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공학석사 학위논문

**Effect of exciplex forming co-hosts  
on the performance of  
phosphorescent dye doped  
organic light emitting diodes**

공동 호스트 구조에서의 엑시플렉스 형성이  
인광 염료 도핑한 유기 발광 다이오드의  
성능에 미치는 영향

2013 년 2 월

서울대학교 대학원  
재료공학부  
이창헌

# Effect of exciplex forming co-hosts on the performance of phosphorescent dye doped organic light emitting diodes

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이 논문을 공학석사 학위논문으로 제출함  
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서울대학교 대학원  
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## **Abstract**

# **Effect of exciplex forming co-hosts on the performance of phosphorescent dye doped organic light emitting diodes**

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Exciplex is an excited state charge transfer complex formed between a donor and an acceptor molecules. Formation of exciplex in organic light emitting diodes (OLEDs) has been considered as an obstacle to increase the efficiency of OLEDs. However, high efficiency phosphorescent OLEDs was reported using an exciplex forming co-host recently. Unfortunately the effect of formation of exciplex in co-host systems on the performance of OLEDs

has not been extensively studied yet.

In this thesis, we studied the effect of the formation of exciplex in co-hosts on the performance of OLEDs. Three exciplex forming co-hosts and two non-exciplex forming co-hosts were selected for the purpose and used to fabricate OLEDs. It turns out that OLEDs with the exciplex forming co-hosts showed lower operating voltages than the OLEDs with the hosts not forming exciplex. We propose that in the exciplex forming co-host systems, electrons and holes recombine to form exciplex first followed by the energy transfer to the dopant to form excitons on the dopant molecules. In contrast, the direct recombination of electrons and holes on dopant molecule rather than the energy transfer from the host molecule is the dominant process in non-exciplex forming co-host system. This process increases driving voltage.

**Keywords: Organic light emitting diode, Exciplex, Co-host system**

**Student Number: 2011-20663**

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# Chapter 1

## Introduction

### 1.1 Organic Light Emitting Diodes

Organic light emitting diodes (OLEDs) have attracted attention for next generation technology. OLEDs are thin solid state devices those can be applied to lightings and displays applications. OLEDs have advantage upon the conventional devices such as LED and fluorescent tubes in terms of light weight, thin thickness, low cost and flexibility.

Figure 1 shows typical structure of OLEDs. It usually consist of organic layers sandwiched between two electrodes, where organic layers usually have structure of multilayer such as a hole injection layer (HIL), a hole transporting layer (HTL), an emission layer (EML), an electron transporting layer (ETL) and an electron injection layer (EIL), the multilayer structure enhances injection of charge carriers to the emission layer.

Light emitting mechanism of OLEDs is as follows<sup>1</sup>; first, by applying voltage, holes and electrons are accelerated to EML. Second, when hole and electron meets, they become to exciton which is bound state

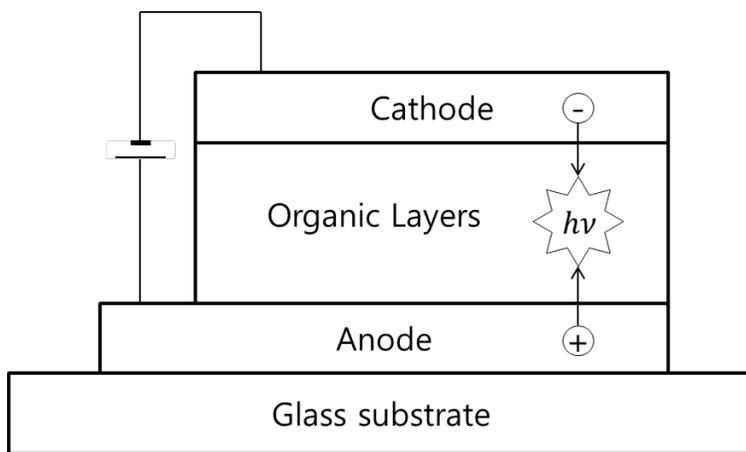
of opposite charged particle. Then emission occurs when electrons fall into energy state of hole and gives off energy. Some of them give off energy as light.

One of main concern of OLEDs is enhancing efficiency of OLEDs because it is closely related to energy consumption and device lifetime. One parameter for expressing efficiency is external quantum efficiency (EQE). It is the ratio of photons escaped from OLED to charge carrier injected into device. The EQE is usually expressed as following equation<sup>2</sup>.

$$\eta_{EQE} = \eta_{out} \eta_{re} \chi \eta_{PL}$$

Where  $\eta_{EQE}$  is the EQE of the OLED.  $\eta_{out}$  is the outcoupling efficiency which means ratio of photon escaped from device to total photon generated in device, max outcoupling efficiency can be calculated to be 30 % without structure for outcoupling<sup>3</sup>.  $\eta_{re}$  is the charge balance factor. If injected hole and electron are same in emission layer. It is considered to be unit in ideal case which means that all injected charge carriers form excitons.  $\chi$  is the ratio of exciton possible to emit light. For exciton states, there are distinctions in spin

alignment. If spin alignment is in parallel state, which is called triplet state, excited electron cannot be relaxed to ground state because this transition violates Pauli's exclusion principle. But if spin alignment is aligned in opposite way, this is called singlet state. This state can emit light by falling to ground state. In the conventional fluorescent OLEDs, this device only utilizes singlet excitons,  $\chi$  is limited to 0.25 because generation ratio of singlet and triplet excitation is 1:3.  $\eta_{PL}$  is the photoluminescent quantum efficiency. This factor is the ratio of excitons which actually emit light to excitons which are possible to emit light. There have been breakthroughs to increase efficiency of OLEDs. Since Tang<sup>4</sup> firstly demonstrated double layers fluorescent structure OLED, many methods to generate photon effectively are studied. One of these methods is utilizing triplet excitons. By using a heavy metal complexes, this material paves the way for light emitting of triplet state by strong spin-orbit coupling with high  $\eta_{PL}$ . For phosphorescent organic light emitting diodes (PhOLEDs) using phosphorescent dyes as dopants, all singlet and triplet exciton of phosphorescent dyes is allowed to decayed radiatively, making  $\chi = 1$ . This results in 4 fold enhancement of efficiency of OLED compared to maximum efficiency of fluorescent devices<sup>5,6</sup>.



**Figure 1.1** The typical structure of OLED device

## 1.2 Exciplex in Organic Light Emitting Diodes

Exciplex is an excited state charge transfer complex formed between donor and acceptor molecules. When donor and acceptor molecules are very close in the ground state beyond the equilibrium, repulsive force arises if they do not form aggregates. However, if a molecule absorbs light and becomes excited state, it can be stabilized by interacting with a neighboring ground state molecule. This phenomenon results in forming exciplex state. Exciplex differs from exciton in that exciplex is excited state charge transfer complex formed between donor and acceptor molecules. Schematic energy band diagram of exciton and exciplex is shown in Figure 1.2 (a).

There is the condition for forming exciplex in OLEDs. First thing is energetic condition. There should be more stable state between two molecules. This means the difference of lowest unoccupied molecular orbital (LUMO) or highest occupied molecular orbital (HOMO) energy level between donor and acceptor molecules should be larger than binding energy of excitons in the donor and acceptor molecules. Second, there is structural condition<sup>7</sup>. If molecule has structure that easy to interact with other molecule such as planar structure, it can

form exciplex when the energetic condition is satisfied. Bis-4,6-(3,5-di-3-pyridylphenyl)-2-methylpyrimidine (B3PYMPM) is good example of this planar molecular structure<sup>2,8</sup>.

