하였을 때 긴 수명을 나타내었다.

주요어 : 유기발광다이오드, 발광층, 호스트구조, 엑시플렉스 형성, 수명
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