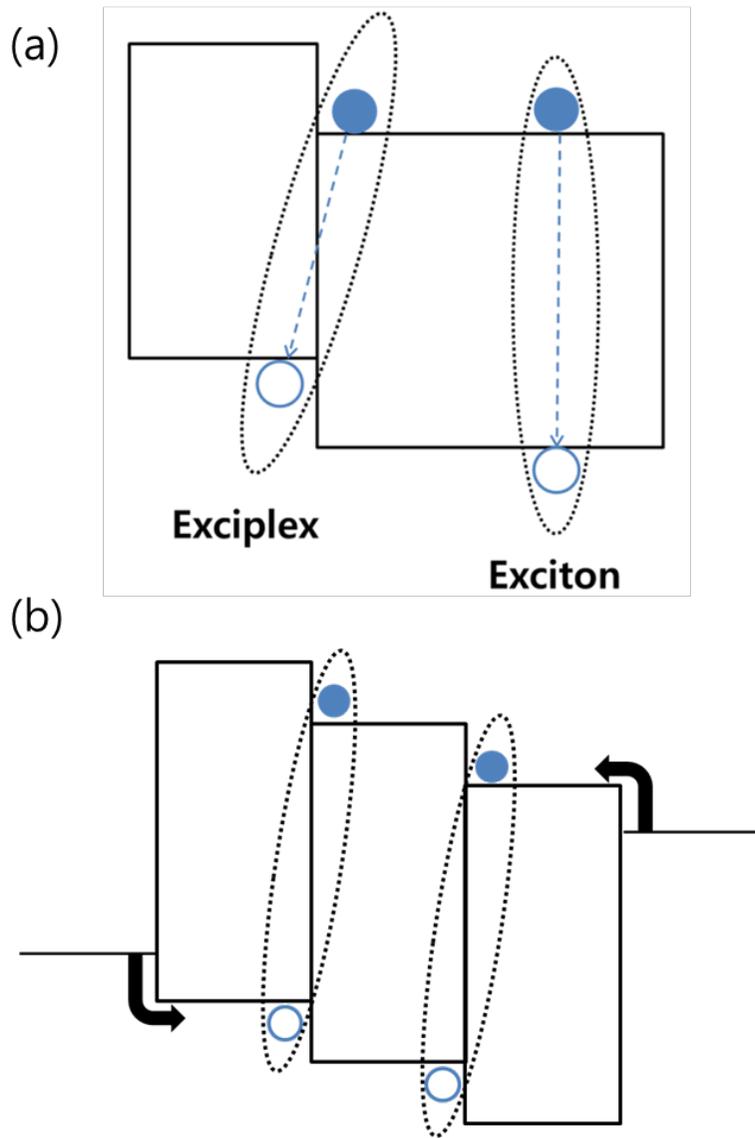
Exciplex had been considered as a quenching site in OLEDs<sup>9,10</sup>. In usual multilayer structure of OLED, charge accumulation near interface of layers leads to form exciplex as shown in Figure 1.2 (b). This usually results in inefficient emission of exciplex. Recently, exciplex is receiving attention for potential to be utilized as high efficiency OLED. One of them is using thermally activated delayed fluorescence (TADF)<sup>11</sup>. Fluorescent OLED device have low internal quantum efficiency because it only utilizes singlet exciton which is one fourth of total exciton generated. TADF is one method to harvest triplet exciton to generate light. If energy level difference between singlet and triplet energy, that is  $\Delta E_{st}$ , is small, triplet exciton can be converted to singlet exciton through reverse intersystem crossing (RISC). This leads to breakthrough of limitation of fluorescent OLED. Exciplex have an advantage on TADF system. Because electron-hole distance in exciplex is large. It results in small exchange energy, it leads to very low  $\Delta E_{st}$ <sup>12-14</sup>. High reverse intersystem crossing of 86.5 % have been reported<sup>14</sup>.

There is another research of high efficiency OLED using exciplex. Park reported phosphorescent OLEDs by using exciplex forming co-host structure<sup>2</sup>. In this study, the OLED device with ultimate efficiency such as high EQE, low turn-on voltage and low roll-off has been reported. The reasons for ultimate efficiency of OLED are attributed to efficient exciplex formation in EML, followed by the energy transfer from exciplex to dopant to form exciton, and the exciton's good confinement of EML.

However, effect of the formation of exciplex in co-host system on the performances of OLEDs has not been well studied. In Park's paper, he studied one exciplex forming co-host system which using tris(4-carbazoyl-9-ylphenyl)amine (TCTA) as hole transporting material (HTM) and B3PYMPM as electron transporting material (ETM). Therefore the conditions for forming exciplex in co-host and the reasons for high efficiency in exciplex forming co-host system are further to be studied.

In this thesis, we studied how exciplex affects performance of devices by comparing exciplex and non-exciplex system in co-host structure. We chose two hole transporting materials and three electron transporting materials for co-host by considering energetic and

structural factors for forming exciplex. Through photo physical study we could identify the exciplex forming co-host system. We investigated the effect of the formation of exciplex in the co-hosts by comparing OLED device of exciplex forming co-host system and non-exciplex forming co-host system. We found that exciplex forming co-host systems have an advantage in operating voltage.



**Figure 1.2** (a) Configurations of exciplex and exciton, (b) Exciplex formation at the interface of multi-stacked layers OLEDs

## Chapter 2

### Experiments

Glass substrates pre-patterned with 70 nm-thick indium tin oxide (ITO) were rinsed and cleaned with acetone and IPA twice, followed by boiling in IPA for 2 minutes. The ITO glass substrates were kept in an 80 °C oven for 15 minutes and treated with ultraviolet (UV)-ozone for 15 minutes before use to clean further and to tune the work function of ITO for good current injection. For PL measurement, we used quartz substrates and fused silica glass substrates which do not absorb light at UV spectrum region. All OLED devices and thin films for PL measurement were thermally deposited at a base pressure of  $< 5 \times 10^{-7}$  Torr without breaking vacuum.

50 nm thick films on quartz substrate were used for PL and absorbance measurement. We used 325 nm monochromatically induced Xe lamp as excitation light source and detect PL intensity by a monochromator attached photomultiplier tube (PMT). We also measured the absolute PL quantum efficiency with an integrating sphere. We used 325 nm He/Cd monochromatic laser and a monochromator attached PMT

(Acton Research, PD-438) detector. Absorbance was measured using a Cary 5000 UV-vis-NIR spectrophotometer.

Current density – voltage – luminescence (J–V–L) characteristics, electroluminescence (EL) spectra and EQEs were measured with Keithley 2400 source meter and Photoresearch PR 650 SpectraScan Colorimeter. EQE of the OLEDs was obtained from the luminance in the normal direction; we corrected EQE with the angle-dependent electroluminescence measurement. A CS-100 Luminance and Color meters instead of PR 650 was used for fast scan of the J-V-L is required.

## Chapter 3

### Result & Discussion

#### 3-1 Photo-physical study of exciplex forming and non-exciplex forming co-host

We used 4,4'-N,N'-dicarbazole-biphenyl (CBP) and TCTA as HTM and B3PYMPM, tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane (3TPYMB) and 1,3,5-tri(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl (TPBi) as ETM. Molecular structures, energy levels, and mobility data of electron and hole of HTMs and ETMs are shown in Figure 3.1, 3.2 and Table 1, respectively. The host materials were selected by considering energetic and structural factor for forming exciplex. CBP and TCTA have similar band gap, but different LUMO level ( $\sim 0.4$  eV) so it controls driving force of transition from LUMO of donor to that of acceptor. And for electron transporting material (ETM), we considered also structural factor. Both CBP and TCTA are known to form exciplex when combined with B3PYMPM<sup>2,8</sup>. It is because of the B3PYMPM's planar structure, it makes easy to interact between

molecules and this leads to form exciplex. TPBi and 3TPYMB have 3-D structure because of steric hindrance of functional group (phenyl and methyl group for each material). Though 3TPYMB and TPBi are not planar, but it is known to form exciplex when combined with m-MTDATA<sup>14,15</sup>. Because m-MTDATA have high LUMO energy of -2.0 eV, so this energy level gives strong driving force to break exciton binding energy because it provides larger LUMO energy level difference. We will show strong energetic factor compensates unfavorable structural condition. We investigated five systems by combining two HTM and three ETM. Band diagrams of systems except for CBP:B3PYMPM are shown in Figure 3.3. CBP:B3PYMPM is proved to form exciplex in the previous study<sup>8</sup>. All system could be candidates for forming exciplex except CBP:TPBi system in which LUMO level of donor is higher than that of acceptor, so there is no stabilized charge-transfer state between CBP and TPBi.

Figure 3.3 shows PL spectra of CBP:3TPYMB, CBP:TPBi system and component of each co-deposition layer. According to the PL spectra of CBP:3TPYMB and CBP:TPBi systems, they do not form exciplex. Peak of CBP:3TPYMB (395 nm) shows similar peak with CBP (395 nm) but more sharper. This means CBP and 3TPYMB do not form

exciplex. Because it does not show red shifted peak which means more stabilized state is produced coming from interaction between two different molecules. CBP:TPBi co-host system does not also show exciplex emission as we expected. PL emission peak of co-host film (382 nm for TPBi, 387 nm for co-host) is not red shifted compared to PL emission peak of each component. CBP and 3TPYMB forms exciplex when it combined with different molecule, for example CBP with B3PYMPM<sup>8</sup> and 3TPYMB with m-MTDATA<sup>14</sup>. Comparing previous report and this result, we concluded that formation of exciplex depends on not only energetic and but also structure factor complexly because B3PYMPM is more planar molecular structure than 3TPYMB and TPBi.

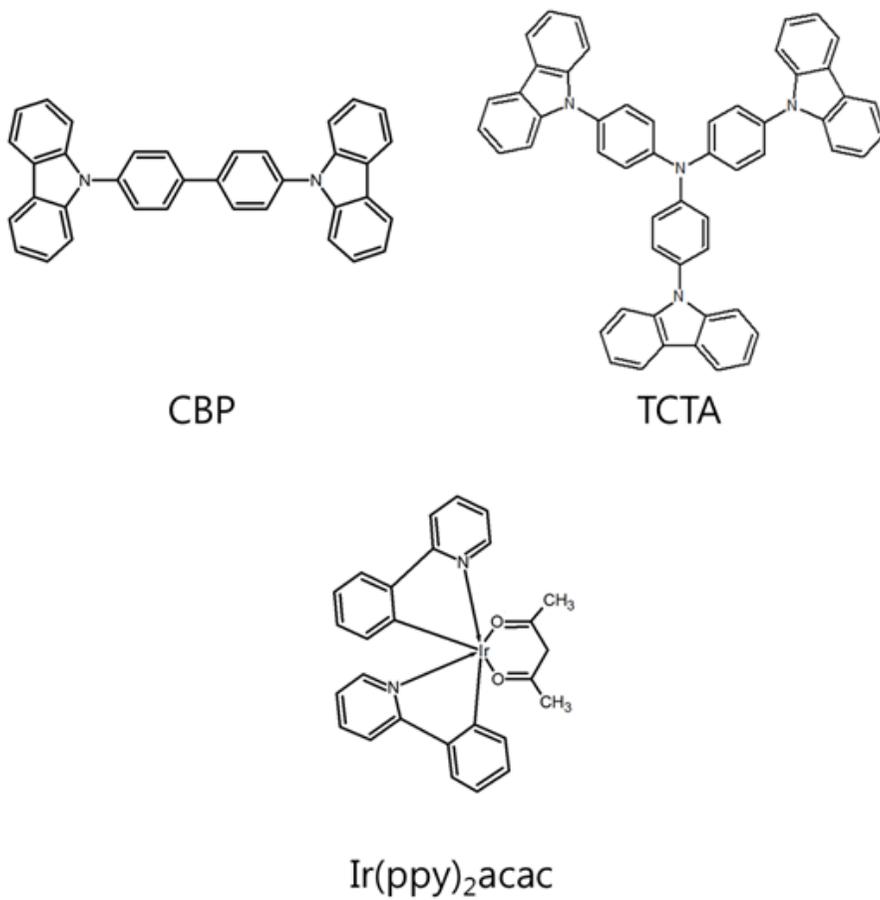
On the other hand, TCTA:3TPYMB and TCTA:TPBi co-host systems formed exciplex. In TCTA:3TPYMB system, PL emission peaks of TCTA, 3TPYMB, and co-host of TCTA:3TPYMB were located at 393 nm, 383 nm and 446 nm respectively. The PL spectrum of TCTA:3TPYMB is broad and red shifted. This PL spectrum cannot be derived from linear combination of PL spectra of TCTA and 3TPYMB, this means new state is formed by two molecules, we know this is exciplex. And for TCTA:TPBi system. Unlike CBP:TPBi system,

LUMO level of TPBi (2.7 eV) is lower than LUMO level of TCTA (2.43 eV). So it can produce exciplex if two molecules interact effectively. In TCTA:TPBi system, PL emission peaks of TCTA, TPBi were located at 393 nm, 382 nm and 438 nm respectively. this red shifted and broader spectrum is the evidence of exciplex formation of TCTA:TPBi co-host.

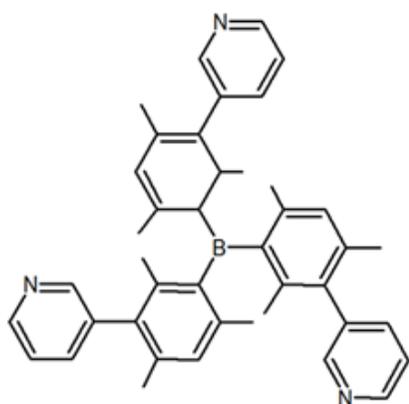
We measured absorbance of each film to identify that this red shifted peak results from exciplex not from aggregates. Aggregate has its own absorption due to energy band splitting. If there are aggregates, there will be another absorbance peak. But for exciplex system, exciplexes don't have absorbance of its own, so absorbance of co-host films have same peaks of superimposed spectra of components. The absorbances of TCTA:3TPYMB and TCTA: TPBi systems are shown in Figure 3.6. We superimposed spectra as volume percent. Though two spectra are not exactly coincided each other. There is no shifted peak from individual component to mixture. This indicates the red shifted peaks for TCTA based co-host systems are coming from not aggregates but from exciplex formation.

Both 3TPYMB and TPBi have 3-D structures not favorable to form exciplex. So when combined these acceptors to CBP donor, these

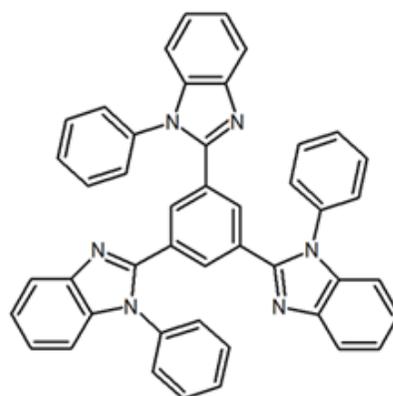
systems didn't show exciplex emission. But when we combined these acceptor to TCTA donor, photo physical study for these system showed there are exciplex states. We explained that this phenomenon is because TCTA has 0.4 eV higher LUMO energy than CBP, it provides stronger driving force to break the binding of excitons. But when CBP is combined with B3PYMPM which have planar structure, this system formed exciplex<sup>8</sup>. The series of these experimental results show that there are indeed energetic and structural factor for forming exciplex and strong energetic driving force compensates structure factor unfavorable to form exciplex such as 3-D structures. We measured also absolute PL quantum efficiency of every co-deposited film we are investigating. From this measurement we found out quantum efficiencies of CBP:B3PYMPM, CBP:3TPYMB, CBP:TPBi, TCTA:3TPYMB, and TCTA:TPBi are 15.4 %, 20.7 %, 39.1 %, 10.8 %, and 8.0 %, respectively. We also measured absolute PL quantum efficiencies of CBP, TCTA, 3TPYMB and TPBi neat films. Each efficiency is 40.2 %, 14.8 %, 3.0 % and 44.1 %, respectively. PL quantum efficiencies of single host and co-host films are summarized in Table 2.



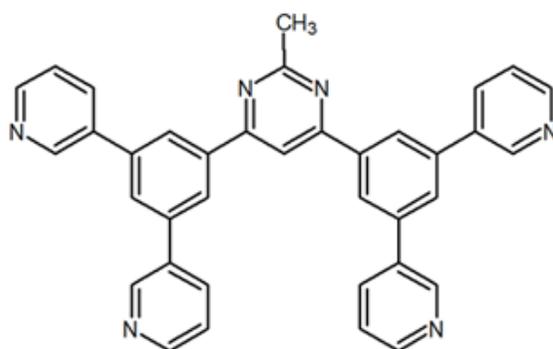
**Figure 3.1** Molecular structure of hole transport materials and dopant



3TPYMB

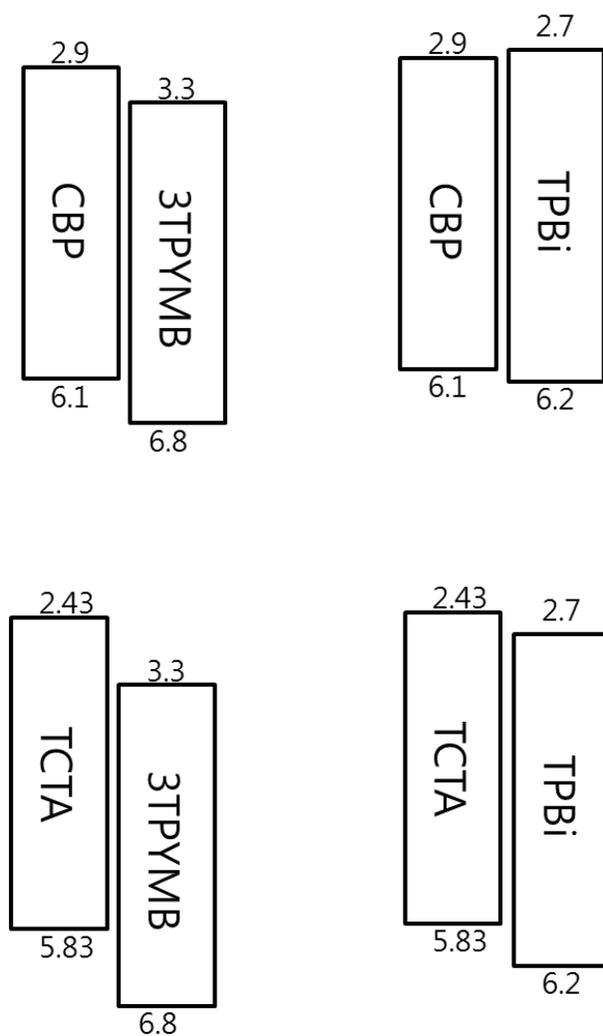


TPBi



B3PYMPM

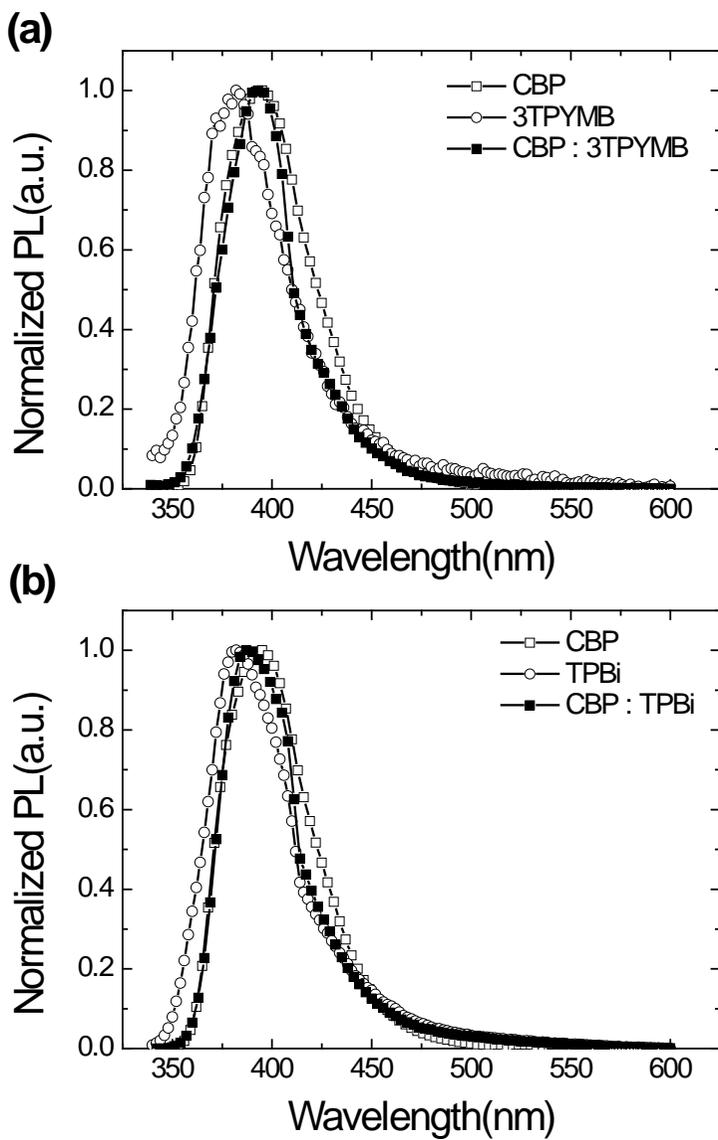
**Figure 3.2** Molecular structure of electron transport materials



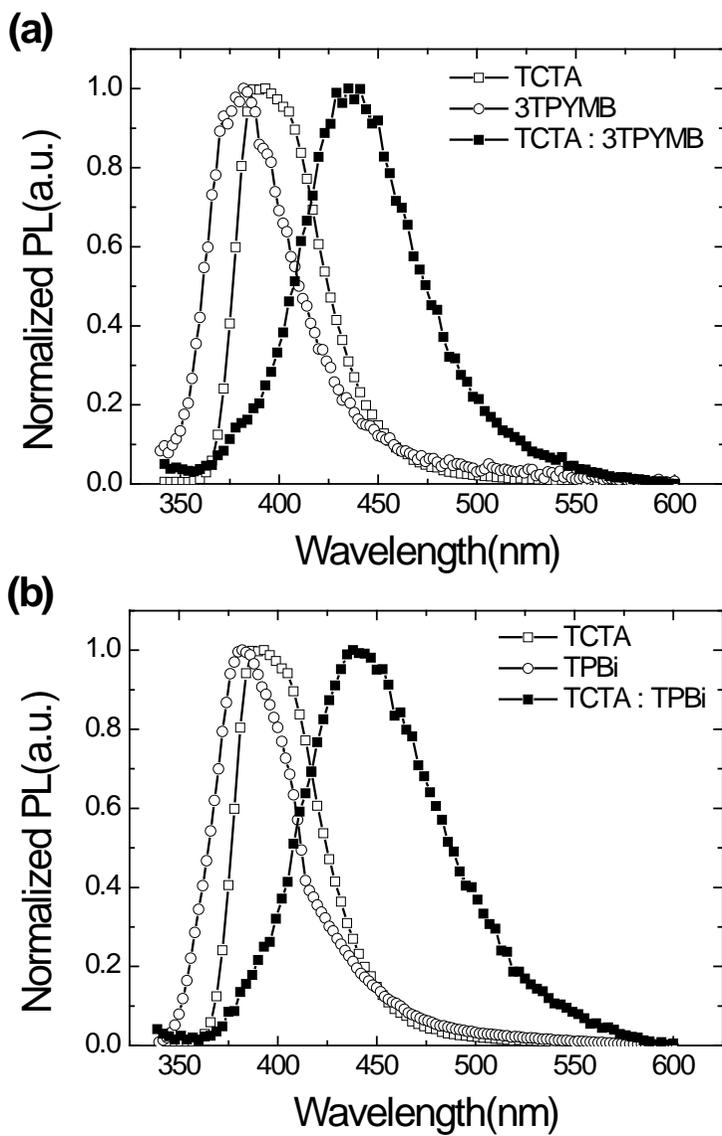
**Figure 3.3** Energy levels of co-host systems which are pair of hole transporting material and electron transporting materials

**Table 1** Energy level and mobility data of host materials

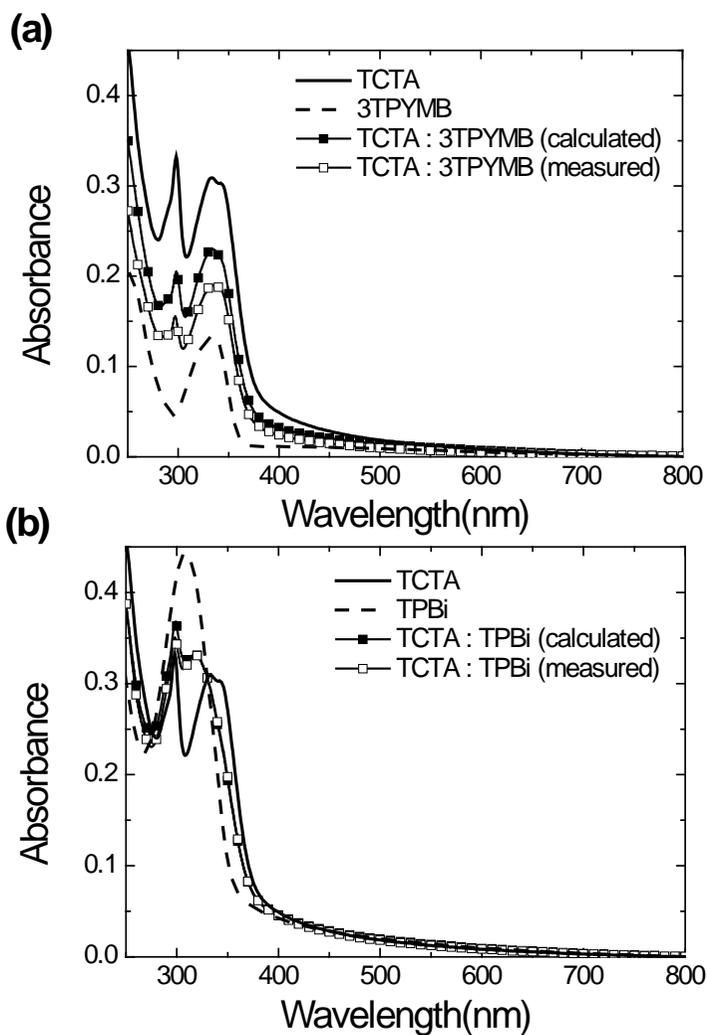
HOST	HOMO (eV)	LUMO (eV)	hole & electron mobility (cm <sup>2</sup> /Vs)	Reference
CBP	-2.9	-6.1	h: $2 \times 10^{-3}$ e: $3 \times 10^{-4}$	2,8,16
TCTA	-2.43	-5.83	h: $3 \times 10^{-4}$ e: $< 10^{-8}$	2,16
B3PYMPM	-3.2	-6.77	e: $1.5 \times 10^{-5}$	8,17
3TPYMB	-3.32	-6.8	e: $1 \times 10^{-5}$	18
TPBi	-2.7	-6.2	e: $\sim 10^{-5}$	19,20



**Figure 3.4** PL spectra of (a) neat CBP, neat 3TPYMB, and CBP:3TPYMB films and (b) neat CBP, neat TPBi, and CBP:TPBi films



**Figure 3.5** PL spectra of (a) neat TCTA, neat 3TPYMB, and TCTA:3TPYMB films and (b) neat TCTA, neat TPBi, and TCTA:TPBi films



**Figure 3.6** Absorbance of spectra of (a) neat TCTA, neat 3TPYMB, measured TCTA:3TPYMB, and calculated TCTA:3TPYMB and (b) neat TCTA, neat TPBi, measured TCTA: TPBi, and calculated TCTA:TPBi system

**Table 2** Photoluminescence quantum efficiencies of single host and co-host

	CBP	TCTA	3TPYMB	TPBi
PL				
Efficiency (%)	20.7	14.8	3.0	44.1

	CBP: 3TPYMB	CBP:TPBi	TCTA: 3TPYMB	TCTA:TP Bi
PL				
Efficiency (%)	20.7	39.8	10.1	8.0
Formation of Exciplex	X	X	O	O

## **3.2 OLED device characteristics using exciplex forming and non-exciplex forming co-host**

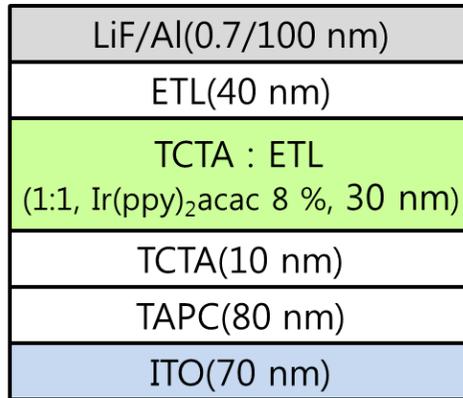
### **3.2.1 Selection of device structure using different HTM in co-host**

When we used TCTA as HTM, we used TAPC as HIL. It has been shown that TCTA device is optimized in exciplex forming co-host system by using TAPC as hole injection layer<sup>2</sup>. It seems that TAPC has higher HOMO level and good hole mobility, It provides effective hole injection for TCTA system. We selected TCTA based device structure as shown in Figure 3.7.

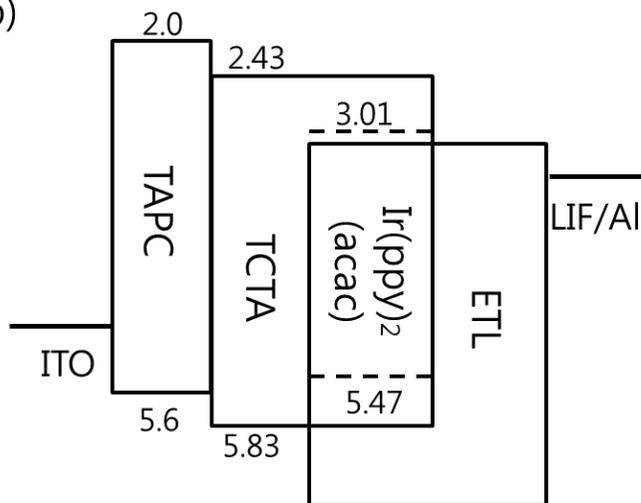
We tried to find HIL for co-host device using CBP as donor. Fixing ETL as B3PYMPM, and EIL as LiF, We attempted to use various HILs such as 70 nm TAPC which is effective for TCTA based co-host system, 1 nm single layer of MoO<sub>3</sub> or ReO<sub>3</sub> and 4 % ReO<sub>3</sub> doped CBP. Among these, ReO<sub>3</sub> doped CBP showed the best maximum EQE and roll-off characteristics. We also varied doping percent of ReO<sub>3</sub> from 4 % to 12 % to optimize HIL as shown in Figure 3.8. Current density and luminance characteristics are enhanced as doping percent increases, but EQE decreases. We

considered this EQE decreasing effect comes from charge imbalance effect. CBP is bipolar host and transport characteristic is good due to high mobility ( $3 \times 10^{-4} \text{ cm}^2/\text{V s}$  for electron,  $2 \times 10^{-3} \text{ cm}^2/\text{V s}$  for hole)<sup>16</sup> and it is higher than B3PYMPM's ( $1.5 \times 10^{-5} \text{ cm}^2/\text{V s}$  for electron)<sup>17</sup>. P-doping on CBP enhances injection and transport property<sup>21</sup>. So, further doping of CBP breaks charge balance by excess hole transport. It seems there is trade-off between charge injection and charge transport enhancement that breaks charge balance. We selected CBP based device structures using 4 %  $\text{ReO}_3$  doped CBP as HIL as shown in Figure 3.9.

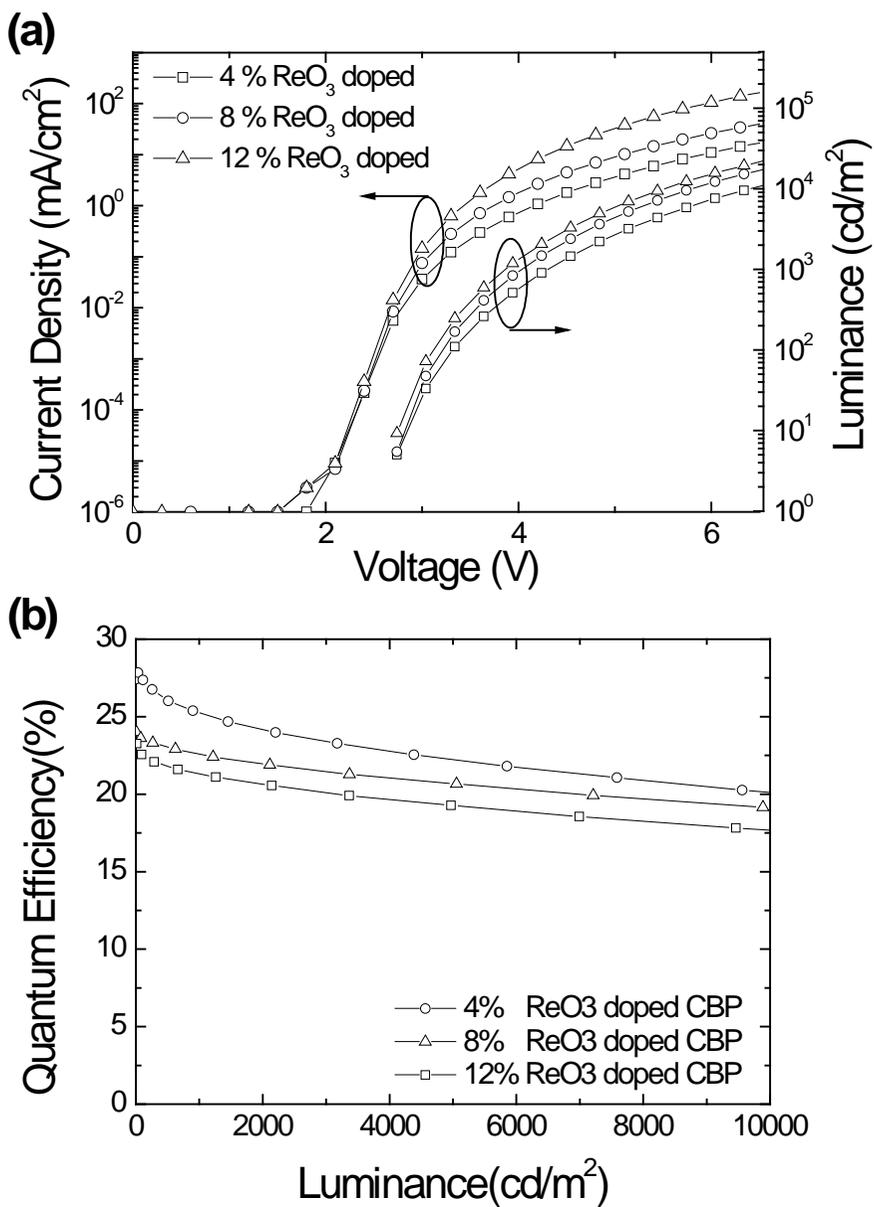
(a)



(b)

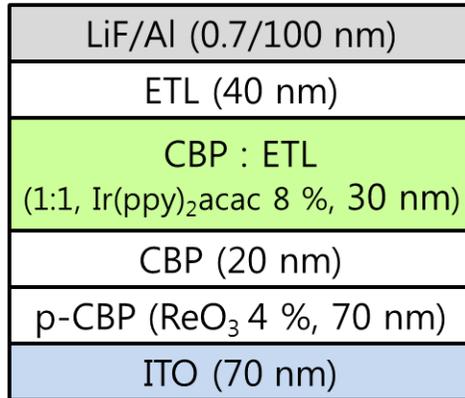


**Figure 3.7** (a) Structure of TCTA based OLED and (b) energy band diagram of TCTA based co-host OLEDs

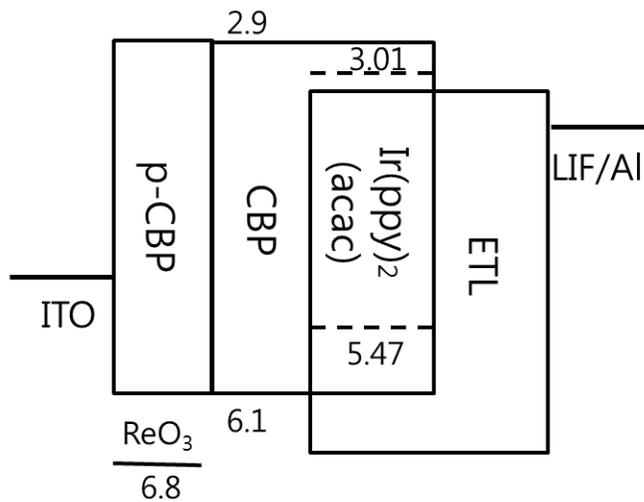


**Figure 3.8** (a) J-V-L and (b) EQE of CBP:B3PYMPM OLEDs as doping concentrations of  $\text{ReO}_3$  in CBP hole injection layer is changed

(a)



(b)



**Figure 3.9** (a) Structure of CBP based OLED and (b) energy band diagram of CBP based co-host OLEDs

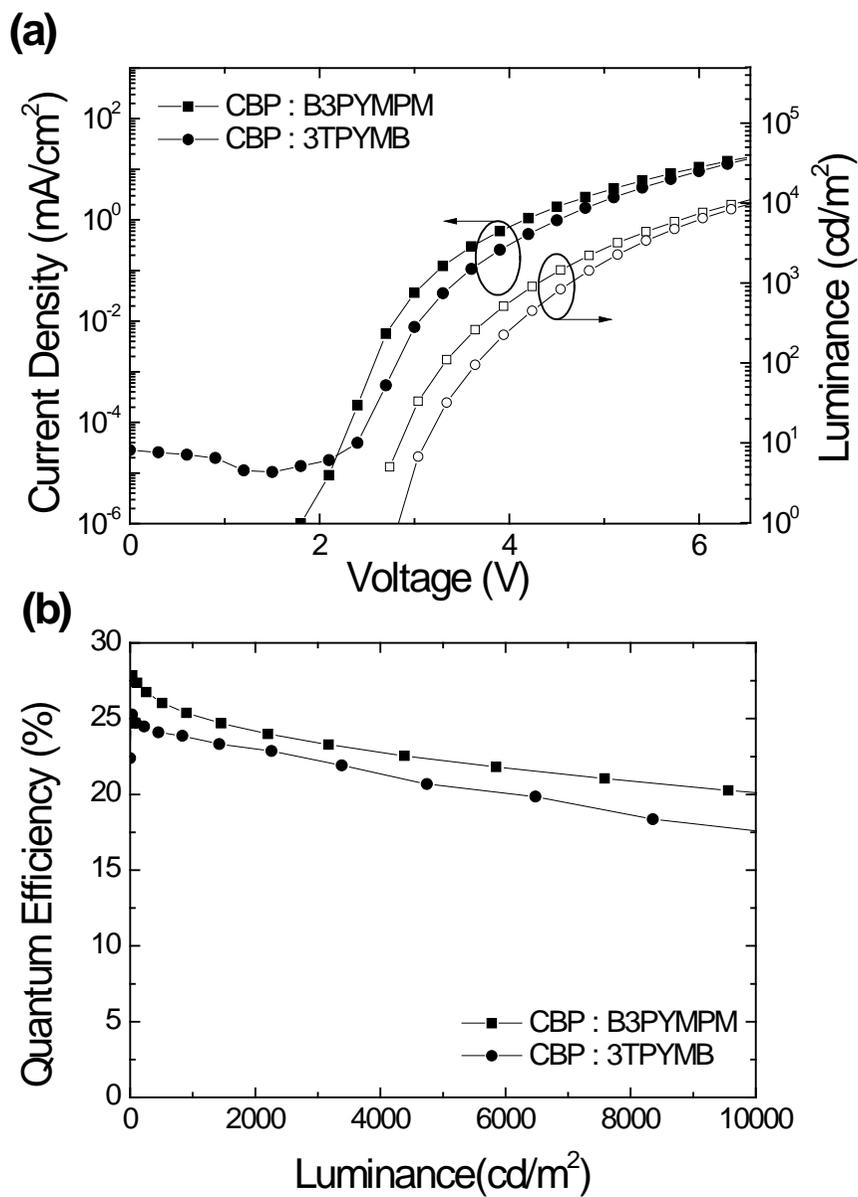
### 3.2.2 Performance of OLEDs with exciplex and non-exciplex forming co-host

We compared CBP:B3PYMPM and CBP:3TPYMB system. 3TPYMB has similar mobility ( $\sim 10^{-5}$  cm<sup>2</sup>/V s) and energy level with B3PYMPM (3.2/6.77 for B3PYMPM and 3.3/6.8 for 3TPYMB). But CBP:3TPYMB system does not form exciplex. We chose two systems because B3PYMPM and 3TPYMB have similar energy level and mobility, but differ in formation of exciplex. So we thought comparing CBP:B3PYMPM system and CBP:3TPYMB system would show how exciplex influence on the performance of OLEDs.

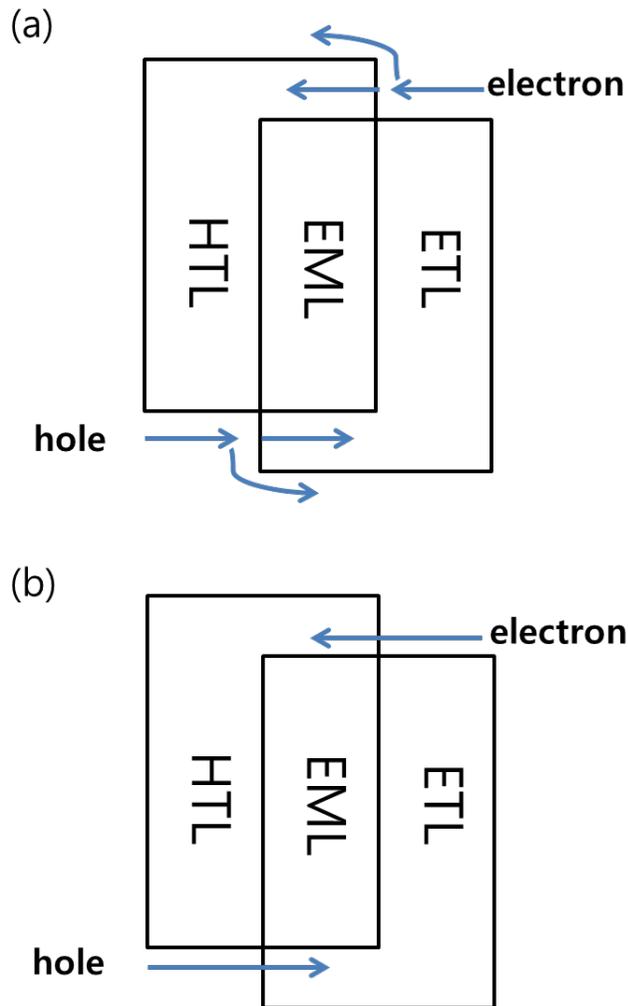
Figure 3.10 is J-V-L and roll-off characteristics of OLEDs with CBP:B3PYMPM and CBP:3TPYMB exciplex co-host. We corrected EQE of devices using angular distribution of electroluminescence. Turn-on voltage of CBP:B3PYMPM device is 2.7 V and that of CBP:3TPYMB device is 3.0 V. To reach 10,000 cd/m<sup>2</sup> luminescence, CBP:B3PYMPM system needs 6.4 V. Maximum EQE is 27.4 % and remain 20.1 % at 10,000 cd/m<sup>2</sup>. Maximum power efficiency is 103.5 lm/W. Turn-on voltage and operating voltage at of device 10,000 cd/m<sup>2</sup> with CBP:3TPYMPM are 3.0 V, and 6.5 V, respectively.

Maximum EQE and EQE at 10,000 cd/m<sup>2</sup> are 25.3 %, 17.6 %, respectively. Maximum power efficiency is 92.8 lm/W.

The difference between two devices can be explained by characteristic of exciplex as shown in Figure 3.11. There is no interaction between the HTM and the ETM forming a co-host such as CBP:3TPYMB system, it is difficult to form exciton at the host molecules because holes and electrons separately exist at the HT molecules and the ET molecules, respectively. Therefore, there are two paths to form exciton at the dopant molecules: (1) Direct charge trapping at the dopant sites to form exciton at the dopant molecules, or (2) the holes at the HT molecules is transported to the ET molecules (or the electrons at the ET molecules is transported to the HT molecules) over the energy barrier to form exciton at the host molecules, and then the excitons transfer to the dopants. Both mechanisms increase the driving voltage<sup>2</sup>. Therefore, over potential should be needed in this case. However, But for CBP:B3PYMPM exciplex forming co-host system, they don't have to jump over injection barrier because there is more stable, lower exciplex energy state. This result in difference of operating voltage. At 10 mA/cm<sup>2</sup>, CBP:B3PYMPM device is 5.9 V and CBP:3TPYMB device is 6.1 V, respectively



**Figure 3.10** (a) J-V-L and (b) roll off characteristics of CBP:B3PYMPM and CBP:3TPYMB co-host

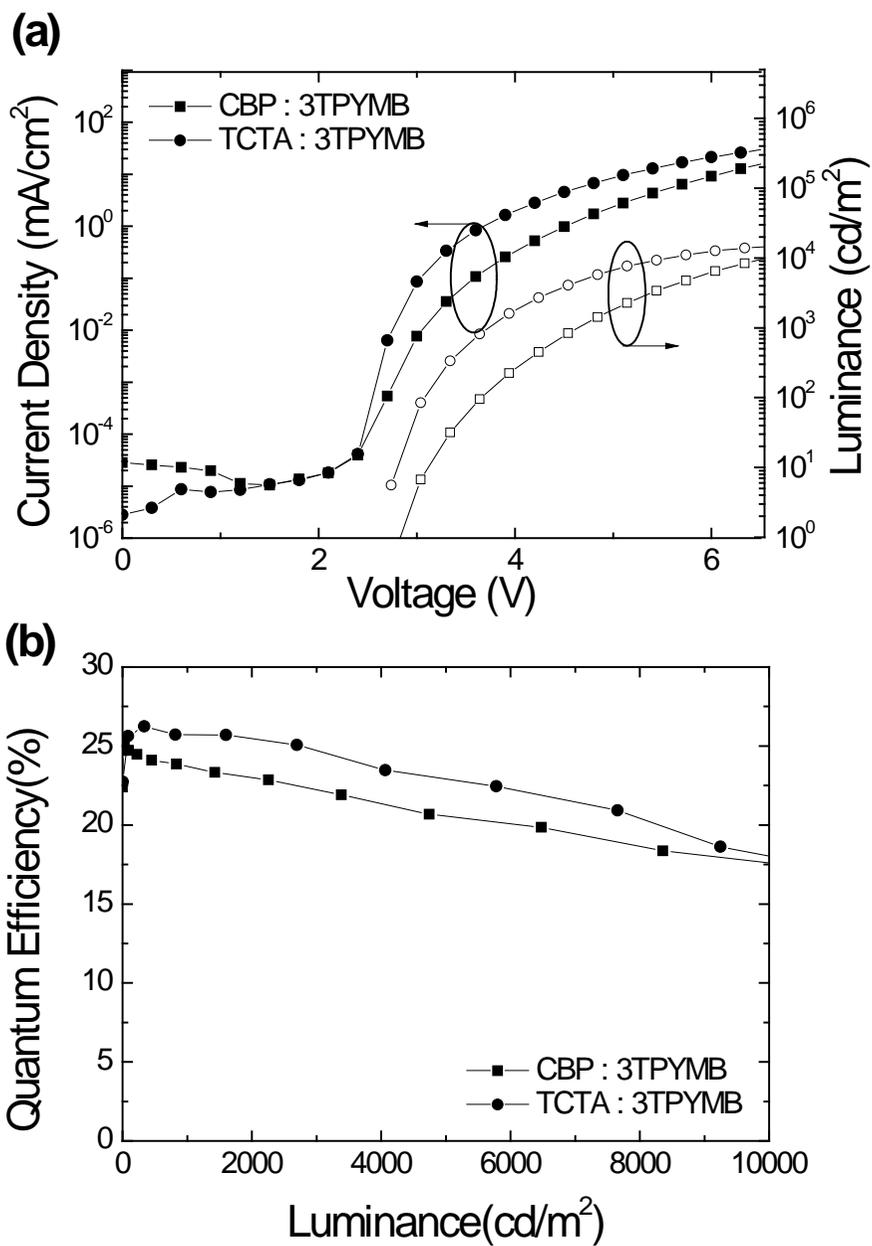


**Figure 3.11** Schematic diagram of charge transport explaining difference of (a) non-exciplex forming and (b) exciplex forming co-host based devices

We also compared CBP:3TPYMB and TCTA:3TPYMB device for non-exciplex forming and exciplex forming co-host system. We fixed ETL material and changed HTL. We studied that TCTA:3TPYMB forms exciplex in chapter 3-1. J-V-L and roll-off characteristics of devices are shown in Figure 3.12. For TCTA:3TPYMB device, turn-on voltage and operating voltage at  $10,000 \text{ cd/m}^2$  are 2.7 V and 5.5 V, respectively. Maximum EQE and EQE at  $10,000 \text{ cd/m}^2$  are 26.2 % and 18 %, respectively.

This result also shows operating characteristics on exciplex forming and non-exciplex forming co-host used in OLEDs, TCTA:3TPYMB exciplex system has lower turn-on voltage because it forms exciplex. Unlike difference between CBP:B3PYMPM and CBP:3TPYMB devices, which current density is less than 1 order different in same voltage, current density difference between CBP:3TPYMB and TCTA:3TPYMB device is near 2 orders. It is due to the difference of hole injection ability of both device structures. For TCTA device we used TAPC as HIL, TAPC is well known materials for efficient hole injection and low injection barrier to TCTA<sup>2</sup>. But for CBP, the HOMO level (6.0 eV) of CBP is very deep, which induce higher over potential to inject hole from ITO to CBP even the electrical doping was adopted

in the CBP layer. In addition, it is prohibited to dope higher concentration in CBP layer because the device efficiency is worse for device with higher doping concentration as shown in chapter 3.1 due to charge imbalance.



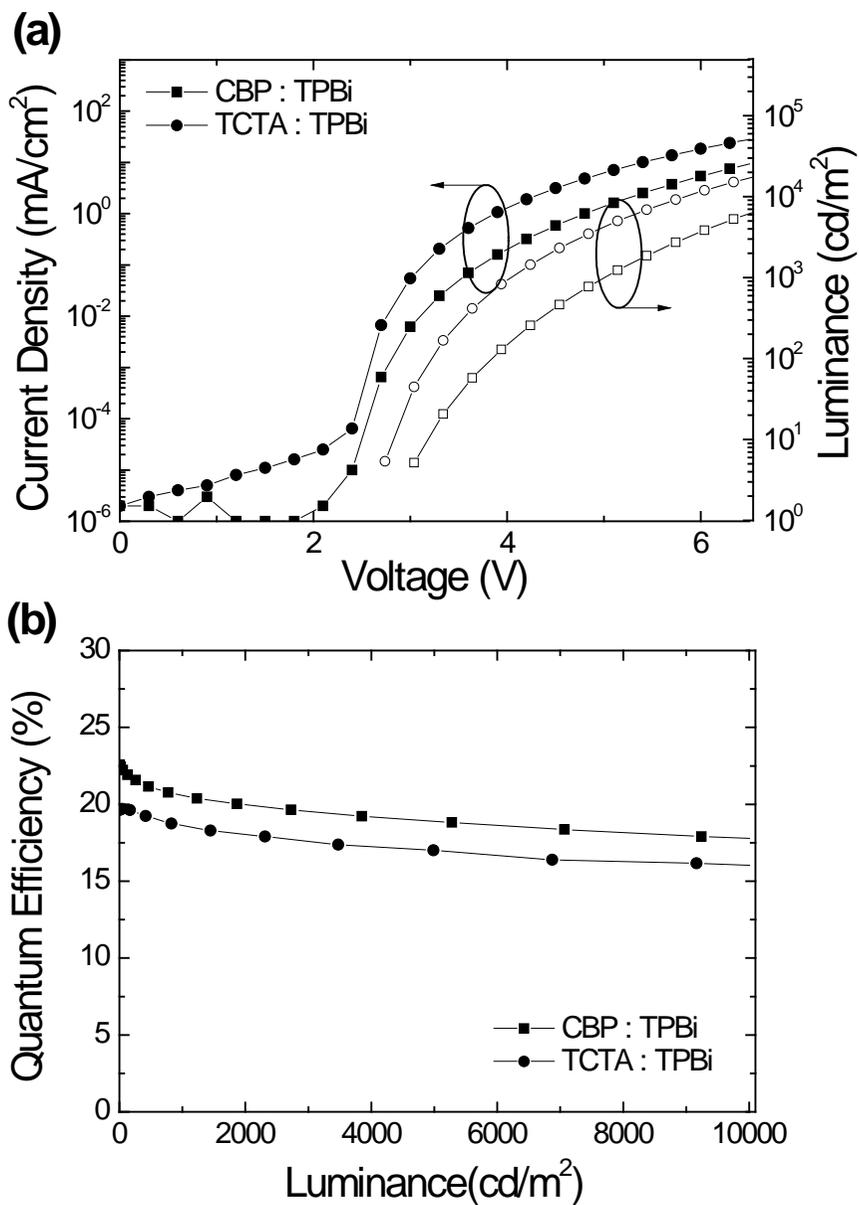
**Figure 3.12** (a) J-V-L and (b) roll off characteristics of CBP:3TPYMB and TCTA:3TPYMB co-hosts

### 3.2.3 Lower EQE case in OLED with exciplex forming co-host

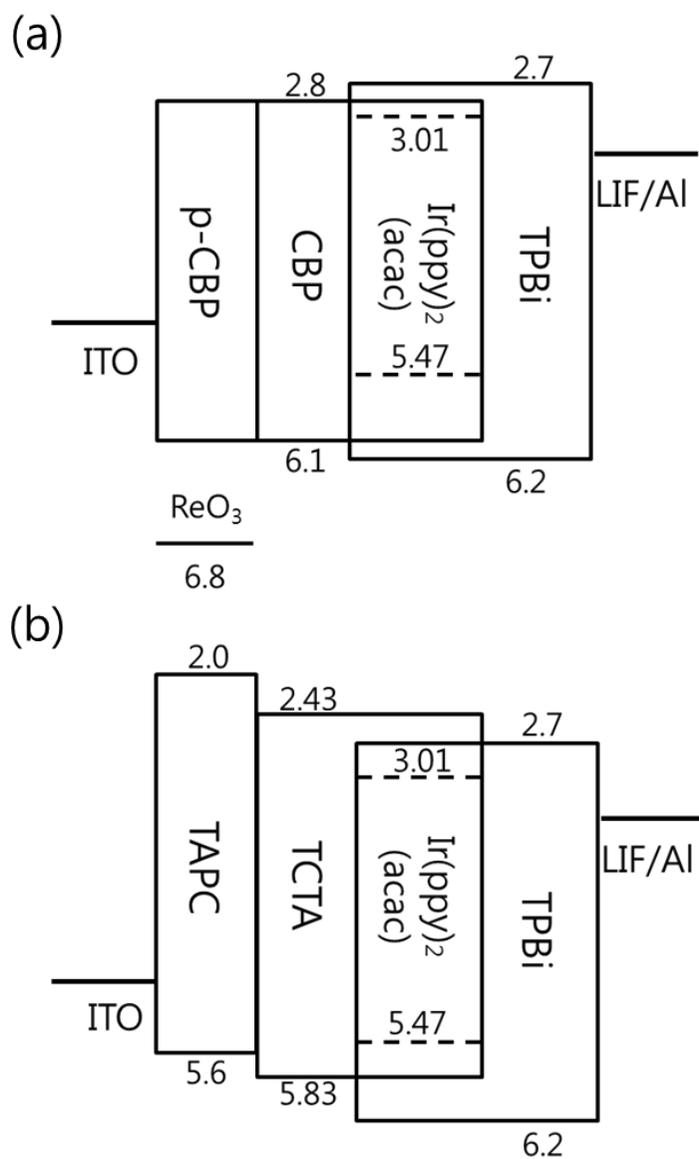
The J-V-L and roll-off characteristic of OLED with CBP:TPBi and TCTA:TPBi is shown in Figure 3.13. Turn on voltage and operating voltage at 10,000 cd/m<sup>2</sup> of device with CBP:TPBi are 3.0 V and 7.0 V, respectively. Maximum EQE and EQE at 10,000 cd/m<sup>2</sup> are 22.6 % and 17.7 %, respectively. Maximum power efficiency is 86.8 lm/W. For device with TCTA:TPBi it forms exciplex and turn-on voltage and operating voltage at 10,000 cd/m<sup>2</sup> are 2.7 and 5.8 V, respectively.. Maximum EQE and EQE at 10,000 cd/m<sup>2</sup> are 19.7 % and 16.0 % . Maximum power efficiency is 93.0 lm/W.

The device with exciplex forming co-host of TCTA:TPBi has lower EQE than that of device with non-exciplex forming co-host of CBP:TPBi. Plausible explanation for this phenomenon is different recombination mechanism. Unlike when using ETL as B3PYMPM and 3TPYMB, Ir(ppy)<sub>2</sub>acac dopant level is lower than LUMO for TPBi as shown in Figure 3.14, so it have condition for electron to trap to dopant site when it injected from cathode side. Behaviors of energy transfer and direct charge trapping are different, further study is needed here to know how dopant trap site behaves differently in

exciton and exciplex system. Performance of all devices is summarized in Table 3.



**Figure 3.13** (a) J-V-L and (b) roll off characteristics of CBP:TPBi and TCTA:TPBi co-hosts



**Figure 3.14** Energy levels in (a) CBP:TPBi and (b) TCTA:TPBi co-host devices

**Table 3** Device performance of OLED devices with different co-hosts

category	HTL : ETL Combination	Voltage		EQE	
		@ 10 mA/cm <sup>2</sup>	@ 10,000 cd/m <sup>2</sup>	Max EQE	@ 10,000 cd/m <sup>2</sup>
Exciplex System	CBP : B3PYMPM	5.9 V	6.4 V	27.4 %	20.1 %
	TCTA : 3TPYMB	5.1 V	5.5 V	26.2 %	18.0 %
	TCTA : TPBi	5.5 V	5.8 V	19.7 %	16.0 %
Non- exciplex System	CBP : 3TPYMB	6.1 V	6.5 V	25.3%	17.6 %
	CBP : TPBi	6.6 V	7.0 V	22.6 %	17.7 %

## **Chapter 4**

### **Conclusion**

We specified exciplex system for CBP and TCTA among five different co-host systems. From this result we found that both structural and energy factor are important for forming exciplex. We also fabricated OLED devices with all co-host systems we studied. By comparing exciplex and non-exciplex forming systems, we found out the devices with exciplex forming co-host have lower operating voltage compared to the device with non-exciplex forming co-host. It is due to the easy formation of excited molecules as form of exciplex in the host molecules. Then the exciplexs transfer to dopant to form exciton at the dopant molecules. For system with TPBi, different tendency of efficiency was shown compared to other systems. It may be attributed to the position of dopant energy level by comparing to co-host energy level.

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## 초 록

엑시플렉스는 이중 분자간의 형성되는 들뜬 상태로서, 유기발광 다이오드에서 효율을 낮추는 원인으로 인식되어왔다. 하지만 최근의 연구에 따르면 전자전달물질과 정공전달물질을 섞은 공동 호스트를 발광층으로 이용하고 여기에 인광 염료를 도핑한 유기 발광 다이오드 구조를 통해, 공동 호스트 중 엑시플렉스를 형성하는 구조에서 고효율을 달성할 수 있다는 것이 보고되었다. 하지만 인광 도판트를 삽입한 공동 호스트 구조에서 엑시플렉스의 형성 유무가 유기 발광 다이오드의 성능에 미치는 영향에 대해서는 연구된 바가 거의 없다.

본 논문에서는 공동 호스트에서 엑시플렉스의 형성 유무에 따른 유기 발광 다이오드 소자효율을 비교하여 엑시플렉스가 효율에 미치는 영향에 대해 분석하였다. 우선 엑시플렉스 형성을 위한 조건인 에너지적, 구조적인 요소를 고려하여 5개의 공동 호스트 구조를 고안하였다. 선행연구 결과와 루미네센스 측정, 흡수 측정을 통해 이중에 3개의 구조가 엑시플렉스를

형성한다는 것을 확인하고 각 공동 호스트 구조들을 이용하여 유기 발광 다이오드 소자를 제작하였다. 엑시플렉스 형성 유무에 따른 전류 - 전압 - 발광 특성, 외부 양자 효율을 비교해본 결과, 각 비교에서 엑시플렉스를 형성하는 구조가 형성하지 않는 구조에 비해서 구동 전압이 더 뛰어난 특성을 보여주었다. 엑시플렉스를 형성하는 공동 호스트의 경우 전자와 정공이 만나 엑시플렉스를 형성하고, 도판트의 엑시톤 상태로 에너지 전이가 일어난다. 반면 엑시플렉스를 형성하지 않는 공동호스트에서는 에너지 전이보다 도판트 분자에 직접 재결합 일으키는 현상이 주로 발생하며, 이것이 구동전압을 증가시킨다.

**주요어:**유기발광다이오드, 엑시플렉스, 공동호스트 구조,

**학 번:**2011-20663

## 감사의 글

대학원에서 2 년의 시간을 보내고 그 결실로서 논문을 완성하게 되었습니다. 이 글을 통해 석사과정 동안 많은 도움을 주신 OPL 여러분들에게 진심으로 감사를 표하고 싶습니다.

한없이 부족한 저에게 큰 가르침을 주신 존경하는 김장주 교수님께 가장 먼저 감사의 말씀을 드리고 싶습니다. 부족한 연구결과에도 항상 아낌없는 격려와 손수 연구자로서의 자세를 가르쳐 주시기를 마다하지 않으셨고, 그 속에서 교수님의 자상함을 느낄 수 있었습니다. 바쁜 일정에도 논문심사에 힘써주신 박수영 교수님, 장지영 교수님께도 감사를 표하고 싶습니다.

바쁜 와중에도 연구 내용을 봐 주시고 조언을 아끼지 않은 실험실의 만형 성훈이 형께 깊은 감사의 말씀을 드리고 싶습니다. 성훈이 형 덕분에 연구를 시작할 수 있었고 연구를 진행하는 와중에도 많은 것을 배울 수 있었으며 논문 또한 완성 시킬 수 있었습니다. 시뮬레이션에 관련하여 많은 도움을 주셨던 세용이 형, 정확한 지적과 함께 논문의 방향을 잡는데 큰 도움을 주셨던 지환이 형, 후배들을 동생처럼 따뜻하게 보살피 주고 챙겨주시는 준혁이 형, 자주 대화하며 멘토가 되어주신 철호 형, 자잘한 질문에도 친절할 도움을 주셨던 정환이 형, 태양전지 연구 때 많은 도움을 주신 태민이 형, 항상 유쾌한 모습을 보여주시는 정범이 형, 항상 근면하게 실험하면서 후배에게 모범을 보여주고 때로는 힘이 되어 주셨던 현섭이 형, 대호 형, 승준이 형 감사합니다. 이분들과 함께 대학원 생활을 해서 행복하고 즐거웠습니다. 지금은 사회에서 활동하시는 선배님들에게도 감사를 표하고 싶습니다. 실험실 일을

가르쳐 주셨던 자상한 형돌이 형, 걸은 무뚝뚝하지만 따뜻하게 후배들을 봐주신 원익이 형, 개인적인 상담도 마다하지 않고 친근하게 보살펴주신 재현이 형, 근면하게 생활을 하시며 롤모델이 되어 주셨던 영서 형, 막 들어온 아무것도 모르는 신입생에게 친절하게 가르쳐 주셨던 동광이 형, 양은 누나 지금 하고 계신 일들이 좋은 결과를 맺기를 바라며 저와 함께한 실험실 생활 동안 도와주신 모든 것들에 대해 감사합니다. 믿고 저를 따라주며 실험을 도와주기도 했던 후배들 민수, 창기, 현, 재민, 그리고 실험실 사람들을 뒷바라지하며 때로는 상담 역할도 해 주시는 지희 누나, 승화정제를 열심히 도와주었던 발랄하고 씩씩한 동생 다현에게도 감사를 표시하고 싶습니다. 늦은 밤에 같이 실험하기도 하며 동고동락하고 고민도 함께 나누었던 동기들에게도 감사의 말을 전하고 싶습니다. 실험에 관해서 자기 일처럼 도와주었던 권현과 항상 개그를 하는 유쾌한 친구 경훈에게도 감사합니다. 이들과 함께할 앞으로의 박사 학위기간이 기대에 벅칩니다.

마지막으로 경상도 남자이지만 따뜻한 마음씨를 지닌 아버지, 어느 때나 저를 걱정해주시면서 물심양면으로 지원해 주시는 어머니, 항상 동생에게 좋은 역할을 보여주면서 고민을 들어주는 형에게 조건 없는 사랑과 앞으로 나아갈 힘을 주어 감사하다고, 사랑한다고 이 글을 통해 전하고 싶습니다.

2013년 1월 30일

이창현